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# ABSTRACT BOOK

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# Content

## Symposium F: Electronic Ceramics 347

# Plenary Speakers

# Structure and Properties of Zeta-Phase Tantalum Carbide

William Fahrenholtz, Evan Schwind, Greg Hilmas

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## Abstract:

Zeta-phase carbides have an unusual combination properties with strengths of more than 500 MPa and fracture toughness values in excess of 10 MPa•m1/2. Zeta phase carbides have a narrow range of compositional stability. These ceramics also have an upper temperature limit for stability and decompose to other carbides above a critical temperature. The zeta phase in the tantalum-carbon system is stable below ~2400°C at a tantalum to carbon ratio of about 3 to 2. Strength and fracture toughness values have been reported at room temperature, but not at elevated temperatures. Our group developed reaction-based processing to produce zeta phase tantalum carbide ceramics that contained up to ~96 wt% of the zeta phase and were nearly fully dense. Zeta phase tantalum carbide ceramics had an electrical resistivity of ~160 ohm•cm at room temperature and exhibited metallic electrical conductivity. The thermal conductivity was about 10 W/m•K, which is about 1/3 of the value of TaC. The strength decreased as temperature increased from about 700 MPa at room temperature to about 180 MPa at 1600°C. Over the same temperature range, fracture toughness decreased from about 10 MPa•m1/2 to 5 MPa•m1/2. In addition, zeta phase tantalum carbide exhibits non-linear elastic behavior that is attributed to its nanolaminate structure. Based on its unusual structure and properties, zeta-phase tantalum carbide can be machined using conventional hardened steel tools. The presentation will discuss the mechanisms underlying the observed properties.

## Acknowledgements:

This research was funded by the Enabling Materials for Extreme Environments signature area at the Missouri University of Science and Technology

# Texture Engineering of Lead-based and Lead-free Piezoelectric Ceramics

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## Abstract:

Texture engineering has attracted significant attention as a promising process for improving not only lead-free piezoelectric ceramics but also lead-based piezoelectric ceramics. Generally, texturing process consists of synthesis of plate-like templates, aligning of templates in the matrix particles using tape-casting or screen printing process, and growth of templates by consuming matrix particles during sintering. Depending on the chemical composition and crystal structure of the template and matrix used, texturing process can be classified into three categories: Templated grain growth (TGG), reactive-templated grain growth (RTGG), and hetero-templated grain growth (HTGG). One of the most important parameters in texture engineering is the behavior of templates during calcination and/or sintering. In this study, the role and behavior of templates in texturing of lead-based and lead-free piezoelectric ceramics were investigated.

## Acknowledgements:

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# Symposium A: Synthesis of Powders

## Invited presentation:

# Highly crystalline boron nitride powders by pyrolysis and mechanochemical synthesis of ammonia borane and alkali metal-containing precursors

Melanie Wynn[1], Elodie De Sousa[1], Yoshiyuki Sugahara[2], Guillaume Cassabois[3], Bernard Gil[3], Julien Haines[4], Samuel Bernard[1]

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## Abstract:

Boron nitride (BN) is a III-V compound which is the focus of important research since its discovery in the early 19th century. BN is electronic to carbon and thus, in the same way that carbon exists as graphite, BN exists in the hexagonal phase. The latter offers an unusual combination of properties that cannot be found in any other ceramics. However, these properties closely depend on the synthesis processes.

BN can be prepared via a simple thermolysis of ammonia borane (AB, $NH_3•BH_3$) without impurities. Indeed, AB is made of the elements of boron nitride in the right amount. However, AB displays several drawbacks among which a fusion upon heat-treatment, the instantaneous evolution of a large quantity of by-products around 135°C and that it leads to a relatively low BN crystallinity (= turbostratic) although a high temperature (1400°C) is applied. We thus investigated the chemical modification of AB by lithium or sodium containing compounds based on the fact that those two alkalis are known to promote BN crystallinity. Thus, we developed a mechanochemical synthesis allowing to form Li or Na modified poly(amidoboranes-co-iminoboranes) with controlled B:Li/Na ratios that could be transformed into pure hexagonal BN or a mixture of hexagonal and rhombohedral BN by pyrolysis at 1400°C under controlled atmospheres without fusion nor release of large amounts of by-products. We particularly showed that the crystallinity, crystalline quality and microstructural ordering of BN - thereby its functional properties - are affected by the synthesis conditions.

## Acknowledgements:

We would like to acknowledge the funding agency "Agence Nationale de la Recherche" (ANR),which supports the work through the "ZEOLIGHT" project (Project number ANR-19-CE08-0016).

# Transition between two solid-solutions: effective and easy way for fine Ce1-xGdxO2-x/2 powders preparation

Adam Alemayehu[1], Dominika Zákutná[2], Soňa Kohúteková[2], Václav Tyrpekl[2]

[1] *Charles Univeristy, Prague, Czech Republic*
[2] *Charles University, Prague, Czech Republic*

## Abstract:

Ceria is an important electrolyte material in solid oxide fuel cells, catalysts, and plutonium surrogates. Even though ceria is a widely studied material, its coprecipitation with the most common doping element, gadolinium, remains mostly superficially studied. We present a comprehensive study of gadolinium-cerium oxalates prepared by coprecipitation of gadolinium (III) and cerium (III) salts by oxalic acid under different reaction conditions and element ratios. For this purpose, we assessed the effects of basic precipitation conditions on the final oxalate size, shape, and conversion into the corresponding oxides. The results showed that coprecipitation with oxalic acid yields and ideal solid solution, which translates into the oxides. This low-cost and straightforward synthetic route provides then high-quality solid solutions of Ge-Gd in the oxide lattice. It has a high industrialization potential, with significant advantages over hydrolysis or hydrothermal techniques.

## Acknowledgements:

This study was funded by the Czech Science Foundation (GAČR), under project 20-20936Y - Microstructural and chemical effects during flash sintering of refractory oxides.

# Study of heteroaggregation between silica particles modified by polyelectrolyte multilayers

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## Abstract:

In recent years, it has been shown that particle heteroaggregation is an important phenomenon in many fields and in particular in the field of ceramic shaping, where it can be used to tailor materials architecture (porosity, homogeneity, etc.). Most of the time, heteroaggregation is obtained with suspension of particles exhibiting very different isoelectric points. In this case, there is a range of pH values where particles are positively and negatively charged and thus heteroaggregate. For systems where such conditions cannot be found, surface modification can be an interesting alternative to pH modification.

In this study we propose to investigate the behavior of silica particles modified on the surface by polyelectrolyte multilayers. After explaining the functionalization method used, we will analyze the behavior of mixed suspensions, composed of 50% of positive particles and 50% of negative particles which have been modified with a different number of polyelectrolyte layers. The study reveals that, for these systems, heteroaggregation is observed in the absence of salt. Thus, surface modification is an alternative to obtain heteroaggregation without modifying pH values of the suspension. Furthermore, when the number of polyelectrolyte layers is large, the stability of the mixed suspensions can be modified by adding salt.

# Microfluidic synthesis of amino- and carboxyl-functionalized magnetite nanoparticles

Cristina Chircov[1], Alexandru Mihai Grumezescu[1], Alexandra Catalina Bîrcă[1], Ovidiu Cristian Oprea[2], Bogdan Stefan Vasile[1], Ecaterina Andronescu[1]

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## Abstract:

In the present study, a series of amino- and carboxyl-functionalized magnetite nanoparticles with uniform properties were obtained through the use of an all-in-one microfluidic lab-on-chip device that eliminates the variations of the intermediary synthesis steps. Specifically, the lab-on-chip device was used for the homogenous mixing of the iron(II) and iron(III) precursors at a 1:2 molar ration, their subsequent co-precipitation in the presence of an alkaline medium, and the collecting and washing of the so-obtained magnetite nanoparticles. The solutions containing the iron precursors were individually injected at the flow of 15 rot/min each, while the solutions containing the precipitating agent (1 M) and the functionalization agent (1, 3, and 5%) were injected through two inlets at 15 and 25 rot/min each. The nanoparticles were removed from the microfluidic chip, dried overnight at 40°C and characterized in terms of composition, structure, crystallinity, morphology, and functionality through X-ray diffraction coupled with Rietveld refinement, transmission electron microscopy, selected area electron diffraction, dynamic light scattering and zeta potential, Fourier-transform infrared spectroscopy, vibrating sample magnetometry, and thermogravimetry-differential scanning calorimetry analyses. The results demonstrated the formation of magnetite as the unique crystalline phase, with narrow nanoparticle distribution sizes, spherical shapes, and concentration-dependent functionalization. In this manner, the present study proved the efficiency of the microfluidic lab-on-chip for the controlled and standardized synthesis of magnetite nanoparticles with uniform properties, which represents a step forward in the field of nanomaterial design and development.

## Acknowledgements:

This work was supported by a grant from the Romanian National Authority for Scientific Research and Innovation, UEFISCDI, project number TE 103, code: PN-III-P1-1.1-TE-2019-1450, entitled Multifunctional lab-on-a-chip microfluidic platform for the fabrication of nanoparticles.

# Powder based on ReB2

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## Abstract:

$ReB_2$ based materials are of interest for hard coating applications. So far, $ReB_2$ based coatings have been deposited by the pulse laser deposition and the magnetron sputtering methods. The resulting coatings have a thickness of few microns. In the case of thermal spraying techniques, where the coating - forming materials are powders, it is possible to obtain coatings with a thickness of 200 microns.

This work presents the attempts to synthesize the $ReB_2$ powder for use as a potential material in thermal spray coating processes. The work presents the synthesis method and characteristics of the $ReB_2$ based powder.

## Acknowledgements:

The work is carried out under the IV edition of the ,,Doktorat Wdrożeniowy" at the AGH University of Science and Technology

# Low-temperature synthesis of nanocrystalline high-entropy oxides and effect of heat treatment on structural changes

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## Abstract:

High-entropy oxides (HEOs) are a fairly new group of materials with a wide range of possible applications. The number of potential interactions between the atoms of various elements in high-entropy oxides is enormous. Consequently, synergistic effects in such materials lead to entirely new properties. The present study discusses the possibility of forming five-, six- or seven-component nanocrystalline high-entropy oxides in the Co-Cu-Fe-Mg-Mn-Ni-Zn-O system. A number of oxide materials with different compositions were designed and obtained using the simple and inexpensive mechanochemical synthesis (MS) method after selecting the appropriate milling time and ball-to-powder ratio. The samples were investigated via X-ray diffraction (XRD) with Rietveld refinement, which revealed that some of the studied systems had a single-phase rock-salt structure (Fm-3m), while the remaining ones also contained an additional spinel phase (Fd-3m) and certain other phases. All samples after MS underwent thermal treatment. Only one Co-Cu-Mg-Ni-Zn-O system retained its single-phase rock salt structure. The other systems were two-phase with Fm-3m and Fd-3m structures and different contents. Two-phase HEOs have not been widely studied thus far and their further examination may reveal advantageous properties.

# Stirring-hydrothermal Synthesis of Uniformity Improved Plate like Potassium-Sodium Niobate (KNN) Templates

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## Abstract:

Improvement of the grain orientation of lead free piezoceramic materials by texturing method is essential to obtain a high piezoelectric performance. Synthesis of plate shaped Potassium Sodium Niobate (KNN) template powders is of quite importance for piezoceramic texturing by tape casting. To this end, hydrothermal synthesis is one of most suitable methods due to its capability to produce shape, composition, and aspect ratio controlled inorganic materials. Hydrothermal treatments of precursor solutions containing $Nb_2O_5$, KOH/NaOH mixtures, and SBDS surfactant were carried out at 190 °C. Upon the hydrothermal treatment of solutions with alkali mixing ratio of KOH/NaOH $\leq$ 50%, $NaNbO_3$ cubes or elongated cuboid aggregates were obtained. A mixture of $K_5Na_3Nb_6O_{19}\cdot 9H_2O$ hexagonal plates and $NaNbO_3$ cubes were obtained when the alkali mixing ratio of the solutions was KOH/NaOH - 80%/20%. Moreover, $NaNbO_3$ cubes embedded in some of $K_5Na_3Nb_6O_{19}\cdot 9H_2O$ hexagonal plates were observed by SEM/EDX mapping images indicating phase segregation. Therefore, we utilized stirring-hydrothermal synthesis method which avoids high concentrated microenvironments in the solution to minimize the phase segregation. Products obtained by stirring-hydrothermal synthesis with all KOH/NaOH mixing ratios showed improved particle size distributions. Upon the stirring-hydrothermal treatment of solution with KOH/NaOH - 80%/20%, hexagonal $K_5Na_3Nb_6O_{19}\cdot H_2O$ (KNN hydrate) plates were obtained as the only product. XRD, SEM/EDX images showed a good phase purity and homogeneous element mixing in these KNN hydrate plates, respectively. Plate shaped KNN perovskite templates with approximate composition of $K_{0.7}Na_{0.3}NbO_3$ were obtained by calcination of those KNN hydrate plates obtained by stirring-hydrothermal synthesis.

# Effects of temperature, aging time, and method of introducing stabilizer oxide into solid solution on properties of Mg-PSZ materials.

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A part of the system in the technology of casting precision aircraft engine parts is a ceramic sealing element, which is also a part of the liquid metal supply system, which takes over the impact of the metal stream, as well as calming and separating the stream of flowing alloy.

In presentd work materials of the partially stabilized zirconium dioxide (PSZ) type were obtained, which meet the stringent requirements for such an element. The properties of these materials strongly depend on the conditions of their production. The appropriate selection of the type of stabilizing oxide precursor as well as the sintering and aging conditions of the materials in the $MgO$-$ZrO_2$ system allowed for the modification of the phase composition and microstructure, which made it possible to obtain a material with good mechanical properties and good thermal shock resistance under conditions of rapid heating (low coefficient of thermal expansion). Materials with the addition of a magnesium oxide (M) precursor, obtained under the same conditions, have higher mechanical properties than materials with the addition of a precursor in the form of a solid solution of $MgO$ in $ZrO_2$. The mechanical strength for the material obtained as a result of two-hour sintering at the temperature of 1640 °C and subjected to the aging process at the temperature of 1420 °C for 2 hours is 250 MPa for the M series material and 214 MPa for the MZ series. Both the Young's modulus and K1C of both these materials are similar and amount to 185 vs. 183 GPa and 4.68 vs. 4.47 MPa · $m^{0.5}$, respectively. Significant differences arise when comparing the coefficient of thermal expansion 5.35 vs. 4.5 $\times 10^{-6}$ L/°C, which has a key effect on thermal shock resistance under sudden heating conditions

# Preliminary Study of the Cold Sintering Process (CSP) for Geopolymer Powders

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## Abstract:

The sintering process is an essential step in transforming particulate materials into dense ceramic materials. Already starting from the Paleolithic, humans made use of this process to create ceramic manufacturers, as shown by the figurine of Venus of Doli Vestonice. Despite its ancient origin, sintering is still nowadays a crucial stage in the production of ceramic products. However, since it needs high temperatures (between 50% and 75% of the melting temperature to theoretical density of 95% of the product), the classic sintering is not so eco-sustainable.

In 2016, Randall and his research team introduced and patented the so-called cold sintering process (CSP) where a ceramic powder is densified with the aid of a liquid phase under an external pressure and limited heating conditions (below 350°C). In doing so, a drastic decrease of the energy amount is obtained, reducing the environmental impact of the process. Up to date, different materials have been successfully processed through CSP with extraordinary results in terms of final properties. In this presentation, preliminary results obtained from the implementation of the CSP for geopolymer powders are reported.Briefly:

a) High geometric density, indicating low residual internal porosity;

b) Very good chemical stability, as confirmed by passing the boiling test. Indeed, materials possessing a not-fully condensed geopolymer network are sensitive to water, undergo swelling, dissolution or total destruction.

The evidence obtained confirms the technological excellence of CSP for the production of geopolymer bodies as an alternative to casting. Obviously, further research will be necessary to understand the diffusion and densification mechanisms that occurs during cold sintering of geopolymer powders

# Study of wet chemistry methods for fabricating potassium sodium niobate materials

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## Abstract:

Materials based on potassium sodium niobate (KNN) have been attracting extensive attention as lead-free piezoelectric materials. Such materials are usually synthesized via a solid-state reaction, which tends to result in powders with inhomogeneous particle size distribution and agglomerates. It is generally accepted that solution-based synthesis offers advantages such as narrower particle size distribution, lower temperature processing, and improved compositional homogeneity. In the present study, a water-based metal-chelate technique was applied to prepare KNN materials. The influence of the type of chelating agents on the stability of sols and the properties of the obtained powders was evaluated. The obtained gels were characterized using thermogravimetric analysis and differential scanning calorimetry to establish the optimal thermal treatment parameters. The structure of powders and sinters was examined using X-ray diffraction and FT-IR spectroscopy. Rietveld refinement was used to analyze the crystal structure of the materials. The results revealed that the obtained powders and sinters were fully crystalline, with an orthorhombic perovskite-like structure of KNN. Morphological observations via scanning electron microscopy showed nanosized powders and sinters with a grain size of 1-5 μm. This indicates that water-based wet chemistry methods are effective at obtaining lead-free KNN ceramics.

# Copper doped ceria nanocatalyst for VOCs oxidation

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## Abstract:

Volatile organic compounds (VOCs) present a major environmental problem, as well as a health hazard. Catalytic oxidation is a promising method for their elimination from anthropogenic emission sources. Ceria ($CeO_2$) is an important and widely applied catalytic material used in three-way catalytic converters, diesel particulate filters, solid oxide fuel cells, water-gas shift reaction, etc. Furthermore, many studies report on its high efficiency in the catalytic oxidation of VOCs. There are two main ways of improving the catalytic activity of ceria. The first one is the reduction of particle size to the nano level, which increases the specific surface area and reactivity of the prepared catalyst. The second one is doping with various metals with lower radius and valence, which enhances the oxygen storage and release capacity of ceria. The aim of this work was to prepare ceria nanocatalysts doped with copper in various amounts via the hydrothermal method. The characterization of the prepared materials was conducted by employing X-ray diffraction analysis, transmission electron microscopy, electron energy loss spectroscopy, $N_2$ adsorption-desorption isotherms and X-ray photoelectron spectroscopy. The catalytic activity of the nanocatalysts was tested for the toluene oxidation process. The results show that copper is incorporated into the ceria crystal lattice in amounts significantly lower than nominal. However, a decrease in particle size and a notable increase of catalytic activity of ceria with the addition of copper were observed, proving copper doped ceria a suitable catalyst for VOCs oxidation.

## Acknowledgements:

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# Low-temperature synthesis of britholite-(La) by sol-gel method

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## Abstract:

Since Nakayama et al. reported that apatite-type structures of compositions $Ln_{10-x}Si_6O_{26+y}$ (Ln = La Sm, Nd, Dy, Gd, x = 8 to 11) materials exhibited high ionic conductivity,[1] rare-earth apatite material with high conductivity have been investigated to develop new electrolytes working at intermediate temperature. Another essential feature of these apatite-type oxides is the wide range of doping possibilities within the La and Si sites, which can be used to enhance conductivity.[2] Ito et al. first synthesized britholite-(La) crystals considered to be of composition $Na_2La_8Si_6O_{24}F_2$, a pseudo-hexagonal $P2_1$ sub-symmetry of the $P6_3/m$ apatite in a study of silicate apatite structures.[3] However, the preparation of apatite usually requires a high temperature of over 1000 °C, and there is no report devoted to the ion conductivity properties of britholite-(La). In this study, we focus on developing a low-temperature synthetic method of the pristine and metal-doped britholite-(La), and the doping effect on its structure and conductivity was investigated. This method reduces the energy consumption required for the preparation of material.

The raw material was prepared by a sol-gel method. In the presence of lanthanum nitrate ($La(NO_3)_3·6H_2O$) and sodium fluoride (NaF), an aqueous solution of sodium metasilicate ($Na_2SiO_3·9H_2O$) was added. The thus-formed solid was calcined at 600 °C twice to afford britholite-(La). The formation of apatite structure was confirmed by powder X-ray diffraction (PXRD) analysis. In addition, it was found that Bi, Fe, and Ce ions can be doped at the La site with maintaining britholite structure. The ion conductivity measurement of pristine britholite-(La) showed a considerably high conductivity of $1.17 \times 10^{-3}$ S cm$^{-1}$.

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# Bio-inspired nanoplatelet-like particles of hydroxyapatite

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*Department of Materials and Ceramic Engineering (DEMaC), CICECO-Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal*

## Abstract:

Nowadays, the synthesis of hydroxyapatite (HA) bioceramics with specific particle size, homogeneous morphology, and chemical composition has been attracting attention due to their distinctive chemical, biological, and physical properties and possible uses in advanced functional materials. Different studies confirmed that surface modification of HA and other calcium phosphate (CaP)-based biomaterials with distinct nano or microstructures could effectively mimic the hierarchical characteristics of native bone tissue and consequently enhance the adsorption of particular proteins in plasma and stimulate cell adhesion, proliferation, osteogenic differentiation, and osseointegration in vivo. Despite the mentioned advances, it is still a big challenge to synthesize and optimize the synthesis conditions of CaP crystals with controllable shapes and specific structures.

In the present work, the synthesis of HA nanoparticles with platelet-like topography was conducted via hydrothermal method, using an anionic surfactant. The effect of the surfactant amount, the precursors´ concentration used and the hydrothermal operational conditions in terms of pH, temperature, and time on the synthesis yield and purity, size and morphology of HA nanostructures was evaluated. A set of representative HA powders were prepared for X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) for crystalline phases and morphological observation, respectively. The results demonstrated the importance of registering the conditions employed in the manufacturing process like the amount of the various compounds, pH, and time during hydrothermal synthesis to ensure the platelet-like HA nanoparticles achievement. It also constitutes a step forward for promising future applications in biomedicine and tissue engineering fields namely in the improvement of mechanical strength and bioactivity of several biodevices.

## Acknowledgements:

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# Novel MAB phases

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## Abstract:

MAB phases are ternary transition metal borides which nanolaminated orthorhombic crystal structures consist of M-B (M - transition metal; B - boron) layers interspersed with aluminum or zinc monolayers or double layers of Al atoms. MAB phases with the following chemical formulas have been defined: MAlB, $M_2AlB_2$, $M_3Al_2B_2$, $M_3AlB_4$, and $M_4AlB_6$.

The name of MAB phases comes from the fact that their structures are similar to nanolaminates of the so-called MAX phases. Thus, it can be said that MAB phases are boride equivalents of MAX phases. The interest in MAB phases is connected with their unique properties combining typical behavior of metals and boride ceramics. Existing literature on MAB phases highlights the significant difficulties associated with their synthesis. Therefore, it is necessary to eliminate thermodynamic difficulties resulting from the unfavorable enthalpy of formation of theoretically predicted MAB phases and metastability of many of them. Despite the mentioned difficulty, there are works in which successful syntheses of MAB phases with the following compositions have been carried out: MAlB (M = Mo, W), $M_2AlB_2$ (M = Cr, Mn, Fe), $Ru_3Al_2B_2$, $Cr_3AlB_4$, and $Cr_4AlB_6$. It should be recognized that the obtaining of these compounds is favored by advances in the design and equipment of synthesis reactors as well as the inventions of new synthesis methods.

Due to the thermodynamic difficulties associated with the synthesis of MAB phases as outlined earlier, there is little literature available on this topic. Additionally, there is a lack of works about some of the interesting MAB phases with special emphasis on titanide based phases. Materials from this group can find application in rapidly growing space industry but also can influence development of energy industry.

# Synthesis of high entropy carbide (Ti, Zr, Hf, Nb, Ta)C

Pavlína Šolcová[1], Matěj Nižňanský[1], Jiří Schulz[1], Petr Brázda[2], Petra Ecorchard[3], Monika Vilémová[4], Václav Tyrpekl[1]

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## Abstract:

This work is focused on simplification of a synthesis of high entropy carbides. Usually, high entropy carbides are prepared by high-energy ball-mining of powders precursors. However, pursued route is based on sol-gel method. The main idea of this synthesis is creating homogenous solution of all precursors. This can be achieved with peroxo-carboxylic complexes of transition metals. Chlorides or oxo-chlorides (e.g. $ZrOCl_2$) are used as metal precursors. Citric acid is used as carbon precursors. Hydrogen peroxide is added to the mixture to form water soluble and stable compounds.

Homogenous solution of all precursors is dried to gel. Next step is pyrolysis at 800 °C in furnace, which leads to creation of amorphous carbon with dispersed nanoparticles of transition metals. This intermediate undergoes carbothermal reduction at 1400°C, 1600 °C and 1900 °C in Spark plasma sintering device. The successful creation of high entropy carbide was at 1600 °C. Both product and intermediate were characterized with powder X-Ray diffraction and scanning electron microscopy. The final product was additionally characterized with transmission electron microscopy and elemental mapping.

## Acknowledgements:

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# Oxalate salts: From oxide powder synthesis to field assisted sintering studies

Václav Tyrpekl, Adam Alemayehu, Anastasiya Zakharanka

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## Abstract:

Oxalate salts are important compounds in the technology of lanthanides, actinides and transition metals. They are inexpensive agents for metal's separation from aqueous solutions This is so thanks to their low solubilities. Moreover, oxalates salt can be easily converted to nanocrystalline or microcrystalline oxides by appropriate calcination cycles.

This contribution gives an overview about synthesis and processing of oxalates in the group of Solid-sate chemistry and nanomaterials, Faculty of Science, Charles University, Czech Republic. For example, we aimed on the synthesis of different morphotypes of cerium oxalate and consequently ceria, solid solutions of cerium-gadolinium oxalate and consequently gadolinia doped ceria. Additionally we developed a synthetic route for lanthanide oxalate "large" microcrystals (~100 µm), which was not straightforward in the past. The oxalate conversion to oxide was also employed in an electrical field assisted sintering study. We have explored the effects of AC and DC electric fields on the "in-situ" solid-state generation and grain growth of oxide nanoparticles.

## Acknowledgements:

This study was funded by the Czech Science Foundation (GAČR), under project 20-20936Y - Microstructural and chemical effects during flash sintering of refractory oxides

# High temperature X-ray diffraction to study the formation of sodium titanates from spray-dried mixtures

Benedicte Vertruyen

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**Abstract:**

The Na-Ti-O system comprises a number of compounds with different Na/Ti ratios and a variety of applications. In particular, several sodium titanates have attracted attention in the field of anode materials for Na-ion batteries, due to the environmentally-friendly character of sodium and titanium and the very low working potential of $Na_2Ti_3O_7$ (0.3 V vs $Na^0/Na^+$). Although precursors with good homogeneity and reactivity can be prepared by solution- or gel-based routes, the synthesis of sodium titanates from cheap, easily available $Na_2CO_3$ and $TiO_2$ starting materials remains of obvious interest. In this communication I will describe how we used in-situ high temperature X-ray diffraction complemented by ex-situ characterizations to investigate the evolution of crystalline phases when heating spray-dried mixtures of $Na_2CO_3$ and $TiO_2$ for ranges of Na/Ti ratios around the compositions $Na_4Ti_5O_{12}$, $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$. I will especially focus on the cases where intermediate phases are involved in the reaction scheme and discuss how a subset of the reflections may display shifts and/or broadening by comparison with the "standard" crystalline phase reported in the crystallographic databases.

# Effect of Y2O3 additive on morphology and phase composition of zirconia solid solutions

Agnieszka Wilk[1], Kamil Wojteczko[1], Marta Gajewska[2], Radosław Lach[1], Piotr Jeleń[1], Maciej Sitarz[1], Krzysztof Haberko[1], Zbigniew Pędzich[1]

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[2] *AGH University of Science and Technology, Academic Centre for Materials and Nano-technology, Kraków, Poland*

## Abstract:

Zirconia and zirconia-yttria solid solution powders within the range of 0 to 8 mol.% $Y_2O_3$ concentration were precipitated and crystallized in NaOH aqueous solution under hydrothermal conditions. The resulting powders were characterized using X-ray diffraction, specific surface area measurements and infrared and Raman spectroscopy. It has been found that morphology and phase composition of the obtained powders are strongly influenced by the $Y_2O_3$ concentration in the system. Low yttria content of 0 and 1 mol. % leads to the elongated particles with monoclinic symmetry. Moreover, an order of magnitude smaller isometric particles appear when $Y_2O_3$ content reaches 2 mol.% and more. They are characterized by tetragonal or even cubic symmetry. It has been shown that $Y_2O_3$ forms solid solution in each zirconia polymorph, i.e. monoclinic, tetragonal and cubic symmetry one.

## Acknowledgements:

The work was financially supported by the National Science Centre Poland under grant no. 2017/25/B/ST8/02217

# Homogeneous precipitation of lanthanide oxalates

Anastasiya Zakharanka, Václav Tyrpekl, Adam Alemayehu

*Charles University, Prague, Czech Republic*

## Abstract:

Oxalic acid is extensively used as a precipitating agent in nuclear chemistry, in preparative inorganic chemistry, and generally in applied science. The f-elements oxalates are extensively studied due to the wide range of applications. Precipitation reactions in solutions can be divided into two categories: heterogeneous and homogeneous. Heterogeneous precipitation is performed by the addition of the precipitating agent directly to the solution of metal ions or vice versa. This creates a high supersaturation and results in the rapid formation of many crystallization nuclei. In homogeneous precipitation, on the other hand, the precipitating agent is being generated in an initially homogeneous system, in a single solution, during a prolonged period. The supersaturation of the solution, in this case, is low and the crystallites grow at a much slower rate, and the morphology of the precipitated particles may be altered. In the past, several heterogeneous actinides and lanthanides' oxalates precipitation routes have been investigated, but homogeneous precipitation remained somewhat underexplored. In the current work, the homogeneous precipitation route of a chosen series of lanthanides was explored. Reaction conditions and kinetics of homogeneous oxalate precipitation by thermal decomposition of oxalic acid derivatives were investigated and described. The characterization (powder roentgen diffraction, thermogravimetry, and electron microscopy) of the representative lanthanide (III) oxalate decahydrates was executed. The homogenous precipitation route allows for a wider range of achievable morphologies.

## Acknowledgements:

This study was funded by the Czech Science Foundation (GAČR), under project 20-20936Y - Microstructural and chemical effects during flash sintering of refractory oxides.

# Symposium B: Ceramic Processing

## Invited presentation:

# Low temperature sintering strategies based on chemical reactivity and control of interfaces

Catherine Elissalde[1], U-chan Chung[1], Etienne Martin[1], Lucas Vilatte[1], Isabel Rua-Taborda[1], Arnaud Ndayishimiye[2], Clive Randall[2], Sylvie Bordère[3], Hélène Debéda[4], Graziella Goglio[1]

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## Abstract:

From field assisted sintering techniques to solvent assisted sintering processes at low temperature (Cold Sintering Process (CSP), Hydro/Solvothermal Sintering (HSS)), significant breakthroughs and developments have been reported in the field of sintering. In particular, the drastic decrease in temperature to sinter functional ceramics have opened wide perspectives in terms of properties and applications. The sintering mechanisms and transport pathways are different, offering a tremedous flexibility in terms of chemical reactivity. Whether it concerns single-phase or multi-materials, expectations are increasingly challenging in terms of performance, and control of defect chemistry, microstructure and interfaces.

In this context, we will illustrate specific sintering strategies to densify functional materials at low temperatures. First, we will focus on the versatility of Spark Plasma Sintering (SPS) to target co-sintering of piezoelectric multimaterials using modified standard set-up and a sacrificial layer approach. Then, we will highlight another strategy to decrease the SPS processing temperature, through the exploration of transient chemistry using specific precursors (hydroxides, carbonates). This approach will be illustrated in the case of zirconia. According to the sintering strategy and the chemical reactivity involved, specific microstructures can be obtained at low temperatures. Finally, a comparison between CSP and HSS devoted to the sintering of ZnO will highlight the current understanding of chemical and mechanical-chemical mechanisms in solvent assisted and low temperature sintering. We will thus demonstrate the complementary of these three sintering methods that cover a wide range of experimental conditions from thermodynamic to off-equilibrium conditions.

## Invited presentation:

# Refining of alumina toughened zirconia composites properties by reactive sintering process

Marek Grabowy

*IEN Institute of Power Engineering, Ceramics Division CEREL, Warszawa, Poland*

## Abstract:

The work concerns the development of ATZ composites containing different alumina content. The selected ATZ composites compounds were fabricated by means of reactive sintering of the mixture of powders composed of precipitated zirconia differing in yttria content. Due to a specific method of preparation, the diffusion intensification during sintering and strong ZrO2 grain-to-grain interactions occurred. Described sintering procedure significantly limits the grain growth process. These phenomena lead to uniquely improved mechanical properties of ATZ composites. Homogenous and fine microstructures with relative densities over 99% were characterized using stereological methods. The ATZ specimens had a hardness of 13.8 GPa, flexural strength higher than 1 GPa and outstanding fracture toughness exceeding 10 MPam1/2. Moreover, the ATZ composites were tribologically tested using the ball-on-disc method up to 500°C. The results proved that the mentioned material had significantly improved wear susceptibility, especially at a temperature range between 350 and 500°C due to the presence of pseudoplastic surface layer, which strongly decreased degradation by limiting of single grains removal. The effects of hydrothermal aging were systematically studied. Highly transformable ZrO2 grains gives the material high resistance to fracture, while making the material very susceptible to hydrothermal aging.

The findings of submitted studies confirm that the ATZ composite material manufactured by the proposed technique had a distinctly improved properties. The investigated ATZ products possess strong potential to be used for reliable machinery parts working in the sliding regime at elevated temperatures, next generation bioceramics for medical devices, high-performance structural elements.

## Invited presentation:

# Rapid Sintering of Ceramics: A Culprit or an Opportunity

Andraž Kocjan[1], Anna-Katharina Hofer[2], Raul Bermejo[2]

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[2] *Montanuniversität Leoben, Leoben, Austria*

### Abstract:

Sintering is a time and temperature-demanding processing step of advanced ceramics, which is associated with densification and grain growth through "slow" solid-state diffusion. Dense and fine-grained microstructures are targeted to obtain superior mechanical and functional properties. Although advanced sintering strategies such as spark plasma sintering (or FAST), flash, ultra-high temperature and cold sintering have all succeeded in the development of nanosized microstructures, they are bound to complex interrelated effects between several competing thermal transport phenomena and to the applied electric current and/or mechanical pressure, thus being limited to simple, limited size-scaled geometries. This poses a challenge for the full exploitation of additive manufacturing (AM) of ceramics. To exploit the geometrical and functional complexity offered by AM, the resurgence of the fast firing (FF), first introduced in the 80`s, is necessary.

The present paper will discuss the possibilities of employing intense thermal radiation (ITR) as a single source of thermal transfer allowing sintering of ceramics with controlled fine-grained microstructure. It is hypothesized that unconventional interface dynamics can foster microstructural evolution via sliding, agglomeration and coalescence of grains, as commonly observed in colloidal systems. This is achieved through immediate (nano)particle consolidation to compensate high surface free energy endowing rapid densification (within minutes) without the need of current nor pressure. As a result, uncontrolled grain growth may be prevented, leading to dense, homogeneous, or tailored microstructures, making ITR ideal as a rapid sintering protocol for 3D ceramic architectures of intricate geometrical complexity.

## Invited presentation:

# Cold Sintering of Functional Materials: A Path to a Possible Sustainable Future

Clive Randall, Zane Grady, Arnaud Ndayishimiye, Javier Mena Garcia, Sun Hwi Bang, Smitha Shetty, Susan Trolier-McKinstry

*The Pennsylvania State University, University Park, United States*

### Abstract:

Cold Sintering involves a transient phase that permits the densification of particulate materials at low temperatures 300 oC and below. Sintering at such low temperature offers so many new opportunities. It permits the integration of metastable materials that would typically decompose at high temperatures. So cold sinter enables a platform for better unification of material science. Now ceramics, metal and polymers can be processed under a common platform in one step processes. With controlling the forming process new nanocomposites can be fabricated. Polymers, gels and nanoparticulates can be dispersed, interconnected and sintered in the grain boundaries of a ceramic matrix phase. With the ability to sinter metal phases, multilayer devices can be co-sintered with electrodes made from metals such as Al, Ag, Fe and Cu. With appropriate binder selection, polypropylene carbonate and its de-binding at 130 oC we can remove organic binders and leave metals and other more stable polymers within the layers that then can be co-sintered under the cold sintering process and form unique combinations of materials in multilayers. This talk will cover some of the fundamentals of cold sintering, as well as some new examples of this technology across different material systems, ranging from ferroelectrics, semiconductors, and battery materials.

### Acknowledgements:

National Science FoundationAir Force Office of Scientific Research

## Invited presentation:

# Trapping a large surface area into a small volume by SPS

David Salamon[1], Miriama Barančíková[2], Jakub Roleček[1], Maliha Siddiqui[1], Haibo Zhang[3], Hua Tan[3]

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[2] *Faculty of Mechanical Engineering - Brno University of Technology, Brno, Czech Republic*

[3] *Huazhong University of Science and Technology, Wuhan, China*

## Abstract:

Spark Plasma Sintering (SPS) method has been developed to preserve a fine-grained structure of the sintered material while the porosity is eliminated. Later the potential of the SPS technique for the fabrication of porous materials has been recognized, but the full potential is not yet explored. Porous ceramic materials have a wide range of interesting physical properties, however, the production of a monolith with shape stability and high specific surface area/porosity is a common problem. This work is aimed to maintain the high specific surface area and produce a monolith with good mechanical stability.

The advantages of the rapid sintering technique for the preservation of high surface area are tested. Two forms of porous silica nanofibers (prepared and milled) were used for partial sintering at different temperatures, heating rates, and dwell times. The specific surface area (BET), density, and compression strength were measured to find optimal SPS conditions.

The low sintering temperature of 600 °C, minimum pressure, and heating rate of over 140 °C·min-1 produced the stable silica machinable monolith, with a compression strength of 2.7 MPa. The BET analysis revealed a surface area of 470 m2g-1, in samples with a porosity of 72 %. The specific surface area preserved in 1 cm3 is over 250 m2, and the macrostructure of the starting powder can tailor the mechanical stability.

## Acknowledgements:

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## Invited presentation:

# Colloidal processing of ceramic-matrix-composites – between capabilities and limitations

Paulina Wiecinska, Marcin Poterala, Michal Kukielski, Joanna Tanska, Anna Wieclaw-Midor

Warsaw University of Technology, Faculty of Chemistry, Warsaw, Poland

### Abstract:

Colloidal processing of ceramics and ceramic-matrix-composites (CMC) is intended to fabricate complex shaped materials of tailored properties and microstructure. Colloidal shaping techniques require effectively working additives, such as: deflocculants, binders, organic monomers, (photo)initiators of polymerization, plasticizers, surfactants, etc. The main challenge in these techniques lies in achieving time-stable, low viscosity aqueous suspensions having high solid loading of well dispersed non-agglomerated particles. Thus, processing agents should accomplish these demanded properties as well as they should realize the trend of "green chemistry". Possibilities of using different organic additives in colloidal processing of CMCs will be presented (e.g. water-based monomers, sugar-based deflocculants, additives used in 3D printing methods). The following issues will be also discussed: multifunctionality of selected compounds, possibilities of the preparation of low-viscosity suspensions containing high concentration of nanopowers, fabrication of ceramic-matrix-composites (ceramic-metal and ceramic-graphene) with the use of tailored precursors of the reinforcing phase.

### Acknowledgements:

This work has been financially supported by Warsaw University of Technology (project number: IDUB TM-1).

# Direct Powder Bed Selective Laser Sintering of Silicon Carbide

Mohamed Abdelmoula[1], Gökhan Küçüktürk[1], Alejandro Montón Zarazaga[2], David Grossin[2], Francis Maury[2], Marc Ferrato[3]

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## Abstract:

Direct-Selective Laser Sintering (D-SLS) is a promising technique for Additive Manufacturing (AM) of pure Silicon Carbide (SiC) powder. The proper values of the process parameters need to be used to succeed the D-SLS of SiC. These process parameters are laser power, scanning speed, hatching distance, and scanning strategies. This study focused on studying the effect of process parameters on D-SLS of SiC and to ensures that these process parameters were appropriately selected. A numerical model was developed to determine the process parameters properly. The results showed that D-SLS of pure SiC powder without any additives is highly possible through the proper selection of the process parameters by using the numerical model. SiC samples were successfully printed using different process parameters obtained from the numerical model, with more than 80% relative density. The relative density can be significantly improved by using functionalized SiC powder or specific post-treatments. Also, Complex geometries were successfully printed using the optimized parameters obtained from the numerical model. Evaluating the mechanical performance should be covered in a future study.

## Acknowledgements:

This project has received funding from the European Union’s Framework Program for Research and Innovation Horizon 2020 (2014-2020) under the Marie Skłodowska-Curie Grant Agreement No. [764935].

# Sintering behaviour of a-alumina containing low amounts of kaolinite and auxiliary molecules

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## Abstract:

Within the framework of the development of ceramic materials based on mixed alumina/mullite compositions, kaolinite appears to be a suitable raw material to consider in the formulation to supply silicon. Natural kaolinite generally crystallizes in the form of pseudo-hexagonal platelets exhibiting a slight thickness (from 1 µm to 100 nm). They are composed of both stacked layers of $SiO_2$ tetrahedral sheets and $AlO_2(OH)_4$ octahedral sheets. After a heating treatment up to 950°C, mullite phase occurs.

This research work consists in the elaboration of multilayer materials by alternating pure alumina and mullite-alumina layers shaped by uni-axial pressing. At high temperatures, the competing mechanisms of sintering and mullite growth control the densification of the alumina matrix. The presence of acicular mullite crystals in the densified matrix and interfaces between the layers contributes to improve the mechanical properties particularly fracture toughness. For this purpose, different compositions of a mixed system based on alumina and kaolinite were prepared varying from 0 to 10%vol the kaolinite content. Two kaolin powders exhibiting a different state of crystallinity were added so as specific molecules (Tiron/Citrate) required to properly disperse both Alumina and kaolinite.

The effect of kaolinite proportion, crystallinity, and the nature of dispersant was then studied on the sintering behaviour of alumina through extensive dilatometric and DTA/GTA analyses (differential and thermogravimetric thermal analysis). It has been highlighted that kaolinite and specific molecule addition leads to a significant modification of the sintering kinetic of the alumina matrix. Secondly, mechanical properties were studied as a function of kaolinite additions and mullite crystallization.

# Ignition of densification mechanisms through applied electric/ electromagnetic fields during spark plasma sintering - application to a pre-oxidized copper powder

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## Abstract:

SPS is a non-conventional and promising sintering method for powder consolidation and densification. However, the whole of the physical phenomena promoted by the combination of high pulsed electric current and mechanical loading has not been clearly understood so far, especially in the early stages of sintering. The role of electrical field is usually narrowed down to the generation of Joule heat. Only few works deal with the potential effects induced by the applied electro-magnetic fields, which can significantly contribute to the enhancement of diffusion mass transport.

This work aims at highlighting the specific phenomena of material transport induced by electric and magnetic fields applied during SPS. For this purpose, the electrical behavior of pre-oxidized copper particles is characterized when exposed to various electro-magnetic waves. Two specific devices simulating the electro-magnetic conditions encountered during SPS have been implemented: one allowing to apply pulsed electric current of high intensity with variable current wave characteristics (i.e. shape, frequency, magnitude), the other characterized by the generation of an electromagnetic wave, produced by an electric spark, in the powder vicinity. Moreover, the electrical response of the granular medium has been studied by modifying its microstructural properties, i.e. initial thickness of the oxide layer on particles surfaces (via controlled reduction-oxidation treatments) and green density of granular compacts. Measured electrical behaviors have been correlated with microstructural evolutions using fine characterization methods such as SEM-FIB. This experimental methodology allows decoupling the effects induced by the electric and magnetic components of the pulsed current imposed during SPS process.

# Production and recyclation of large REBCO sputtering targets

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## Abstract:

With the constant growth in the production of coated conductor REBCO tapes (CCs), the demand for REBCO sputtering targets has also been steadily increasing. The current production capacities will not be able to meet the demand of CCs in upcoming years. The production of REBCO targets is very tricky, as the peritectic decomposition of the main superconducting phase ($REBa_2Cu_3O_x$) is very close to the sintering temperature. In this work, the optimization of precursor powder and process parameters for conventional sintering has been studied. Furthermore, field-assisted sintering technique (FAST) and hot pressing (HP) have also been studied as a means to significantly scale up the production. Finally, the novel method suitable for R&D purposes "target infiltration" was developed. Last but not least, a general recycling technique for REBCO materials will be presented as a means of addressing the shift in phase compositions in the remains for used sputtering targets.

## Acknowledgements:

This work was supported by the Czech Science Foundation, grant number 20-03253S and Ministry of Industry and Trade, program TRIO, pro-ject no. FV40201

# Exploring the potential of Calcia (CaO) dopant for the stabilization of Tetragonal and Cubic ZrO2 nanoceramics as an alternative to Yttria (Y2O3)

Aditya Arun, Lakshaman Kumar, Anirban Chowdhury

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## Abstract:

Synthesis of 3 and 10 mol% CaO doped $ZrO_2$ nanoparticles using our novel "Burst nucleation" assisted co-precipitation technique yielded ultrafine particles with a mean particle size of 11 and 3 nm respectively, w/o usage of any surfactants/ligands. Dense (~97%) CaO-stabilised $ZrO_2$ ceramic was stabilized with minimum (3 mol%) doping (reported to date) and processed via conventional sintering at a low temperature (~1200°C); compositional analysis via X-ray fluorescence confirmed the CaO doping accuracy. Phase-pure tetragonal structure (characterized via both X-ray diffraction and Raman spectroscopy) along with uniform nanograins (90 nm) of the ceramic ensured the evolution of no monoclinic phase even after vigorous low-temperature degradation experiments (both thermal and hydrothermal aging for 80-100 h). The sintered ceramic recorded a high hardness value (~15 GPa). The remarkable structure-property correlations in the 3 mol% CaO-stabilised $ZrO_2$ ceramic suggest that the same may be worth examining for suitable future applications (e.g., in dental ceramics). 10 mol% CaO doped $ZrO_2$ ceramics with near theoretical density (~100%) obtained at just 15 minutes dwell time during conventional sintering (at 1500°C). The ceramics showed a mixture of cubic (83 wt.%) and tetragonal phase (17 wt.%) through Rietveld analysis. Sintered ceramics showed a high hardness value (~14 GPa) compared to previously reported cubic CaO doped $ZrO_2$ ceramics; small grain size (Mean grain size: 0.9 μm) was a key factor to achieve this. Crystal phase, hardness, and toughness of 3 mol% CaO doped $ZrO_2$ ceramic were comparable to a 3 mol% yttria-stabilized zirconia system. The sintered 10 mol% CaO doped $ZrO_2$ ceramics showed comparable hardness and toughness with popular 8 mol% $Y_2O_3$ doped $ZrO_2$ ceramics (8YSZ).

## Acknowledgements:

Aditya Arun and Lakshaman Kumar are indebted to the financial support provided by the Indian Institute of TechnologyPatna.

# Design and elaboration of Polymer-Derived Silicon Oxycarbide (SiOxCy) parts by Stereolithogtaphy (SLA)

Anthony Ballestero[1], Laurence Boyer[1], Florent Deliane[2], Cécille Dulucq[2], Natacha Duée[2]

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## Abstract:

Because of its high accuracy, Stereolithography (SLA) is an Additive Manufacturing process that enables to build complex shapes with high performance materials. This process is a layer-by-layer method based on the local and controlled curing, of a photosensitive feedstock after an UV exposure with an appropriate wavelength

Today, the main strategy to shape high performance ceramics by SLA is to use a resin made of ceramic particles dispersed in photopolymerizable monomers and oligomers. On account of the absorbance of silicon oxy-carbide particles in the UV wavelengths, $SiO_xC_y$ ceramics are difficult to elaborate by SLA. To get round the problem, the Polymer-Derived Ceramics (PDCs) route seems to be a convenient way to obtain $SiO_xC_y$-based printed parts because it deals with a polymer instead of a loaded paste. These polymers present the advantages to be custom tailored in liquid state and to react under UV light enabling their photopolymerization and combines the properties of a polymer feedstock and the ability to be converted into ceramic materials such as (oxy)-carbides by a thermal treatment.

RESCOLL and the CTTC have jointly developed a new smart resin which offers a long-term stability and the ability to be processed under UV light and sintered to get $SiO_xC_y$ ceramic structures.

We will present synthesis formulation (stability, rheology and reactivity), definition of printing parameters, photopolymerization and optimal shaping and thermal treatment for the conversion into ceramic. Characterizations and properties of the final ceramic part will also be discussed.

## Acknowledgements:

The authors want to acknowledge the Nouvelle- Aquitaine region for the financial support.

# 3D printed proton-conducting substrates for hydrogen separation

Andrea Bartoletti[1], Alex Sangiorgi[2], Angela Gondolini[2], Elisa Mercadelli[2], Alessandra Sanson[2]

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## Abstract:

Ceramic composites based on Barium Zirconate-Cerate perovskites have recently received renewed interest as high temperature proton conductors as membranes for $H_2$ purification and membrane reactors for their full selectivity, high thermal and chemical stability, and intrinsic lower cost in respect to the Pd–based technology. The microstructure of the substrate plays a fundamental role to increase the gas diffusivity through the porous support. In this work, BCZY-based supports were manufactured for the first time through direct ink writing (DIW). Honeycomb-type geometries were designed as ideal porous membrane supports, due to the possibility of combining low pressure drop and high gas diffusion rate with suitable mechanical resistance. Different inks preparation methods were evaluated to obtain high solid loading (> 40 vol%) "green" suspensions (water based or solvent-free). Printable inks with optimal shear thinning behaviour were successful microextruded through 410 μm diameter nozzle, depositing up to 3 stacked layers without shape modification, structural collapse or nozzle clogging. Drying and thermal post printing treatments were carefully optimized to obtain defect-free and easy to handle green bodies. The optimization of the whole process leads to BCZY-based supports with a high degree of engineered porosity.

## Acknowledgements:

This work has been funded by the agreement between the Italian Ministry of Economic Development and the Italian National Research Council ''Ricerca di sistema elettrico nazionale''

# Additive manufacturing of ceramic components by fused deposition modelling technology.

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## Abstract:

Fused deposition modelling (FDM) is one of the AM processes in which a thermoplastic filament is extruded through a nozzle and deposited in semiliquid state in the form of roads to fill each layer of the 3D part on to a platform. Depending on the feedstock materials this low-cost technology can be widely used not only for hobby purposes but also for structural and high-tech applications. The aim of this study was to develop, and test composite filaments highly filled with Al2O3 powders for additive manufacturing of 3D ceramic prototype (e.g. Ceramic Package for Electronic Devices) with max dimensions of 50 x 50 x 30 mm using FDM technology. Within this work, two composite filaments with different alumina powders with different surface area and average particle size were developed, manufactured, and used for feasibility study of 3D printing of ceramic objects. Both filaments were first used for the printing of cylinders which were applied for the determination of bulk densities after each processing step (3D printing, debinding and sintering). Results revealed the maximum relative density of sintered cylinders prepared from fine grade alumina reached up to 94 % at 1500 °C for 5h depending on printing parameters. The microstructural analysis, coefficient of thermal expansion, thermal conductivity as well as mechanical properties were determined.

## Acknowledgements:

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# Formation and influence of plasma in flash sintering of ceramics

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## Abstract:

Flash sintering uses external electrical fields to achieve full densification of ceramics at lower furnace temperatures and in a shorter time, compared to conventional sintering. The reason for the rapid densification in flash sintering is still under debate and a variety of possible fundamental mechanisms have been proposed.

One mechanism, sometimes considered in flash sintering, is the formation of a plasma. In this research the possibility of plasma formation is investigated experimentally and discussed with respect to plasma theory. In particular, the formation of a plasma in the first stage of flash sintering and a change from indirect plasma heating to direct Joule heating can be achieved under certain conditions. Whether and how the plasma influences some of the final properties of the material is another issue which will be addressed in this presentation. Most of the results presented relate to plasma formation during flash sintering of boron carbide and silicon carbide but the possibility of a plasma formation during flash sintering of 3YSZ and other oxides is also investigated. The formation of such a plasma might be an explanation for several apparent contradictions presented in the literature, which are still controversial.

# Role of atmosphere during flash sintering of NiO/8YSZ composite

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## Abstract:

Composites of nickel oxide and 8 mol.% yttria stabilized zirconia (NiO/8YSZ) are widely used as anode materials in solid oxide fuel cells (SOFC) owing to their high catalytic activity towards oxidation of fuel gas, sufficient electrical conductivity, comparable thermal stability and chemical compatibility with other adjoining components. Fabrication of these composites, by conventional sintering methods, requires a relatively high temperature of 1400-1450°C with holding time of few hours. Flash sintering has recently emerged as an energy efficient sintering process to densify ceramic materials in a few seconds, at relatively low furnace temperatures. In this context, this work assesses the viability of using flash sintering technique to densify the NiO/8YSZ composite. Two different composites with varied NiO content i.e, below percolation limit (10 vol. % NiO) and above percolation limit (50 vol. % NiO) were processed in this study. The densification behavior and microstructure of the flash sintered samples was investigated in detail. Furthermore, the influence of the oxygen partial pressure on the onset of flash temperature, densification and microstructure of the composite sample was systematically studied. During flash sintering, the extent of densification in the composites was influenced by the NiO content and the sintering atmosphere. With careful optimization of the processing parameters, nearly full densification of the composites was achieved in air at a furnace temperature of 900°C and in just 30 s of hold time. Nevertheless, this was a preliminary investigation to understand the densification behavior of the composite. Real operation of the sintered components under SOFC conditions in not the focus of the present work.

## Acknowledgements:

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# Gadolinium-doped ceria electrolytes by ultrafast high-temperature sintering

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## Abstract:

Ultrafast high-temperature sintering (UHS) is an emerging consolidation technology that allows densification of ceramic components within a few minutes under extreme heating/cooling conditions. Gadolinium-doped ceria (GDC) is one of the most "popular" oxygen ion conductors, with potential application in intermediate temperature solid oxide fuel cell (SOFC), although it is characterized by relatively low sinterability by conventional heating usually requiring several hours at about 1400-1500°C.

Herein, we explored the opportunities offered by UHS for manufacturing dense GDC-based ceramic electrolytes. Both commercial and chemically synthetized (oxalate synthesis) GDC powders were considered. The microstructural evolution of small pellets produced by uniaxial pressing was studied as a function of UHS parameters. Preliminary impedance spectroscopy characterization of the ceramics was also carried out. The results show that UHS allows the production of dense components in a short time with attractive electrochemical properties. In particular, some results point out the activation of oxygen conductivity at extremely low temperatures after UHS.

As a proof-of-concept, a symmetrical SOFC constituted by GDC electrolyte sandwiched between Sr-Co ferrite electrodes was also consolidated by UHS.

## Acknowledgements:

The work is supported by Caritro Foundation (Cassa di Risparmio di Trento e Rovereto) within the project "Innovative processing routes to green high entropy ceramics with enhanced functional properties (HiEnCer)".

# A novel approach to processing of doped hafnia ceramics

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## Abstract:

Doped hafnia is an interesting candidate as an electrolyte for potentiometric sensors in sodium. However, the processing methods described in the literature seem unable to reach the microstructure specific for this application: high purity, micrometric grains, high density, almost full fluorite structure for high ionic conductivity. Two novel synthesis routes were then proposed based on wet chemistry processes. The cations ($Hf^{4+}$ and $M^{3+}$ dopants Gd or Y) were precipitated as hydroxide nano-crystallites with ammonia or as oxalate with oxalic acid. Several dopant rates were tried from 10 to 30 % (moles of cations). The powders were then calcined at 700 °C to obtain oxide, with high specific surfaces (25 $m^2.g^{-1}$).

The fluorite phase was the only one found in calcined powder coming from hydroxide precipitation, whereas monoclinic phase was also detected through the oxalate route. Then, only the powders from hydroxide route were pressed in pellets and sintered at 1600 and 1800 °C. After sintering, the low doping rate pellets with both dopants exhibit two phases, while only fluorite was detected above 20 %. The lattice parameter of the cubic phase was found to increase only above 20 % of dopants. The density after sintering was poor at 1600 °C. Dilatometric studies indicate that the shrinkage was not achieved at 1600 °C. A better result was obtained at 1800 °C with 20 % of Y.

# New water-thinnable acrylic polymeric binders in processing of BST/polymer composites

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## Abstract:

BST/polymer composites are very attractive for many applications since they combine properties which are typical for polymers, like good flexibility and forming capability, with high electroactivity responses of BST. In order to meet the expectations of high-frequency technologies, it is necessary to develop a material with sufficiently low stresses that will allow movements of the ferroelectric domains in the polymeric matrix. However to create a composite material with the best properties, it is necessary to optimize their composition and the process of their production. The properties of the BST/polymer composite depend to a large extent on the polymeric binder used in their processing. Chain length of polymers, glass transition temperature and variable hydrophobic to hydrophilic polymer part ratio will effect on the rheological behavior of ceramic suspensions and on the mechanical and electrical properties of the BST/polymer composites.

In the research the ceramic-polymer composites based on barium-strontium titanate and water-thinnable acrylic polymeric binders were investigated. Barium strontium titanate was synthesized by the high temperature solid-state reaction. Polymeric binders were synthesized using emulsion polymerization process from acrylate monomers with different chemical structure. The ceramic-polymer composites were obtained by tape casting. The properties of the synthesized BST powder and the influence of the chemical structure of the polymeric binder on the rheological properties of the slurries and on physicochemical and electrical properties (characterized by Broadband Dielectric Spectroscopy) of BST/polymer composites were investigated.

## Acknowledgements:

This work was financially supported by the Polish National Science Centre, project No 2018/30/Q/ST8/00205. Research has been conducted within Polish-Chinese International Collaboration.

# LTCC tapes for a new generation of SICER silicon-ceramics composite substrates

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## Abstract:

Silicon and LTCC tapes (Low Temperature Cofired Ceramics) are standard substrate materials in micro sensors and microsystems technology. Established methods of micro-technology, as well as methods of assembly and connection technologies can be applied to both materials, resulting in efficient microsystems fabrication options for various product areas. Through combination of both materials into a common SICER substrate system, micro systems with significantly higher complexity might be developed.

Subject of the research project High Performance Sensors (HIPS) is the development of an inorganic platform for highly integrated electronic systems with extended sensor functionality. It is based on a composite sintered substrate at wafer level, which consists of silicon and a glass-ceramic LTCC multilayer laminate. It also enables applications of the SICER substrate with higher operating temperatures, such as IR emitters or thermally activated gas sensors.

The LTCC technology is a state-of-the-art technology that allows to fabricate integrated multilayer circuits that enable completely new interconnection and packaging solutions. The LTCC green sheets are mechanically structured, printed with metal thick-film pastes, laminated and sintered at about 900°C.

The poster presents a new LTCC material developed for the SiCer technology. The required glass- and ceramic powders were selected and a composition that enables a CTE adapted to Si was calculated and experimentally validated. The preparation of the casting slurry was carried out with these compositions. Casting experiments were performed which allows to provide 6“ceramic wafers for the SiCer process. A continuous casting process for green tapes with a width of 300mm and thicknesses of 50-200 µm was developed.

## Acknowledgements:

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# Effect of physical and geometrical parameters on the stability of flash sintering and the quality of flash sintered parts

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## Abstract:

Flash sintering of ceramics results from the simple application of an electric voltage to a preheated compact of conductive ceramic, without mechanical load. This apparent simplicity indeed hides a set of coupled phenomena that make the technique difficult to control. The intrinsic electro-thermal instability tends to amplify any defect of the material, thermal losses at sample boundaries or power supply. The viscoplastic deformations associated with rapid densification during sintering also contributes to make the process sensitive to boundary conditions. Making the original technique a real a manufacturing process for ceramics therefore remains an issue.

A finite element model was developed for describing the flash sintering of single component or multilayered cylindrical compacts. The model takes into account the coupling the 3 aspects of the process: electrical, thermal and mechanical (densification by sintering and viscoelastic behavior). The numerical simulations have been associated with experimental work on single component pellets and multilayer parts of different ceramics such as 3YSZ and typical battery components (LCO, LATP, LVP).

On this basis and with the background of recent literature, the paper will examine and discuss the effect of physical mechanisms, materials properties, geometrical and process parameters on the densification behavior of the specimens during flash sintering with a view to making this technique a manufacturing process for ceramics.

## Acknowledgements:

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# Fast processing of complex ceramic components by robocasting and microwave sintering

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## Abstract:

The CERAPIDE project* investigated the fabrication of complex ceramic parts from submicronic alumina and zirconia powders, including shaping by robocasting and consolidation by microwave sintering. Robocasting (also called Direct Ink Writing) is a 3D printing technique that produces complex objects by depositing successive layers, wire by wire, of a powder-filled paste. Various paste compositions were characterized by rheometry and printed. The features determining the printability of a paste, i.e., its ability to provide precise and flawless parts, were then identified. Notably, polyethylene glycol was found to be a promising alternative to the widely used Pluronic. Also, several strategies to process composites and multi-materials were developed. Microwave sintering, which takes advantage of the coupling of ceramics with an oscillating electromagnetic field, is attractive because of its speed and energy efficiency. Two procedures were compared, direct microwave heating and indirect heating assisted by silicon carbide susceptors. In direct heating, the major role of the dielectric properties of the material, which determine its microwave-coupling properties, was highlighted and the control of the sintering of both powders was found to be very difficult for distinct reasons. In contrast, indirect heating allowed the sintering of parts with various shapes, architectures and compositions (alumina, zirconia, composites) in a controlled, efficient and homogeneous way and in very short times (10 to 20 min), provided the susceptors are properly positioned. The microstructure and the mechanical properties of the sintered parts were found to be suitable and even comparable to classically processed materials.

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## Acknowledgements:

Agence Nationale de la Recherche

# The study of diamond regrowth in High-Pressure High-Temperature sintered polycrystalline diamond materials

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## Abstract:

High-Pressure High-Temperature (HPHT) sintered polycrystalline diamond (PCD) material has been applied in the oil exploration and mining industries due to its superior wear resistance and excellent fracture resistance[1,2] One factor that can affect these mechanical properties is the diamond regrowth during sintering. The regrown diamond will connect the isolated diamond grains to form an integral structure while breaking the continuous binder phase into individual islands during the HPHT sintering. It is claimed that the regrown diamond shows a low defect density, including, colour centres such as the NV centre, dislocations, twinning and stacking faults. However, little attention has been paid to qualitative and quantitative identification of differences in the regrown diamond between PCD materials. Based on these different characteristic defect densities between original and regrown diamond, in this work we study the regrown diamond by various characterization techniques, including SEM-FIB tomography, EBSD, hyperspectral cathodoluminescence and TEM. The characterization results are compared and correlated with one another. The results indicate that the regrown diamond could have been partially plastic deformed, causing the identification of regrown diamond to be more difficult. Other methods, such as the connectivity, shape and the area-to-volume ratio of binder pools, may provide an indirect way to study the regrown diamond.

# Chemical modification of silicon carbide precursors for Direct Ink Writing

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## Abstract:

There is a trend toward more performant or competitive materials with the objective to improve the efficiency of actual systems and to repel technological boundaries. Carbides can be considered as such strategic materials. They attract increasing interest due to their properties targeted for future materials and technologies especially in aerospace. Inherent difficulties to the traditional techniques for manufacturing such dense materials with a complex geometry can be overcome by the development of new manufacturing approaches on the first hand, and the deployment of synthetic paths where chemistry of materials and ceramic science are combined rationally to process multi-scale complex solid state architectures. This second part can be investigated by the Polymer-Derived Ceramics (PDCs) route, which offers new opportunities in ceramic sciences. The molecular origin of preformed preceramic polymers such as polycarbosilanes and the possibility of modifying them to be then shaped and transformed into advanced ceramics such as silicon carbide (SiC) play a major role in the elaboration of ceramics endowed with properties that reach far beyond those of existing materials. Here, the aim of this work is to modify SiC precursors with boron and/or nitrogen elements to fit in various manufacturing techniques including Direct Ink Writing technologies (such as Aerosol Jet Printing) and design SiC components with complex shapes at relatively low temperature. The chemistry behind the synthesis and pyrolysis behaviour of these polymers as well as their processability will be presented and discussed. The characterization of the materials will be done at each step of their elaboration process. As a proof of concept, we will introduce Aerosol Jet Printing realizations.

## Acknowledgements:

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# Nanostructured rutile TiO2 ceramics fabricated by High Pressure Spark Plasma Sintering : effect of high pressure on physical densification phenomena

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## Abstract:

Rutile is the most common and stable polymorph form of titanium oxide $TiO_2$ at all temperatures. Nanocrystalline $TiO_2$ has attracted increasing interest as a ceramic. For example, the doping of rutile $TiO_2$ with a small amount of niobium is known to induce a large increase of the electrical conductivity, broadening its technological interest towards new emerging fields such as the thermoelectric conversion of waste heat. In this work, high-density bulk $TiO_2$ was fabricated from a nanopowder of anatase $TiO_2$ by high pressure spark plasma sintering (SPS) technique. It is shown that by applying high pressure (76 MPa to 1 GPa), densification and phase transition start at lower temperature and are accelerated. Thus, it is possible to dissociate the two densification steps (anatase then rutile) and the transition phase during the sintering cycle. Regardless of the applied pressure, grain growth occurs during the final stage of the sintering process. However, twinning of the grains induced by the phase transition is enhanced under high pressure resulting in a reduction in the crystallite size. Thus high pressure SPS technique has allowed to vary the grain size of pellets from 300 to 170 nm. The sintering behaviour of $TiO_2$ doped with Nb concentration of 2% and un-doped are studied. It seems that t its presence at grain boundaries modify densification behaviour and grains growth kinetics. Grain growth activation energy has been calculated to show the impact of pressure during sintering thermal treatment.

# Net-shape zeolite monoliths by bulk crystallisation of 3D printed aluminosilicate slurries

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## Abstract:

Zeolites are microporous aluminosilicate materials which are widely used in industry as catalysts or adsorbents due to their significant Specific Surface Area (SSA), thermal and chemical stability and the exceptional selectivity induced by the highly ordered nature of their porosity. Their synthesis, however, usually proceeds through the hydrothermal treatment of dilute aluminosilicate suspensions, with low yield and high costs.

The authors present here a novel two-step route to produce net-shape zeolite monoliths by Additive Manufacturing. In a first step concentrated aluminosilicate slurries are subjected to mild heat-treatments in non-hydrothermal conditions to induce bulk crystallisation of zeolites; depending on the slurry composition and choice of reagents, either zeolite Na-X or Na-A can be obtained with negligible amorphous residues. The product is milled into a powder and added as a solid filler to a second slurry, allowing to modify the rheological properties and achieve a high viscosity suitable for 3D printing through the Direct Ink Writing technique without introducing extraneous components into the final material. After shaping, the monoliths are subjected to the same crystallisation treatment yielding net-shape zeolite components; by altering the composition of the second slurry a tuneable fraction of amorphous binder can be conserved in the final monoliths, providing mechanical cohesion and the ability to better withstand aqueous environments for successive functionalisation steps such as ion exchange.

The final 3D printed monoliths contain a significant fraction of zeolite Na-X or Na-A (60% or higher, depending on the amorphous binder content) and display high SSA and $CO_2$ adsorption capacity, making them attractive for applications such as Carbon Capture.

# Hybrid additive manufacturing for the fabrication of freeform silica glass components

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## Abstract:

AM of ceramics has been developed extensively over the past years. A deeper understanding of the various technologies has revealed their specific strengths and limitations: DIW, for example, requires an ink with a distinct rheological behaviour in order to retain the shape once extruded and is limited in the choice of geometries. With DLP, consolidation depends on UV light absorbance by the photocurable molecules; suspended particles scatter and absorb light, decreasing the resolution and the curing depth. Here, the prototype of a hybrid DIW-UV AM process will be presented as an attempt to overcome the limitations and exploit the benefits of both technologies. Thanks to their combination, it is possible to extrude a filament able to maintain its shape thanks to the photo-polymerisation of its outer shell, avoiding the fine-tuning of the ink rheology as well as any light scattering issue. A system composed of an UV LEDs array mounted over the printer head of a DIW equipment was developed. Complex and free-forming shapes were fabricated after the formulation of a photo-curable colloidal silica-based suspension. TEOS was employed as additional silica precursor. TEGDA/HEMA and HEMA/POE ratios were optimized to produce an ink with adequate rheological behaviour, reactivity and ceramic yield. Transparent glass components were obtained upon debinding and sintering heat treatments.

## Acknowledgements:

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# Enhancing the geometrical capabilities and performance of functional ceramics fabricated with Freeform Injection Molding

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## Abstract:

The distinct characteristics of ceramics in terms of material preparation, processing and geometrical capabilities are setting limits on their performance and application potential. Process development is an important aspect that will determine the future of innovative ideas. The use of water-soluble, 3D-printed moulds has established a novel manufacturing approach capable of producing freeform geometries with Ceramic Injection Molding (CIM). The single-cavity mould can offer the advantages of numerous design iterations at a reduced cost and lead times, with remarkable material versatility. We expand the material portfolio to customised feedstocks and different material formulations, aiming to produce functional parts for advanced applications. We examine the process capabilities of Freeform Injection Molding (FIM) in terms of geometrical complexity, quality of 3D structures and characterisation of functional piezoelectric properties in Pb-free ceramics. The challenges encountered are crucial for their functional properties, and we present the approaches adopted to improve their performance with material development and process parameters optimisation.

## Acknowledgements:

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# Surface Reactivity and Processing Properties of Metal Oxide Nanoparticles for Ceramics

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## Abstract:

Powders of composite metal oxide nanoparticles are promising starting materials for nanoscale grained ceramics with improved functional properties. A major challenge in their utilization is related to the control over characteristic material properties and associated changes these materials undergo during processing of particle powders to ceramics.

We compared MgO nanoparticles with and without Ba admixtures. Vacuum annealing of Ba-Mg-O nanoparticles induces Ba segregation and produces compositional gradients.[1] The enhanced surface reactivity promotes particle coarsening and produces a bimodal particle size distribution with a fine fraction of morphologically well-defined particles below 10 nm and a coarse fraction of larger and less-defined particles. Exposure to water vapor at room temperature leads to a size dependent dissolution of Ba-Mg-O nanocrystals and to their transformation into hydroxides with altered microstructures.[2] The impact of surface impurities on sintering will be discussed.[3] This study underlines for dispersed materials of enhanced surface reactivity that adsorption of components from the ambient significantly affect sintering properties and resulting microstructures.

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[3] Bourret, G.,R.; Diwald, O.; J. Mater. Res. 34 (2019) 428-441; DOI: 10.1557/jmr.2018.429

## Acknowledgements:

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# Large Scale Binder Jetting of Inorganic Components Using a Geopolymer

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## Abstract:

Additive manufacturing of construction materials is an innovative, challenging research field, with the potential of producing parts with complex structures, and specific functional or structural properties. In the current research, a large-scale binder jetting printer was employed to fabricate geopolymer-based components. The printing bed was comprised of lightweight aggregates, reactive metakaolin, and waste materials, which were activated by the selective deposition of an alkaline solution (silicate-based solution). The reaction parameters were controlled to achieve an adequate setting time enabling rapid printing with the suitable resolution, and the building up of a structure at the macro-scale (meter-size). The main chemical, physical and mechanical characteristics of the printed parts were investigated. This work was carried out in the framework of the IDEAL project (Industrial ResiDues for Smart FirE-resistAnt PhotocataLytic Components; KAVA Reference Number: 19040).

## Acknowledgements:

This activity has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under the EU Framework Programme for Research and Innovation, Horizon 2020. This work was carried out in the framework of the IDEAL project (KAVA Reference Number: 19040).

# The investigation of ZnO dopant on flash sintering of 3YSZ: Grain growth with electrochemical reactions

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## Abstract:

Conventional sintering of Zirconia ceramics typically requires a high temperature and long soaking hours. Recently, Flash Sintering (FS) one of the new methods of field-assisted sintering has shown tremendous promise in reducing the sintering time and the temperature. However, significant heterogeneity in densification was observed in the flash sintered sample. In this work, we investigated the effect of ZnO dopant on the microstructural heterogeneity in flash sintered 3YSZ. Detailed microstructural analysis were performed at the cross-sectional and longitudinal sections of the samples. Heterogeneity in grain size across the sample was observed in ZnO doped 3YSZ. A substantial increase in grain size was observed with an increase in dopant concentration. With the addition of 2 mol% ZnO dopant in 3YSZ, a small improvement in densification and significant prevention of sample cracking was observed. The extent of electrochemical blackening was observed to be increasing with the increase in dopant concentration. The blackened phase was analysed with Raman in detail. The blackened phase was found to be distorted tetragonal Zirconia which revert back to the tetragonal phase after thermal treatment.

## Acknowledgements:

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# Engineering of ceramic oxides microstructures using low temperature reactive sintering processes and Flash SPS

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## Abstract:

Among many materials present in our daily lives, technical ceramics occupy numerous fields. Their applications go from energy, biomedical to transport (automotive, aeronautics, space, etc …) sectors.

In the last decades, the development of more energy efficient and environmentally friendly manufacturing processes has encouraged intensive research on low-temperature and/or ultrafast sintering processes. These efforts have led to the elaboration of new materials, multi-materials and composites for applications in different socio-economics fields.

In this communication, we will discuss the original strategies developed and demonstrate the possibility of producing oxides nanostructured ceramics with engineered grain boundaries (alumina, $Al_2O_3$; lanthanum phosphate, $LaPO_4$; stabilized zirconia, 3Y-$ZrO_2$) by reactive sintering of hydroxide precursors using low-temperature processes (HP-SPS and CSP) or Flash-SPS of oxide powders. The mechanical properties of the nano-ceramics obtained are discussed with regard to their structures and microstructures.

# Flash sintering of Li3V2(PO4)3, a mixed cationic/electronic conductor as an electrode active material for Li-ion All-Solid-State Battery

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## Abstract:

Flash sintering (FS) is an ultra-fast current-assisted densification technique which is an attractive tool for the shaping of energy material multilayer system. Various studies showed the feasibility of FS with oxygen vacancies (like Yttria-doped Zirconia) or mixed (ionic/electronic) conductive materials, traditionally used for SOFC. However, very few studies deal with FS of purely $Li^+$/$Na^+$ cationic or mixed conductors as used in ceramic All-Solid-State Batteries (ASSB). Our previous work(1),(2) highlighted the need of a reversible electrochemical reaction to ensure charge transfer from the current collectors to the ion charge carriers in the ceramic. This reaction is easily obtained thanks to oxygen in air in the case of Yttria-Stabilized Zirconia, but not for purely cationic conductors. A simple way to allow the current flowing into a $Li^+$ electrolyte is to use an intermediate $Li^+$/$e^-$ mixed conductor between the platinum electrodes. This system actually forms the architecture of an ASSB.

In this study, we focus on the process of FS with a mixed cationic/electronic conductor. We have chosen to use the mainly ionic $Li_3V_2(PO_4)_3$ (LVP) electrode material for its chemical stability with specific $Li^+$ electrolyte materials. Here, densification properties, microstructure, structural stability in temperature and conductivity of LVP are compared between conventional sintering and FS. Especially, the formation of hotspot during FS is analyzed, coupled with numerical simulation of the phenomenon. This study represents an important first step in the making of Li-ion ASSB by flash sintering.

## References

(1) Caliman, L.B. et al. J. Eur. Ceram. Soc. 36 (2016) 1253-1260.

(2) Lachal, M. et al. J. Amer. Ceram. Soc. (2021) 104(8), 3845–3854.

## Acknowledgements:

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# Additive manufacturing-assisted shaping of ceramics with complex shape

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## Abstract:

Successful production of advanced ceramics requires a connection of few factors such as application of high quality starting materials, shaping methods which allow near-net-shaped ceramics to be formed with tailored properties, good handling strength, good microstructural homogeneity as well as a limited amount of production waste. Hence, the shaping methods like gelcasting, slip casting, additive manufacturing (3D printing) are intensively developing. Due to low cost of equipments, relative ease of use and good mechanical properties of green and sintered samples, gelcasting seems to be a promising shaping method that meets the desired requirements.. However, the complexity of obtained sample strictly depends on complexity of used mold. Thus, only the combination of gelcasting with molds produced by one of the additive manufacturing methods will provide a sufficient elasticity and efficiency in manufacturing of complex shaped ceramics.

In this work, the new approach to Jinlong Yang et al. modification of gelcasting procedure was proposed [doi.org/10.4028/WWW.SCIENTIFIC.NET/KEM.280-283.739]. Thanks to that it was possible to simplify the process by increasing the initiator amount what significantly decreases the gelation time and in such a way reduce an influence of oxygen inhibition on the condition of green bodies. The proposed solution also facilitates the application of gelcasting in production. In contrast to the classic gelcasting, there is no need to use all prepared ceramic suspension during one casting. Casting procedure can be now freely stopped and even postponed for several hours or days. The application of 3D printed forms allows obtained a complex shaped molds followed by complex shaped green bodies and sintered parts.

## Acknowledgements:

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# Using Organic Acids to Densify Ceramics

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## Abstract:

Cold sintering process was used to fabricate dense monolithic samples of zinc oxide. A series of organic acids were used to compare the impact on densification, tensile strength, and microstructural evolution. Dense ceramics were achieved with relatively high densities (>90%) and high tensile strengths (80-100 MPa) using organic acids solutions as transient solvents, mild temperature (<150 °C), and under pressure for 30 minutes. The microstructure of the sintered pellets was characterized through SEM to study average grain size, triple points, coarsening and necking. We report that the tensile strength was comparable to conventionally sintered samples, achieved at 1000 °C. Phase purity was maintained, low amount of residual organics and water content in the cold sintered samples with content below <3%.

# Multiphysic and multiscale investigation of the setting process of hydraulic binders: the case of gypsum

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## Abstract:

Because of their setting ability, hydraulic binders are used in different applications (e.g. mineral construction materials, bone substitutes, ...).

Such process is continuous and always initiated by mixing one or several fine powders with an aqueous solution. The dissolution of the initial reactive powders results in the formation of a viscous and moldable paste, which properties evolve with time to form a porous monolithic ceramic through the nucleation and precipitation of more stable phases.

The need to control the rate of reaction and final properties requires the precise understanding of the setting process in a multiphysic and multiscale approach. This issue has already been addressed in studies that were somehow limited regarding one or several aspects:

- only one aspect of the setting process was studied (e.g. chemical reaction, evolution of the mechanical properties or of the microstructure), without looking at the other aspects.
- only one length scale was investigated when phenomena occur at multiple scales.
- the setting process was stopped at discrete terms, prior to characterization, preventing the follow-up of one specific sample.

In this study, gypsum plaster is studied in standard conditions (e.g. liquid to solid mass ratio), to develop in-situ and ex-situ multiphysic and multiscale characterization techniques to monitor the evolution of:

- the phase composition (rate of dissolution and precipitation) using XRD and FTIR,
- the microstructure using SEM and µ-CT,
- the mechanical properties using DMA, rheology and compression tests.

This panel of techniques enables to monitor and to correlate the different physical transitions occurring during the setting process and to draw a global picture of the on-going phenomena.

## Acknowledgements:

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# Effect of Sodium on phase transformation of alumina

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## Abstract:

Alumina is the most advanced ceramic material that is highly available powder, and g-alumina is the most common alumina phase. To obtain high-density ceramic, gamma-alumina undergoes several polymorphic transformations. This phase consists of the transition phase of alumina, q-alumina, which occurs in a specific order before converting to a-alumina.

Although significant progress has been made so far in considering the effect of Na on the properties of alumina, its influence on gamma-alumina is still incomplete.

This work aims to investigate the effects of Sodium on the phase transformation of gamma-alumina. The transition behavior and the microstructure of the samples have been investigated. The results show that the ratio of sodium affects the transition behavior of alumina.

## Acknowledgements:

Prof. Dr. Mehmet Ali Gulgun

# Mechanical activation and HIP of ZrB2-TiB2 based composites for hypersonic system

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## Abstract:

Ultra-high temperature ceramics, such as $ZrB_2$, are convinient for application in hypersonic systems due to melting point higher then 3000 °C and excellent ablation resistance. For such application further improvement by addition of second phases, including SiC or $CrB_2$, has additional benefits in domain of oxidation behavior, while $TiB_2$ doping reduces material's weight. A powder mixture of $ZrB_2$, $TiB_2$, $CrB_2$ and SiC was high energy ball-mill trough four steps. Obtained milled powder was subjected to hot pressing following different thermal cycles. Subsequent annealing was applied to remove oxide phases and reduce micro-cracking. Due to different termal treatment, various microstructure and hardnes were occure. We reached fully dense ceramics, and with different oxide-phases content depending on sintering conditions. Maximal obtained hardness was 24 GPa. Ongoing activity regards the study of the strength and oxidation resistance to assess the suitability of this multi-phase system for hypersonic applications.

## Acknowledgements:

This study was performed and financed within NATO project SPS G5767 - "Super Strong Ceramics for Protection in Harsh Environments and DefenCE" (SUSPENCE)

# Paste rheology, photopolymerization and mechanical behaviour of tough ceramics prepared by Stereolithography

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## Abstract:

Ceramic laser stereolithography (SLA) offers a high degree of design freedom and resolution required for the design of complex and dense ceramic pieces, notably useful for implants development. In this context, we will discuss here three SLA aspects of prime importance: I) the paste rheology, II) the photopolymerization and III) the mechanical behaviour of dense SLA-ceramics.

SLA pastes are made of numerous organic components including a high content of ceramic particles (ca. 50 vol.%) making their mechanical response quite difficult to rationalize without a fine structural analysis, particularly while flowing. To address this question, we ran rheological investigations with the aim of: 1) providing quantitative parameters describing the paste "printability", 2) characterizing the paste ageing behaviour and their possible reuse over one year, and 3) understanding particle restructuration under shear stresses.

Besides, the laser energy received per element of volume has been estimated in order to better understand the effects of printing parameters and laser pattern on the photopolymerization of the paste. Solidification was investigated by FT-IR, NMR and compared to Jacob's equation results. In particular we made emerged superimposed Jacob's linear regressions for samples printed with different laser parameters, showing that there are several ways to adjust these parameters to achieve the same energy and solidification degree. In addition, a high correlation between depth of polymerization and monomer conversion supports the existence of equivalent printing programs.

We finally close this discussion by showing promising mechanical properties on dense ceramics prepared by SLA from a recently developed Ce-TZP-based paste.

# Fast and high resolution volumetric 3D printing of SiOC components

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## Abstract:

Light-induced additive manufacturing techniques, such as stereolithography (SLA), digital light processing (DLP) and continuous liquid interface production (CLIP), are among the most successful for the fabrication of ceramic components thanks to their high resolution; however, they all share the common motifs of pointwise or layered generation, which result into long printing time and inhomogeneity at the interfaces. Such limitations are overcome by volumetric 3D printing, i.e. the simultaneous 3D growth of a cross-linked object within a liquid volume.

We demonstrate for the first time the use of a volumetric 3D printing method named xolography for the fabrication of polymer-derived ceramic components. Xolography is a dual color technique, which uses photoswitchable photoinitiators to induce local polymerization upon linear excitation by intersecting light beams of different wavelengths. The technology has specific requirements in terms of viscosity, reactivity and transparency; therefore, it is not well suited for slurries but works best with all-liquid systems. We tested preceramic polymer formulations with ceramic yield ranging from $10\%_{wt}$ to $38\%_{wt}$. We optimized process parameters such as printing speed, UV radiation dose and photoinitiator-coinitiator amounts and successfully fabricated complex components with high resolution and short printing time, which convert to crack-free SiOC parts after pyrolysis.

# Novel approach to fabricate C/C-SiC by applying additive manufacturing based on the fused filament fabrication

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## Abstract:

Currently, ceramic matrix composites (CMC) are fabricated by subtractive manufacturing processes, like cutting, milling and grinding of semi-finish components. Additive manufacturing (AM) of CMC enables a cost reduced manufacturing process due to the near net-shape processing and the possibility to align the fibers in load direction for an optimized mechanical performance. Within this study, carbon fiber reinforced SiC (C/C-SiC) was fabricated by additive manufacturing, applying the fused filament fabrication (FFF) technique and the LSI-process (liquid silicon infiltration). Due to the FFF method it is necessary to use thermoplastic filaments. Therefore ("CF-PEEK") filaments with thermoplastic polyetheretherketone (PEEK) as the matrix and C-precursor, and carbon short-fibers ($< 250$ µm) as reinforcements were applied in order to fabricate the near net-shape CFRP (C-fiber reinforced plastic). In order to prevent the re-melting of the thermoplastic PEEK within the as-printed CFRPs during pyrolysis at 1000 °C, a prior crosslinking step below the melting temperature is required. Therefore, a dwell time of 48 h at 325 °C in air was introduced to stabilize and crosslink the CFRP. Due to the stabilization and the printing of degassing channels for the pyrolysis, near net shape and complex CMC parts were obtained by the liquid silicon infiltration process (LSI). The thermal induced crosslinking step with a variation of temperature and dwell time was characterized by differential scanning calorimetry (DSC). The microstructure and the flexural strength of C/C-SiC material were studied and promising results obtained, e.g. the C-fibers were preserved during the whole LSI-process and strength of almost 60 MPa were measured.

## Acknowledgements:

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# Efficient optimization of thermal processes in ceramic processing

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## Abstract:

Debinding and sintering are critical steps in ceramic processing with respect to time, cost, energy as well as product quality. Hence, significant improvements can be achieved by optimized heating cycles.

In order to minimize the efforts a modular approach has been developed for the optimization of a specific debinding or sintering process. The approach is based on a thorough understanding of the process and material requirements, precise material characterization and experimental data based finite element simulation. Finally the results are validated before transfer to the production facilities.

For example, whereas constant debinding rates, based on TGA-measurements and the kinetic field approach are sufficient for small components, more material properties like heat transfer, reaction enthalpies and gas composition as well as gas permeability and mechanical strength have to be evaluated as a function of temperature and the state of debinding for large components or high binder contents.

In sintering the determination of the sintering kinetics and the application of the kinetic field or a master sintering curve will improve the time-temperature cycle but deformation due to friction or gravity can only be simulated using material-, temperature- and state of sintering dependent viscous properties of the material. In order to include these data both experimental methods and FE-simulation have been improved.

The aim of the presentation is to explain and demonstrate the chosen approach and methods. This also includes the presentation of user-apps which have been recently developed to allow a simple on-site adaptation of heating cycles based on a characterized material systems for varying component geometries and process conditions.

# Homogeneous densification of large YSZ cylinders by Flash Sintering

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## Abstract:

The Flash Sintering (FS) process has raised a great interest in the past few years due to its ability to densify a large variety of ceramic materials in a few seconds and at lower temperatures than conventional sintering. The simultaneous application of electric and thermal fields allows an ultrafast densification and consequently a drastic reduction of time and cost of the sintering process.

Since the first article on FS published by Cologna et al. [1], yttria-stabilized zirconia (YSZ) is one of the most studied ceramic due to its ability to undergo the Flash phenomenon under suitable electric field and furnace temperature. Most works deal with dogbone shape, which mainly lead to small sintered samples. Moreover, a constant direct current is generally applied while the furnace temperature increases gradually. However, DC fields are known to produce polarity induced effects, which cause electrochemical reductions at the electrodes in the case of ionic conductors.

This study is focused on the Flash Sintering of large YSZ cylinders (green dimensions, 20 mm in diameter and 10 mm in thickness) in a furnace at constant temperature. Different parameters were tested: AC or DC current, current or voltage ramp (with respectively, limit in voltage or current), flash sintering duration. The influence of these parameters on the sintered samples was analyzed in terms of density and microstructure homogeneity.

[1] M. Cologna, B. Rashkova and R. Raj, 'Flash sintering of nanograin zirconia in < 5 s at 850°C', J. Am. Ceram. Soc., 3556–3559, 2010.

## Acknowledgements:

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# Flash Sintering of Alpha-SiC

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## Abstract:

Flash sintering produces high density specimens in shorter timescales and at lower furnace temperatures than are achievable through conventional, pressureless sintering methods. This work shows, for the first time, that pressureless flash sintering in an alumina tube furnace at 1500 °C can densify SiC to 96% T.D. in the solid state (B and C additives) in a few minutes. The sample temperatures required to achieve this were similar to conventional sintering temperatures of SiC (2100-2200 °C). The optimum processing conditions will be discussed (power limit, furnace temperature, hold time, thermal management and atmosphere) along with their effect on sample microstructure and mechanical properties (Vickers hardness, 3-point bend strength and SEVNB toughness). The Vickers hardness of the samples created using the optimised flash sintering conditions was 28.5 GPa ± 0.2 GPa, compared with 24.5 GPa ± 0.5 GPa measured for conventionally sintered specimens of the same powder. Preliminary investigation has shown that the increase in hardness was not directly related to grain size or density.

## Acknowledgements:

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# Printability by micro-extrusion of innovative alumina pastes, based on environmentally friendly additives

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## Abstract:

Additive manufacturing refers to a set of shaping processes enabling to build 3D ceramic parts with a layer-by-layer approach, by combining material and computer sciences. Among them, micro-extrusion process is based on forcing a paste through a nozzle whose inner diameter is at the submillimeter scale. The final quality of micro-extruded parts mainly depends on the rheological behavior of the paste, strongly related to the nature of organic additives.

The most common organic additives come from the petrochemical industry and are potentially harmful to the environment or operators' health. Hence, this project aims to develop an eco-friendly ceramic paste for micro-extrusion process, in accordance with green chemistry requirements.

The paste formulation was performed using alumina powder as a reference material. In order to satisfy the environmental needs, an aqueous medium with both natural dispersing agent and binder were chosen. Particular attention is paid to the chemical interactions between the additives, their influence on paste properties and printability. Porous scaffolds were printed by digitally controlling the movement of a homemade extrusion device, with a 400 µm inner diameter nozzle. After heat treatment, the sintered parts show a density up to 98%. Moreover, a study on the mechanical properties of dense parts is investigated by analyzing their microstructure after sintering and performing mechanical tests, such as four-point-bending tests.

The first promising results show the feasibility of 3D parts by micro-extrusion, with a ceramic paste having environmentally friendly additives. Process parameters and printing paths can be further optimized in order to reach more complex geometries, which are usually not achievable by conventional processes.

# Ceramic cores for reproducing internal cooling channels in high pressure turbine aircraft blades

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## Abstract:

High-pressure turbine blades with internal precise channels are manufactured by the investment casting process with the use of thin-walled ceramic cores of high accuracy with complicated shapes. The developed silica-based material for core fabrication satisfies rigorous requirements regarding mechanical strength, surface roughness, shrinkage, coefficient of thermal expansion, microstructure, pore size distribution and dimensional precision. The thin-walled ceramic cores were formed by the high pressure injection moulding method. The post-shaping process of the cores included water and thermal debinding, sintering, precision machining and dimension measurements. The cores machining after sintering required application of a specially profiled stand, tools selection and elaboration of parameters for machining, which protected the brittle cores from surface damage. The measurement process of the ceramic core was performed on a coordinate measurement machine with the use of a specially designed stand. The manufactured cores were positively verified in the process of high-pressure turbine blade casting under production conditions.

## Acknowledgements:

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# Investigation of densification mechanisms in Ultrafast High-temperature Sintering (UHS)

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## Abstract:

Ultrafast High-temperature Sintering (UHS) was proposed in 2020 by Prof. Hu et al. on sintering of LLZO. Like other pressureless fast firing methods, UHS allows consolidation of ceramics in a very short period, while showing a more controllable experimental condition. People have also reported that this method has the potential of creating finer gran size ceramics. However, the mechanism causing this abnormally rapid densification compared with conventional sintering remains under debate.

This research investigated the sintering behaviour of $\delta$-$Al_2O_3$ under different sintering condition using conventional sintering and UHS. For UHS, the specimen was heated up within a carbon felt under argon atmosphere, from room temperature to 1800K. $\delta$-$Al_2O_3$ densities of up to 99.8% were achieved in 60s using this method. The density and microstructure were characterised as a function of sintering conditions, enabling the sintering trajectory and Master Sintering Curve to be plotted according to the measured temperature profile. Compared with conventional sintering, UHS showed a different sintering behaviour, suggesting that a different densification mechanism may be taking place at earlier stages of densification. Possible explanations are discussed.

# Optimization of Alumina Toughened Zirconia Inks for Direct Ink Writing Applications: Rheological Characterization And Printability

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## Abstract:

Direct Ink Writing (DIW) is an extrusion-based additive manufacturing technique that allows to produce high-density ceramic parts with complex shape. A computer-aided design (CAD) model is used to control the movement of the nozzle, where ink is extruded, to build the object with high process precision. The extruded "ink" is determining for the quality of the printed part. One of the primary issues in DIW is extruding a continuous filament of ink without clogging the narrow nozzle while ensuring the shape fidelity.

To achieve the required rheological properties, the ink should behave like a viscoelastic fluid, so that the viscous (fluid-like) behavior is dominant during deposition and the elastic (solid-like) behavior is dominant after deposition. This can be achieved with the use of a gelation agent and/or a colloidal suspension. Gel-embedded inks do not depend on the particle interactions and therefore are more stable. Pluronic F127 hydrogel, a 3D hydrophilic polymeric network, is used in this study because of the easy control over its gelation behavior. The printability of the slurries with different solid loadings of alumina toughened zirconia ceramic powder is studied based on rheological properties.

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# Robocasting of piezoelectric ceramics

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## Abstract:

Ink formulation is one of the main challenges with ceramic 3D printing. Here, we present a new, reactive-colloidal hybrid ink for 3D printing by robocasting of $BaTiO_3$-based ceramics. The hybrid ink combines a titanium isopropoxide-based sol-gel base with a colloidal dispersion of powder, here demonstrated with $BaTiO_3$ both as the sol-gel (by reaction of titanium isopropoxide and barium oxide) and colloidal (by addition of $BaTiO_3$ powder) parts. Addition of glycerol was necessary to avoid fast precipitation and poor dispersion of $BaTiO_3$ from the re- action of BaO and Ti-isopropoxide. With a solid loading of 40 vol% $BaTiO_3$, 10 mm tall structures could be printed with minimal deformation from slumping. The $BaTiO_3$ shows good piezo-, ferro- and dielectric properties after sintering, with a piezoelectric charge coefficient ($d_{33}$ of 159 pC/N) in the range commonly reported for $BaTiO_3$. The hybrid inks developed in this work are therefore suitable for robocasting of $BaTiO_3$-based electroceramics.

# Pre-debinding processes of alumina parts printed by stereolithography

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## Abstract:

Indirect ceramic additive manufacturing techniques such as stereolithography (SLA) require the use of organic compounds for the formulation of feedstocks (resin, pastes…). However, these phases must be removed before sintering in order to obtain a dense ceramic part. This debinding process is generally carried out in a thermal way, at a slow heating rate, to allow time for the gases resulting from the decomposition of the organic material to escape from the raw part without damaging it. However, despite relatively long debinding times, obtaining defect-free parts remains a challenge. To solve this problem, pre-debinding cycles or specific treatments could be done before the thermal cycle.

The aim of this work is to assess the relevance of supercritical extraction with $CO_2$ (SC) as a pre-debinding step and compare it with conventional water debinding on SLA-printed parts. The influence of both soaking time (from 1 to 6 hour for SC and from 1 to 48 hours for water) and cubic specimen size (10 and 20 mm) have been evaluated by measuring the mass loss and performing TGA analysis. Supercritical extraction was carried out at 60°C under a pressure of 20 MPa in a dynamic mode to renew $CO_2$ atmosphere during the process. 10 mm specimen sintered after both water and SC pre-debinding showed no defect (delamination or cracks). However, 20 mm specimen showed delamination and broke during sintering. Surface specimen characterization has been performed by contactless rugosimeter and SEM analysis in order to evaluate the effect of pre-debinding treatment on pore formation. Considering soaking time and extraction time (limited at 6 hours due to used equipment) no preferential pre-debinding treatment has been clearly identified.

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# Rapid sintering of 3D-printed parts with exceptional high strength

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## Abstract:

Nowadays, numerous technologies for additive manufacturing (AM) ceramics are being developed, opening the path to fabricate ceramic components of high geometric accuracy and complexity. Stereolithographic 3D-printing technique is commonly used to print ceramics from slurries containing a relatively high amount of polymeric binder. As a result, debinding and further sintering of the printed parts are time and energy demanding processing steps, which may limit the mass production of certain ceramic products. In this regard, rapid sintering technologies, such as FAST or SPS have been recognized as a game-changer that can densify ceramics with fine-grained microstructures within a few minutes, raising the question on how the mechanical properties may be affected.

Whereas the mentioned rapid sintering technologies are limited to simple geometries, in this work, a pressure-less rapid sintering process was used to obtain the ability of rapid sintering ceramic parts of complex shapes. In a hollow cylindrical graphite die, alumina ceramics were sintered through radiation heat transfer within less than 20 minutes. It was investigated, how temperature and dwelling time effects microstructural, physical and mechanical properties. Dense, pure alumina with a grain size below ~0.5 μm could be manufactured, resulting in a biaxal strength ($\delta_0$=860MPa) 30% higher than that of conventionally sintered alumina parts. This increase may be associated with the fine-grained microstructure and low internal micro-residual stresses, opening the path to sinter complex 3D-printed alumina parts in very short times.

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# Successful Use Cases of LCM Ceramic 3D Printing in Industrial Mass Production

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## Abstract:

With 3D printing technology being adopted in more fields than ever before, the economic potential and capacities of additive manufacturing are rapidly expanding. Industry reports also forecast that the market for ceramic 3D printing will grow multiple times over the next few years and the implementation of ceramic AM is already creating geographically independent, yet globally connected 3D printing production systems. However, ceramic parts used in demanding applications must have properties including absolute precision, impeccable material quality and a zero tolerance policy in quality management, making the path to unlocking this potential very challenging indeed. This contribution will present exemplary real world use cases where it was possible to successfully optimize the LCM process to combine these material properties with the profit-oriented requirements of scaled-up industrial mass production. These use cases, including a successful manufacturer whose annual output now reaches 12,000 parts, will show how companies have already integrated 3D printing and digital production into their workflow and have entered into serial production of highly accurate and intricate 3D-printed parts. An assessment of the potential of ceramic 3D printing will demonstrate how far serial production in ceramic additive manufacturing has already come, while also looking at the future potential of this technology and where the industry is headed. Thus, this talk will also highlight key factors in successfully implementing ceramic AM into an existing company workflow, better understand the real potential of ceramic 3D printing systems and know the current status of LCM technology employment in industrial mass production.

# Graded ceramic solid-state electrolytes as an example of FAST/SPS-based research and production

Jens Huber

*Dr. Fritsch Sondermaschinen GmbH, Fellbach, Germany*

## Abstract:

Dr. Fritsch and the Fraunhofer institute IPA in Stuttgart, Germany, are partners in a research project for the development of new mixing and sintering techniques for the development of graded ceramic solid state electrolytes. While today´s Lithium-Ion cells are quite common, they show significant disadvantages which are not accepted by most consumers: limited storage capacity which results in a small vehicle operating range, the risk of explosion and the decrease of loading capacity which further decreases the operating range and also the value of the vehicle after some years.

However, a technology which is not accepted by consumers will not be successful in the long run.

The breakthrough may come if so-called "all solid state lithium-ion batteries" are successfully keeping what they promise. Ceramic electrolyte is in the focus of the research work because it offers many advantages. Oxide-based electrolytes (oxide and phosphate ceramics) are characterized by a good conductivity and high electrochemical stability when being in contact with the cathode material. Ceramic materials are usually hot pressed. However, the disadvantages of hot pressing such as long sinter cycle times of several hours, the energy intensive operation of the hot presses and the negative effects of the long exposure to heat on the material properties such as grain growth which results in poor homogeneity and lower density are not acceptable for the solid state battery applications. FAST/SPS reduces such issues to a minimum by drastically reducing the sinter cycle time. In this presentation the development of graded ceramic electrolyte is taken as an example for the multiple advantages which FAST/SPS sintering has got to offer for ceramic material development, not only for the battery industry.

## Acknowledgements:

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# Microstructural evolution of Inconel 625 – WC system in different heating condition

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## Abstract:

The research on Inconel 625 – WC composite obtained by laser cladding method proved that it is a promising technique of manufacturing of this type of composites. However, due to its complexity (in terms of elements present in the system), analysis of microstructure and phase composition of the material is challenging. To better understand how microstructure of the material evolves while exposed to different heating conditions, powder mixtures of Inconel 625 and WC were subjected to Differential Thermal Analysis (DTA). Total amount of six mixtures with different addition of WC powders (DWC1 ≈ 3,88 μm and DWC2 ≈ 6,13 μm) were prepared with addition of dextrin binder. Usage of DTA allowed for controlled heating rate of systems which allowed to determine how it affects microstructure evolution and hardness of the material.

This research was funded by National Science Center Poland, PRELUDIUM 13 grant “Protective composite coatings for high temperature applications obtained by laser-cladding method” number [UMO-2017/25/N/ST5/02319]. The funders had no role in the design of the study, in the collection, analyses, or interpretation of data.

# Reactive Laser Sintering of SiC coatings on Inconel 625 substrate

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[2] *Empa Swiss Federal Laboratories for Materials Science and Technology/ Laboratory for High Performance Ceramics, Dübendorf, Switzerland*

## Abstract:

The aim of the proposed research visit is to manufacture highly porous SiC ceramics by reactive laser sintering technique. The idea for reactive laser sintering came from combination of traditional methods of SiC ceramics production and development of Selective Laser Sintering (SLS) as an additive manufacturing (AM) method. SiC ceramics need high temperature in order to form liquid phase necessary for sintering. Because of that small amount of different sintering aids can be used to enhance their sinterability. In case of this research involving SLS method, reactants in form of SiC/Si/C were prepared in form of granulate. In order to obtain powders with desired morphology and flowability, spray drying was selected as a method of choice. Obtained spherical granulates were then sprayed onto Inconel 625 discs and subjected to laser treatment in Nitrogen atmosphere. Because of high absorptivity of Nd:YAG fiber laser wavelength ($\delta =$ 1064 μm) by SiC of about 80%, process is energy efficient. Conducted SEM-EDS, XRD and Raman spectroscopy analysis, showed presence of SiC, Si and small amount of $Si_3N_4$ in samples.

This research was funded by Swiss National Science Foundation, Scientific Exchanges grant "Reactive laser sintering of silicon based ceramics" number [IZSEZ0_201435]. The funders had no role in the design of the study, in the collection, analyses, or interpretation of data.

# Optimized spray granules for dry pressing by means of slurry destabilization and ultrasonic atomization

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## Abstract:

The homogeneous introduction of organic additives is a prerequisite for good processability of ceramic powders during dry pressing. The addition of organic additives by wet route via ceramic slurries offers advantages over dry processing. The organic content can be reduced and a more homogeneous distribution of the additives on the particle surface is achieved. In addition to the measurements of zeta potential and viscosity, sedimentation analysis by optical centrifugation was also tested and successfully used to characterize the ceramic slurries and accurately evaluate of the suitability of different types, amounts, and compositions of organic additives.

Spray drying of well-stabilized slurries usually results in mostly hollow granules with a hard shell leading to sintered bodies with defects and reduced strength and density. By purposefully degrading the slurry stability after dispersion of the ceramic powder, the drying behavior of the granules in the spray drying process and thus the granule properties can be influenced. Destabilization of the slurry and thus partial flocculation was quantified by optical centrifugation. Spray drying of the destabilized alumina slurries resulted in "non-hollow" granules without the detrimental hard shell and thus improved granule properties.

Further improvement of the granules was achieved by installing ultrasonic atomization in the spray dryer. A narrower granule size distribution was achieved, which had a positive effect on, among other things, the flowability of the granules.

Specimens produced from this granules had fewer defects of smaller size, leading to better results for the density and strength of the sintered bodies. The observations made for alumina could be transferred to zirconia and as well to ZTA with 20 wt% zirconia.

# Influence of paraffin wax addition on rheological properties and printability of ethylene vinyl acetate based feedstocks for fused filament fabrication of alumina

Aljaž Iveković[1], Milan Vukšić[2], Marko Bek[3], Lidija Slemenik Perše[3], Andraž Kocjan[1]

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## Abstract:

Fused filament fabrication (FFF) of ceramic components enables rapid prototyping of complex shaped ceramic components. Rheology of the feedstock material is crucial for the optimal performance during printing. However, due to the nature of the FFF which utilizes thermoplastic behavior in order to melt and extrude the feedstock which upon solidification retains its shape, not only the behaviour of molten feedstock, but also room temperature properties must be considered.

In order to investigate the effect of different rheological conditions on the printability of highly filled ceramic filaments, various amounts of paraffin wax (0, 20, 40 wt. %) were added to the ethylene vinyl acetate (EVA) based binder. Feedstock materials containing 50 vol. % of alumina powder were processed into continuous filaments and characterised in terms of filament flexibility (bending strain), buckling (compression modulus - viscosity ratio), printability (G'', G') and interlayer welding (relaxation modulus G(t)). As expected the increase in paraffin wax concentration significantly affects the rheological properties of the thermoplastic feedstocks and printing behaviour of thermoplastic filaments. Although higher paraffin wax concentration resulted in a higher filament flexibility and handling, overall optimal printing behaviour was observed for filaments produced with 20 wt.% wax addition.

## Acknowledgements:

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# Does flash sintering involve plastic flow?

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## Abstract:

During flash sintering, very rapid densification of a ceramic powder compact occurs during a thermal runaway induced by electrical power dissipation from an applied voltage and current. The mechanisms of densification within seconds are still not well understood. The present study investigates the impact of plastic flow on densification of strontium titanate during flash sintering. After sintering, a high dislocation density of $10^{14}$ $m^{-2}$ was observed by transmission electron microscopy. Uniaxial compression tests at 1150°C revealed that deformation rates are about one order of magnitude higher for flash sintered samples compared to conventionally sintered samples. This plasticity after flash sintering is likely caused by the high pre-existing dislocation density.

It is argued that the dislocations are generated and migrate during sintering resulting in the occurrence of plastic flow. This becomes possible by the very high heating rates, which conserve high driving forces for sintering up to high temperatures by minimizing neck growth by surface diffusion during heating. Sintering stresses of several 10 MPa can be achieved, which is above the flow stress of $SrTiO_3$. Thus, plastic flow becomes possible. In this light, the most important parameter of flash sintering is the extremely high heating rate. The current findings can be compared and extrapolated to other fast sintering processes as e.g. spark plasma sintering (SPS), microwave sintering, laser sintering, and ultrafast high-temperature sintering (UHS). Among these, there are multiple examples for the occurrence of dislocations after sintering.

# Scanning transmission electron microscopy studies of segregation behavior in iron doped strontium titanate.

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## Abstract:

Perovskite oxides, such as strontium titanate, are of interest for a variety of energy related applications due to their many advantageous properties, including their ionic conductivities. Of particular importance to material performance is the presence of space charge layers at the grain boundaries, which arise from the segregation of charged defects in the material. Space charge regions often contribute to a blocking behavior of the grain boundary to ionic conduction. Dopant species, added to impact material processing or performance, will tend to segregate to grain boundaries and interact with the space charge layer. As a result, studying the segregation behavior of dopants in strontium titanate is critical for a full understanding of material performance.

In this work, the effects of dopant segregation on space charge are investigated using scanning transmission electron microscopy (STEM), allowing for characterization of grain boundaries on the nanoscale. Bulk $SrTiO_3$ material was synthesized with a variety of iron doping levels, with the goal of understanding the segregation response of dopants at grain boundaries in the system. In addition to STEM, other analyses are utilized to characterize the materials, including XRD, SEM, and electrochemical impedance spectroscopy. Among the points examined is the dopant segregation width in relation to the space charge layer at the grain boundary, and how a variation in dopant level affects the observed grain boundary segregation, microstructure evolution and electrical properties

# Hierarchical compositional control of ceramic composites

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## Abstract:

In this presentation we will discuss the use of oil/water emulsions as templates to prepare dense ceramic composites with controlled 3D structures. This is achieved by dispersing an oil suspension of one powder in a water suspension of another. By using emulsions as templates, we can: 1- control the microstructure at the droplet scale (a few microns) and 2- shape the emulsion into 3D objects via multiple simple and scalable techniques such as slip casting. The inner structure of a composite can be designed by controlling the droplet size, shape, composition, and spatial arrangement, opening the opportunity to achieve tailored microstructures, and improved structural or functional properties. Here, we introduce this approach with a model system using zirconia and alumina. Zirconia is dispersed into the oil phase, decane, and alumina is dispersed into the water phase. PVA is used as surfactant to stabilize the emulsion. We analyze the rheology of the different suspensions in order to formulate stable emulsions that can be shaped into dense composites using slip casting. Our results show that it is possible to prepare stable suspensions of zirconia in decane with solid contents as high as 19 v. %. The emulsion are shear thinning with viscosities of the order of 10 to 0.1 Pa.s. The microstructure and mechanical properties of the final composites are assessed and related to the processing conditions. The results could be extended to other materials and open a new way to tailor the microstructure of composites.

# Cold or Fast: Sintering of Al doped LLZO solid state electrolyte by cold-sintering and flash-sintering

Gareth M. Jones[1], Christopher Green[2], Dinesha Dabera[1], Parinaz Tabrizian[1], Scott Gorman[3], Sherry Ghanizadeh[2], Sandra Fisher John[2], David Pearmain[2], Geoff West[1], Emma Kendrick[3], Claire E. Dancer[1]

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## Abstract:

Solid-state ceramic electrolytes are a crucial component of solid-state batteries, however the processing conditions for these ceramic materials is challenging, requiring elevated temperatures during sintering to produce suitably dense layers. As solid-state electrolytes (SSEs) start to reach market, there is an increasing drive for faster and more energy efficient sintering methods, especially methods that can reduce the volatilization of lithium during typical sintering. We show the result of two different advanced sintering methods, cold-sintering, and flash-sintering, on the oxide SSE aluminium doped lithium lanthanum zirconium oxide (Al-LLZO). The two methods provide an interesting contrast between processing conditions: the high pressure, low temperature and solvent dependent nature of cold-sintering and the rapid high temperature conditions of flash-sintering. The contrast between these two methods is compared through examination of the sintered ceramics microstructural features by scanning electron microscopy, X-ray diffraction, and Raman spectroscopy. The optimization and important parameters of both methods are discussed in detail, such as the effect of pressure, temperature, solvent quantity and time during cold-sintering, and the effect of furnace temperature, current profile, and various electrode configurations during flash-sintering. Results for both contact mode flash-sintering (two electrodes in contact with the sample) and contactless flash-sintering (where the electrode rasters over the sample surface) are made.

## Acknowledgements:

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# Shaping of ceramic by binder jetting

Enrique Juste[1], Qirong Chen[1], Marie Lasgorceix[2], Anne Leriche[2], Charles Dutertre[3], Fabrice Petit[1]

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## Abstract:

Additive Manufacturing by binder jetting is becoming increasingly popular to process ceramics. This layer-by-layer technique consists in building up a part from powder beds on which a binder is selectively deposited. Such technology is not only highly productive but also all-material compatible and is one of the few truly "free form" additive technologies. Unfortunately, it suffers from a series of limitations that are not yet fully resolved. These include the low density of the sintered parts, which makes them unsuitable for structural use, and the rather rough surface of the parts produced. A significant research effort is underway to overcome these limitations. The literature is full of attempts to improve this technology either with extensive work on the powders or with significant hardware modifications.

This presentation reports preliminary results obtained on a new type of hybrid binder jetting equipment used to manufacture of alumina parts. The system is not only an additive one but also a subtractive one: it comprises an in-situ mounted laser whose purpose is to refine the contour of each printed layers thus enhancing the overall part resolution and smoothness.

The presented results describe the optimal operating conditions with two different binders to ensure a maximum densification after sintering. The benefit of a post-infiltration of parts with a loaded suspension is highlighted. Alumina parts with densities up to 88% of the theoretical density have been produced.

# Microwave sintering of zirconia bulk and lattice samples shaped by DLP-based stereolithography

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## Abstract:

Nowadays, shaping by additive manufacturing and rapid sintering processes are of particular interest to produce technical ceramics with reduced time and energy consumption. Additive manufacturing processes enable to overcome many different issues of conventional shaping processes, especially fabricating complex geometries. Among them, stereolithography is based on the layer-by-layer polymerization of a photosensitive resin. It was highly studied to produce oxide ceramics such as alumina or zirconia. Rapid sintering such as microwave (MW) sintering is interesting to reduce the duration of thermal treatments. MW sintering is a fast volumetric heating of the samples by direct MW/materials interaction. It leads to dense samples with fine microstructures. The combination of shaping by additive manufacturing and MW sintering has been rarely studied these last years.

Therefore, the aim of this study is to couple these two processes to produce zirconia samples. For this purpose, bulk and lattice-type pellets were printed with Digital Light Processing (DLP) based stereolithography process. A ready-to-use 3 mol% yttria tetragonal zirconia (3Y-TZP) slurry was used. The sample were then submitted to a thermal debinding in a conventional (CV) furnace. The printed samples were sintered in a MW multimode cavity. CV sintering was also applied for comparison. Highly dense samples with fine microstructures were obtained with MW sintering with shorter thermal cycles in comparison with CV sintering (i.e., higher heating rates and lower holding times). MW sintering of bulk and lattice-type samples led to a homogeneous microstructure.

# The Powder Aerosol Deposition Method – Possibilities and Actual Limitations

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## Abstract:

The Powder Aerosol Deposition (PAD) Method is one of the most interesting ceramic deposition technique in the last years. PAD allows to deposit pure ceramic powders without organic additives. Thus, dense ceramic films can be achieved without any high-temperature steps. This property opens new opportunities in combination with completely different materials like ceramics on polymers.

The PAD process is rather simple. The ceramic particles that are distributed in carrier gas are driven by pressure difference between the aerosol and the deposition chamber. Thus, they are accelerated up to several hundred m/s, impact on a substrate, and they are fragmented into nanometer-sized pieces, and form a dense ceramic layer. Detailed explanation of the process can be found in [1], [2], or [3].

This contribution shows possible applications of the PAD method in the areas of gas and temperature sensing, energy harvesting, thermoelectric generators, superconductors, solar cells, and solid-state batteries. Although the PAD method is very promising, some actual limitations of the process exist. These problems and some possible solutions will be discussed.

## Ref.

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# Hydrothermal synthesis of multi-cationic high-entropy layered double hydroxides

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## Abstract:

High-entropy materials (HEMs) have become the subject of increasing attention in the materials science community. In general, HEMs are obtained by incorporation of multiple, randomly-distributed elements, typically ≥5 different cation species, all accommodated within a well-defined crystal structure. What has drawn particular interest is their tunable material properties resulting from the configurational entropy caused by the incorporation of these randomly-distributed elements. High-entropy materials originated with high-entropy metal alloys; recently, the principle has been applied to high-entropy ceramics (HECs) with the discovery of high-entropy oxides (HEOs).

Since the field of HEOs is relatively new, focus so far has been primarily given to synthesizing different crystal structures and chemistries rather than powder synthesis to achieve uniform powders or different morphologies. One route to achieving uniform powders has been wet-chemistry techniques, where precursors are first synthesized, then calcined to produce HEOs.

One such precursor is layered double hydroxides (LDHs), but most previous work on LDHs has focused on syntheses with less than 5 cations in the structure; synthesis techniques for incorporating >5 cations (thus increasing the configuration entropy into a more interesting range) are still needed. This work explores the range and extent of different compositional combinations for high-entropy double layered hydroxides (HE-LDHs). Specifically we focus on synthesis of combinations of 8, 7, and 6 cations (Mg, Al, Fe, Cr, Co, Cu, Zn, Ni) in the LDH structure by utilizing a hydrothermal synthesis method. The synthesized materials were then studied by X-ray absorption, X-ray diffraction, and electron microscopy with electron dispersive X-ray spectroscopy.

# Additive manufacturing of high strength zirconia ceramics via digital light processing

Dmitrii Komissarenko[1], Gurdial Blugan[1], Thomas Graule[1], Simon Roland[2], Benedikt Seeber[2]

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## Abstract:

DLP 3D printing is one of the most promising additive manufacturing techniques as it allows for the fabrication of ceramic parts with a complex shape, precisely controlled internal architecture and fine surface finishing. The method is based on the layer-by-layer solidification of photosensitive ceramic suspension via UV-light projection followed by debinding of organic components and sintering. To achieve a high density and quality of the final ceramics it is generally considered that the solid content in the slurry must be higher than 40 vol. %. However, this leads to an increase in the viscosity of the slurry and artefacts during 3D printing.

The present study demonstrates the possibility of the 3D printing of high quality zirconia ceramics with relatively low solid content via development of a proper formulation, optimization of 3D printing parameters and design of the debinding program. The acrylate-based slurries with 35 vol. % of tetragonal zirconia were developed with appropriate rheological properties and curing behavior. The 3D printing of ceramic samples with 25 μm of the layer thickness was performed on the desktop Asiga Pico II printer. It was shown that the density of the sintered semi-translucent parts was over 99%. The cross-sectional SEM images of the zirconia ceramics did not reveal severe defects in the structure and the size of the pores did not exceed 2 μm. According to the ball-3-ball test, the ceramic samples have a flexural strength higher than 1 GPa.

# Additive manufacturing of aluminum nitride ceramics with high thermal conductivity via lithography-based ceramic manufacturing

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## Abstract:

Owing to its outstanding thermal properties, aluminum nitride (AlN) is a highly promising material for advanced thermal management applications. Its sensitivity towards hydrolytic decomposition, however, limits its use in various ceramic shaping techniques, thus placing significant limitations on part geometries accessible.

In this contribution, the development of a materials system facilitating additive manufacturing (AM) of AlN via lithography-based ceramic manufacturing (LCM) is presented. In a first step, a suitable ceramic materials system was developed leading toward materials with adequate thermal and structural properties, which was evaluated by in-depth characterization of specimens obtained through conventional cold-isostactic pressing. At this stage, the effect of starting materials, sintering additive composition, and heat treatment parameters were systematically investigated, yielding thermal and mechanical benchmark values.

Subsequently, the materials system was implemented into an LCM-compatible slurry system. By monitoring the oxygen content during various steps along the processing chain, detrimental hydrolytic decomposition processes could be ruled out.

A thorough control of process parameters in particular during printing and debinding, were found crucial for obtaining crack-free AM materials. AlN specimens fabricated by additive manufacturing exhibited characteristics comparable to specimens obtained through conventional compaction, yielding relative densities above 98 %, thermal conductivities higher than 160 W $m^{-1}$ $K^{-1}$, and flexural strength values ranging from 320 to 498 MPa.

With respect to prospective novel use cases in future thermal management applications, a variety of crack-free demonstrator parts were successfully fabricated.

## Acknowledgements:

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# Synthesis of K-b-Al2O3 solid electrolyte for battery applications

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## Abstract:

The production of alternative ceramic electrolytes is the most promising for large-scale storage of renewable energy due to its high energy efficiency and good cycle life. The state of the art Na-b''-Al2O3 electrolyte is used in molten salt batteries (ZEBRA). However, the disadvantage of these batteries is high operating temperature of about 250 °C. This elevated operating temperature significantly increases the production and maintanence cost of the batteries and causes safety problems. The Potassium-doped to b''-$Al_2O_3$ can potensialy operate at much lower temperatres.

The research and development of the K-b''-$Al_2O_3$ electrolyte was performed with three different methods:

- Ion exchange of a solid ceramic precursor to directly produce K-b''-$Al_2O_3$ solid electrolyte.
- Ion exchange of a precursor Na-b''-$Al_2O_3$ to K-b''- $Al_2O_3$ powder.
- Production of K-b''-$Al_2O_3$ powder by calcination.

The optimal composition and the influence of particle size for the production of green and sintered electrolyte bodies were investigated. In addition, preparation by different methods included the optimization of the debinding and sintering conditions in order to achieve a higher relative density. The structural characterization of the produced K-b''-$Al_2O_3$ was studied by the fraction of b''-phase in the b-phase system, which was based on the state of the art Na-b''-$Al_2O_3$. The investigation of the ionic conductivity of the sintered K-b''-$Al_2O_3$ discs showed 0.057 S/cm at 300 °C, which is similar properties to commercial products.

# Obtaining high fire resistance, backing material clinker using local raw materials - dolomite, quartz ore sand (Georgia) and production waste

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## Abstract:

Purpose: The purpose of the work is to obtain high fire resistance, backing material clinker using local raw materials - dolomite, quartzoresand (Georgia) and production waste- by magnesite bricks loam. Determine their ratio.

Method: The study was carried out by thermal, X-ray and electron microscopy methods. The clinker is obtained by pressing samples in a semi-dry way at a hydraulic pressure of 100 MPa and firing at 1450-15000 C.

Results: intheprocess of firing, CaO of dolomite and SiO2 of raw sand combine to form a high-melting calcium silicate, and the amount of MgO increases due to the residual of magnesite bricks, which is obtained in the form of periclase.

Conclusion: For the saturation coefficient KN (KN = 0.85), the ratio of dolomite and sandstone was chosen 4:1. The composition of the theoretically desirable newly formed minerals has been calculated. Their content is determined by the ratio of the mixture taken and the firing temperature. This leads to an increase in the amount of MgO in the clinker. Compressive strength 980 MPa, open porosity no more than 8.8%, temperature of the onset of deformation 0.2 MPa at a load of -15000 C.

# Ceramic-graphene composites obtained by slip casting: rheological studies and analysis of possible interactions

Michał Kukielski[1], Artur Kasprzak[1], Radosław Żurowski[1], Justyna Zygmuntowicz[2], Piotr Wieciński[1], Paulina Wiecińska[1]

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## Abstract:

Up to day research on preparation of ceramic-graphene composites focuses mainly on powder metallurgy methods. However due to deterioration of graphene platelet size and inhibition of sintering process, resulting in increased porosity, performance of obtained materials was below of what was predicted. The use of colloidal processing methods should decrease the amount of steps needed for preparation of ceramic-graphene composites and reduce the defragmentation of graphene platelets during the process. The reason for the low interest in colloidal processing route is the high viscosity of suspensions. This makes it hard to prepare suspensions with high content of well dispersed graphene enabling breaching percolation threshold. Literature reports suggest that the solution for similar problem in case of polymer-graphene composites turned out to be modification of graphene oxide surface with other compounds increasing its affinity with the continuous phase of the dispersion. It should be possible to apply similar approach in case of ceramic-graphene composites. In this work Authors' aim is to understand interactions which occur in aqueous suspensions containing ceramic powder and graphene oxide through investigation of zeta potential and rheological properties of the suspensions. Furthermore, Authors propose functionalization of graphene oxide as an effective way to decrease the viscosity of ceramic-graphene oxide suspensions.

## Acknowledgements:

This work has been financially supported by Warsaw University of Technology (project number: IDUB TM-2).

# ‘Shape strain’ in Nanoceramics

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## Abstract:

Strain contributions in the ceramic bodies are due to various reasons, e.g., induced via doping, nanosize, heat treatments (sintering or annealing parameters) etc. In this work, we introduce the concept of ‘shape strain’ in nanoceramics for the first time. The concept of ‘shape strain’ has been introduced to illustrate its beneficial effect to control/avoid any undesired phase transition via consolidation/densification of ceramics. Low (4 mol%)-doped $ZrO_2$ ceramics with various dopants have been used for investigation. With ionic radii size difference (of dopant ion and $Zr^{4+}$) above 30%, CaO-doped zirconia ceramics showed the effect most prominently. The effect was also dependent on the grain boundary mobility of dopants.

We also illustrate the benefits of the ‘shape strain’ effect in undoped ceramic systems (e.g., $TiO_2$ and $BaTiO_3$). Our studies indicate that this effect can still be relevant without any influence of dopants (i.e., thus making the effect more generic). Along with retaining a phase purity, the ‘consolidation strain’ effect was found to be effective in maintaining a correct stoichiometry for the ceramics as well. It also helped in avoiding the emergence of extra/new phases (e.g., for $BaTiO_3$), depletion of ions, creation of unwanted vacancies in the system etc. Dependencies of various possible factors on this ‘shape strain’ effect have also been highlighted. Controlling final phase evolutions in ceramics is difficult and this effect may serve as remedy if tried with different size fractions of starting powders.

# Influence of temperature gradients on flash sintering onset and quality

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## Abstract:

Flash sintering, a novel ceramics densification process, has gained interest due to its rapid densification effect and the associated possibilities of energy efficiency improvements and microstructure control. While its general effectiveness has been demonstrated in a range of oxide materials, upscaling remains a major challenge due to inhomogeneous densification and hot-spot formation.

We report on in-situ IR thermometry measurements of flash sintering events in barium titanate green bodies of different geometries. Both the change in temperature during the flash event as well as the temperature gradients on the sample surface were monitored. An expected exponential increase in temperature, proportional to the increase in current density for the flash event, was recorded. However, no correlation between the peak temperature and the sample density could be established. A temperature gradient of up to 200 °C was identified on both sides of the sample in field direction due to heat energy transport through the electrodes. For non-symmetrical samples the formation of a significant gradient orthogonal to the field direction was recorded as well demonstrating incubation of hot-spots due to the differences in heat energy losses through radiation and convection.

## Acknowledgements:

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# Discontinuous Powder Aerosol Deposition Method: Formation of ceramic films at room temperature using small powder quantities

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## Abstract:

The Discontinuous Powder Aerosol Deposition (DPAD) allows for the formation of ceramic dense films from ceramic raw powder at room temperature using smallest powder quantities of less than 100 mg. It is a variation of the Powder Aerosol Deposition Method (PAD) where powder quantities with a minimum of several grams are required. Two major differences between DPAD and conventional PAD exist:

First, the discontinuous mode of operation allows for the use of smallest powder quantities, as a constant aerosol formation is not necessary anymore. The coating process is more of a “shot-like” type and is completed within seconds.

Second, a defined and adjustable gas pressure is used to accelerate the particles through a nozzle in a vacuum chamber. The resulting adjustment of the momentum of the impacting ceramic particles yields two further advantages: First, one may tune the impact velocity for optimum deposition efficiency of the powder-of-interest. Second, changing the momentum of the ceramic particles may reduce a sandblast effect and therefore allows the coating of more sensible (soft) substrate materials.

With the small powder quantities, only small areas can be coated. Therefore, we see the potential application in the following fields: Testing of new materials where only small powder quantities can be synthesized and sensor applications where small coating areas are sufficient.

[1] M. Linz, J. Exner, J. Kita, F. Bühner, M. Seipenbusch, R. Moos: Discontinuous Powder Aerosol Deposition: An Approach to Prepare Films Using Smallest Powder Quantities, Coatings, 11, 844 (2021), doi: 10.3390/coatings11070844

## Acknowledgements:

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# Capibilities of large single-domain bulks REBCO prepared by TSMG

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## Abstract:

Since the discovery of stable levitation in type II superconductors, the number of applications of superconducting magnetic bearings for contactless machinery or strongest magnets has increased significantly. At the same time, other applications such as table-size MRIs or generators for offshore wind turbines. These applications require the production of single-domain bulks with the largest dimensions and at high capacity. In this work, large-single domain bulks were prepared by the top-seeded melt growth (TSMG) technique under air conditions. The monocrystalline MgO covered with a thin layer of Nd-123 phase was used as seed. TSMG is a demanding technique, even small temperature deviations (0.5 K) can induce the formation of secondary nucleations. Additionally, for very large bulks, it takes weeks until the growth is finished. In this work, we present a study of trapped magnetic field maps and levitation forces for different sizes of prepared RE-Ba-Cu-O (RE = Y, Gd, Eu) bulks with sizes from 14 to 155 mm.

## Acknowledgements:

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# Fabrication of ZrB2–hardened Zr3Al2 intermetallic composites by high-energy ball-milling and reactive spark-plasma sintering

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## Abstract:

A powder metallurgy route combining high-energy ball-milling (HEBM) of elemental powders and reactive spark-plasma sintering (SPS) is proposed for the controlled fabrication of novel composites based on a Zr–Al intermetallic matrix hardened with a ceramic second-phase, and its suitability demonstrated on ZrB2–hardened Zr3Al2. Specifically, commercially available powders of ZrH2, Al, and B were first combined in molar ratios of 2:1:1, to give an intermetallic–ceramic composite nominally formed by ~76.8 vol.% Zr3Al2 plus 23.2 vol.% ZrB2, and were intimately mixed and mechanically activated by HEBM, in the form of dry shaker milling for 30 min, next identifying by a dilatometric SPS test at 50 MPa pressure that the densification window of these composites is ~975–1275°C. Subsequent densification SPS tests at 50 MPa pressure in that temperature interval, and also at 1350°C, plus the microstructural and mechanical characterisations of the

resulting materials, established 1175°C as the optimal SPS temperature. It was also identified that densification takes place by transient liquid-phase sintering with molten Al, and that it occurs gradually, not abruptly, because most molten Al disappears in a flash by reacting with Zr to form in situ the intermetallic. It is also shown that the combination of HEBM plus reactive SPS yields Zr3Al2+ZrB2 composites with fine-

grained microstructures formed essentially by multitude of ZrB2 nanograins dispersed into a matrix of submicrometre, or nearly submicrometre, Zr3Al2 grains. Importantly, these intermetallic–ceramic composites were found to be very hard (i.e., ~11.5 GPa), attributable to the hardening provided by the ZrB2 nanograins, and sufficiently tough (i.e., ~4.5 MPa·m1/2), and therefore potential candidate materials for multitude of structural–tribological applications. Implications for future study are finally discussed.

## Acknowledgements:

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# Flash sintering of BZT-BCT ceramics: tuning the microstructure for properties enhancement

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## Abstract:

Due to environmental concerns, piezoelectric technologies require a robust cyclic reliability from manufacturing to recycling. In this perspective, extensive research has been carried out to develop high performance lead-free piezoceramics able to replace commercial lead-based materials. Lead-ree $Ba(Zr_{0.2}Ti_{0.8})O_3$-$(Ba_{0.7}Ca_{0.3})TiO_3$ system has emerged as candidate for room temperature transducer applications because high piezoelectric charge coefficient is achieved in this system for compositions at the morphotropic phase boundary. However, conventional ceramic processing of these eco-friendly piezoceramics demands high energy consumption because long-time, high-temperature heat treatments are required. Therefore, faster kinetics sintering routes should be explored in order to mitigate the environmental impact of the ceramic processing. In this context, the field-assisted flash sintering has started to be used since the application of a proper electric field has proven to significantly reduce sintering time and temperature. In this work, $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ ceramics are obtained by flash sintering of nanopowders. An exhaustive control of the sintering parameters allows tailoring the microstructure, thereby improving functional properties of the flash-sintered ceramics. Results suggest that a proper electric current control leads to customized grain size and, consequently, enhanced properties.

## Acknowledgements:

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# Rapid pressure-less sintering of advanced oxide ceramics

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## Abstract:

Pressure-less rapid rate sintering in a specially designed furnace with the heating rates from 100 °C/min up to 1500 °C/min has been found as a possible way for preparing defect-free and nearly dense alumina and zirconia ceramics of a relatively large size. This finding represents a crucial benefit for the big-scale sintering process in the ceramic industry. Moreover, the mechanisms of heat transfer and the role of surface diffusion during rapid heating are discussed in detail. The origin of the so-called core-shell structure formed during rapid sintering of zirconia ceramics was discovered and possible ways of its elimination are shown. The capability of rapid rate sintering is demonstrated on sintering of lead-free piezoceramic materials, when BCZT powder compacts were for the first time sintered by rapid heating rates within one hour of sintering, while achieving good piezoelectric properties.

## Acknowledgements:

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# Microstructural evolution of barium titanate at applied non-conventional rapid sintering

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## Abstract:

Lead-free $BaTiO_3$ is a widely used electroceramic material. Its electrical and mechanical properties depend mainly on mean grain size and density. Therefore, precise grain growth control during the thermal treatment plays a crucial role. To explore microstructural evolution at non-standard conditions, rapid sintering, or fast firing, was applied in this work. Stoichiometric sub-micron $BaTiO_3$ powders were uniaxially pressed and sintered with heating rates up to 200 °C/min at temperatures ranging from 1100 °C up to 1250 °C. The abnormal grain growth and transition to bimodal grain size distribution were reported at sintering temperatures between 1275 – 1325 °C at conventional conditions. Our results suggest that this behaviour can be dramatically affected by the type of heating. Moreover, the influence of microstructural changes on density, phase composition, mechanical and electrical properties was investigated and discussed. The stoichiometry of grain boundaries of abnormal grains was observed.

## Acknowledgements:

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# Hard ferromagnetic ink-jet printed CoFe2O4 thin films

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## Abstract:

Cobalt ferrite ($CoFe_2O_4$) is a magnetic oxide with inverse spinel structure that exhibits moderate saturation magnetization, high magnetocrystalline anisotropy and high coercivity, good chemical stability and mechanical properties. In the form of films, such characteristics make the material a good candidate for application in hard magnetic devices, magneto optical devices, high-density recording media, and MEMS. Cobalt ferrite thin films have been prepared by several methods: spray pyrolysis, pulsed laser deposition, atomic layer deposition, sol–gel technique, RF magnetron sputtering, and molecular beam epitaxy. In this work, we propose a simpler process for producing patterned $CoFe_2O_4$ nanometric thin films by means of ink-jet printing. Cobalt ferrite films were successfully printed onto Silicon substrate by using a nanoparticles' suspension of $CoFe_2O_4$ and a dedicated ink-jet printer apparatus, and then sintered to promote densification and andhesion. Jetting and printing parameters were carefully studied and fixed in order to ensure a reliable printing process. Squared patterns of 5 mm of side were printed onto a silicon substrate and polyimide-coated silicon. Printed films present an average thickness ranging from 39 nm (for single layer) to 220 nm (for 6 layers) and their nanostructure, profile and magnetic behaviour have been investigated. Results for a 6-layered film show a well sintered nanostructure, with a "hard" ferromagnetic behaviour with moderate anisotropic effect, with a saturation magnetization of 201 emu/$cm^3$, remanent magnetization of 110 emu/$cm^3$ and a coercive field of 223 mT for out-of-plane measurement and 188 mT for in-plane measurement.

## Acknowledgements:

This research was carried out in the framework of the Joint Research Laboratory between Politecnico di Milano and STMicroelectronics with the aim at developing innovative MEMS devices and technological processes. Authors would like to acknowledge the financial support by STMicroelectronics, the "Functional Sintered Materials (Funtasma)" Interdepartmental Laboratory of Politecnico di Milano and PoliFAB, where this research activity was developed.

# Preparation of ready-to-print a-alumina granulated powders by spray-drying

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## Abstract:

Binder jetting (BJ) is an indirect AM technique suitable for ceramic production. However, ready-to-print powders are lacking on the market, even for common materials as alumina. Indeed, BJ requires micrometric spherical particles that ensure sufficient flowability and packing without compaction. At the moment, ready-to-press commercial powders features too large granule size for BJ, which would generate large internal porosity that are challenging to eliminate during pressureless sintering; on the other side powders synthesized by thermal spray may have an optimal size distribution, but their low surface energy hinders diffusion mechanisms, thus preventing densification.

Our work aims at describing an optimised procedure for granulating ultrafine particles by spray-drying to achieve ready-to-print a-$Al_2O_3$ powders. The study started from the identification of raw materials suited for the process through complete characterisation of particles shape, size, and surface properties (SEM, granulometry, BET and zeta potential measurements). Then, dispersion in diluted and concentrated water-based suspensions was achieved thanks to a cationic polyelectrolyte (polyethyleneimine, PEI) and gradual dispersant addition effect was assessed by zeta potential and aggregates size variation. Suspensions rheology was studied and modelled through Krieger-Dougherty equation to identify the maximum solid loading allowing sufficient feeding through the spray-dryer nozzle. Finally, optimisation of the granulation conditions (solid loading, nozzle diameter and chamber temperature) was performed.

The procedure has allowed to achieve bimodal and monomodal size distributions with $d90<50$ µm, thus allowing printing with reduced layer thickness, and Hausner ratio $< 1.3$ ensuring sufficient flowability.

## Acknowledgements:

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# Shaping KNN powder by binder jetting

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## Abstract:

The demand for complex-shaped functional ceramics to optimize performance, allow miniaturization, and reduce material consumption, pushes the study of 3D printing techniques to fully exploit their potential. There is a growing interest towards the binder jetting (BJ) technique, with yet a limited number of feasibility studies mostly focused on metals, with only a few papers on ceramic-based compositions. Here we present our preliminary study of the application of the technique to the shaping of KNN-based materials, mainly focusing on microstructure control. Achieving high green density is difficult, which leads to final porous structures that can only be exploited in a limited range of applications, so that additional strategies for pores filling must be considered. Disk-shaped samples for electrical characterization, as well as complex-shaped specimens were produced. Porosity, grain size distributions, and phase composition were studied using SEM, XRD and MIP (Mercury Intrusion Porosimetry), and correlated to binder saturation, number of layers, and powder morphology. Results are compared to those measured on die-pressed pellets. $d_{33}$ values of 80-90 pC $N^{-1}$ were achieved for the undoped KNN composition. Possible applications to underwater acoustics are discussed based on the materials' figure of merit.

# Role of Surface Carbon Nanolayer on the Activation of Flash Sintering in Pure Tungsten Carbide

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**Abstract:**

Flash sintering of ceramics requires the activation of a thermal runaway phenomenon, during which the electrical resistivity of the green specimen decreases exponentially with the temperature. The negative dependence of the specimen resistivity with temperature restricts the flash phenomenon to a certain class of ceramics. However, flash sintering conditions were recently achieved at room temperature for green samples of tungsten carbide (WC), thanks to the interaction of the electrical current with the green electrical properties. The high initial green resistivity decreases exponentially upon applying the current, approaching the value of the bulk material and enabling a transitory thermal runaway to occur. An electrical contact resistance model has been developed to study: (i) the role of the constriction resistance, (ii) of the pressure and (iii) of the surface chemistry on the electrical properties of granular WC compacts. The comparison of experimental with simulation results reveals how surface chemistry rules the resistance at particles contacts. In the specific, powders richer in carbon content show a higher overall resistivity with respect to oxidized ones. An ultrathin surface carbon layer, firmly bonded to the particle surfaces, is responsible for the large increase in green resistance. HR-TEM observations confirm the presence of a highly disordered carbon nanolayer, between 10-30 Å in thickness. Subsequent ion sputtering, during XPS analyses, highlights the strong bond character between the bulk WC lattice and surface carbon, which cannot be removed by the intense etching. The strong electronic and chemical affinity between WC and the carbon layer suggests a new approach for activating flash sintering on a metallic ceramic.

# Additive Manufacturing of Porous Ceramic Bodies by Extrusion of Capillary Suspensions

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## Abstract:

The use of additive manufacturing technologies for the fabrication of ceramic bodies allows the production of complex geometries that would not be possible with traditional manufacturing techniques, such as dry pressing, extrusion or slip casting. By employing direct ink writing (DIW) in combination with the capillary suspension concept, we are able to 3D print complex geometries with high open porosity > 60%. Capillary suspensions are ternary liquid-liquid-solid systems, in which the addition of a secondary fluid, immiscible to the main phase, changes the flow properties of the suspension drastically. This is due to the formation of a sample spanning particle network controlled by strong attractive capillary forces coming with the addition of the second immiscible liquid. This network structure reduces shrinkage and suppresses crack formation, making capillary suspensions ideal precursors for manufacturing of highly porous bodies, with the possibility to tune porosity and pore size, simply by varying particle size and volume fraction. Capillary suspensions display a high yield stress and strong shear thinning behavior, which makes them good candidates for extrusion-based 3D printing processes. The former guarantees a superior shape accuracy and enables large ratios of unsupported length over filament diameter ratios (»10) and printed feature sizes below 0.1 mm. In this study, we will present 3D printed structures to be used as filters, with geometries not achievable by traditional fabrication processes. Porosity and pore size will be analyzed and their influence on mechanical strength will also be discussed. Furthermore, the influence of sintering temperature on pore structure and how this affects permeability will also be addressed.

# New hardness model for fine fibrous eutectic ceramics prepared by laser-heated floating zone (LFZ)

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## Abstract:

The fabrication of two eutectic ceramic systems ($MgAl_2O_4$-MgO and $Y_2O_3$-MgO) with fine fibrous microstructure by laser-heated floating zone (LFZ) method for optimization of their mechanical properties was studied. The low growth rate causes coarsening the fibre interspacing which is detrimental for the hardness. Gradual enhancement of hardness happened for eutectic ceramics fabricated at higher growth rates. Favourably, it showed elevated hardness at 750 mm/h growth rate (15.5 GPa from Vickers indentation for $MgAl_2O_4$-MgO and 11.5 GPa from Vickers indentation for $Y_2O_3$-MgO). It is found that hardness scales with the interfiber spacing l according to a law of the type lnl/l, different from the assumed Hall-Petch-like dependence. This proposed law can be explained in terms of dislocation hardening induced by the MgO fibers.

## Acknowledgements:

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# Novel approach to fabrication of porous polymer-derived SiOC ceramics by 3D printing of High Internal Phase Emulsions

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## Abstract:

In this work, a new method for the fabrication of porous SiOC ceramic components is presented. Three W/O High Internal Phase Emulsions (with aqueous phase amount of 81%) based on poly(hydromethylsiloxane) and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, differing in secondary porogen content (chlorobenzene) were fabricated by mixing with aqueous phase (0.02M NaCl) in the presence of non-ionic surfactant (DBE-224). The rheological parameters of the emulsions were tested to assess their influence on the Direct Ink Writing (DIW) process. 3D printing of the emulsion resulted in the formation of porous scaffolds, which after curing and drying formed preceramic foams. The components converted to SiOC ceramic structures by pyrolysis at 1000°C in inert atmosphere, undergoing isotropic shrinkage. They possessed a designed, open macro-porosity (70 vol%) as well as interconnected pores in the struts (82 vol%). The resulting structures possessed hierarchical porosity as high as 94 vol%, with a corresponding high compressive strength.

## Acknowledgements:

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# Impact of high-energy ball milling on piezoelectric properties of the "lead-free" BCZT (Barium Calcium Zirconate Titanate) piezoceramics.

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## Abstract:

Over the last few years lead-free piezoceramics have gained particular attention as a class of materials to replace the commercially used lead zirconium titanate (PZT)[1]. Currently, among lead-free materials, BCZT (Barium Calcium Zirconate Titanate) is considered one of the most promising lead-free piezoceramics due to its lower density (6 g/cm3) and higher d33 (620pC/N) compared to PZT ceramics and lower volatility of precursors than KNN, that leads to better stoichiometric control, in spite of a low Curie Point (120°C). [2] According to previous studies, the BCZT piezoelectric properties are intimately correlated with an optimized microstructure (i.e. grain size, microporosity, etc.), that results strictly influenced by some critical steps of the fabrication process [3]. Among the parameters, particle and grain sizes homogeneity seems to play a crucial role in the optimization of the BCZT piezoceramics fabrication [4]. In this view, the present study aims at elucidating the effect of a second ball milling step, after calcination, on the microstructural and piezoelectric properties of the processed BCZT ceramics. Both particle and grain sizes evolution as a function of the mechanical treatment were evaluated through SEM/TEM, light scattering analysis and XRD technique. Piezoelectric properties were determined and related to the microstructure of each pellet realized. As preliminary result, it emerges that uniformity of particle and grain size is a key factor for processing BCZT ceramics with enhanced electromechanical properties.

The effect of second ball milling time on particle size, microstructure, phase evolution was evaluated through SEM analysis, DLS analysis, XRD analysis. Furthermore, piezoelectric properties were evaluated and related to microstructure.

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# The role of fluoride additives in the densification of ceramics – How does it work?

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## Abstract:

Fluoride sintering additives are frequently utilized for the densification of various ceramics, but the current comprehension of the mechanism by which they affect densification is lacking behind empirical experience. A prominent example is LiF, which is commonly used in the preparation of transparent ceramics ($MgAl_2O_4$, $Y_2O_3$, YAG, MgO). It is generally accepted that LiF melt allows the rearrangement of particles, enhances densification and later in the process escapes from the system due to its high vapor pressure, so ideally no secondary phase is present in the final product. However, the second – and the most essential – step of enhanced densification is a source of scientific dispute. It is not clear if oxygen vacancies are responsible for this enhancement and if so, under what circumstances are they created. The present work tries to shed more light on fluoride additives and how they work throughout the whole process of preparation. The results suggest that the mutual dissolution of sintering additive and the base ceramic is the key aspect.

## Acknowledgements:

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# Processing and mechanical evaluation of oxide-oxide ceramic matrix composites manufactured using automated fibre placement

Thomas Nelson

*University of Birmingham*

## Abstract:

Traditional oxide-oxide ceramic matrix composite (CMC) manufacture can involve manual slurry infiltration into pre-cut fabric sheets, followed by hand lay-up onto a mould of required shape. Automated fibre placement (AFP), previously used for production of polymer matrix composites, promises a capability for highly reproducible laminate production of complex geometries using towpreg feedstock. The process of AFP involves using a computer controlled loaded roller to place layers of towpreg material, containing a dry matrix, onto a mould. However, the optimal parameters for further processing of laminates from the as-laid state to final sintered component are currently unknown.

This poster will present the results of a processing study of AFP laminates undertaken using both heat press curing, which tends to result in delaminated samples after final sintering, and the use of autoclave-based curing cycles for which the pressure and temperature were optimised over several runs. The eventual aim of this project is to compare the mechanical performance of optimised, commercially available AFP laminates to those manufactured in-house, from spools of towpreg material. Practical processing considerations will also be explored, such as the towpreg tack and behaviour of green bodies after AFP. Imaging of the material using non-destructive techniques, such as micro-CT, may give an insight into defect distribution to allow greater understanding of the mechanisms occurring during processing.

# Fabrication of Porosity Graded Ceramics by Lithography-based Ceramic Manufacturing (LCM)

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## Abstract:

Porous ceramics have always been attractive materials in applications where low density, high thermal shock resistance, or high thermal insulation is demanded. In recent years, ceramics exhibiting gradient in porosity (i.e., Porosity Graded Ceramics) with a controlled amount of both open and closed pores is of high interest for several applications such as thick barrier coating, cores for precision casting, biocompatible implants, and fabrication of functionally graded metals through infiltration. Conventional methods (e.g., packing of ceramic powders with different density and partial sintering, multilayer lamination of layers with different densities or different amounts of some additives, direct foaming, and replica templates) have limitations in manufacturing of complex and near-net shaped porosity graded ceramic structures. Lithography-based Ceramic Manufacturing (LCM), a method developed by Lithoz GmbH as an enhancement of Stereolithography (SLA) and Digital Light Processing (DLP) technology, is an indirect additive manufacturing method that allows the precise fabrication of complex ceramic designs by layer-by-layer deposition of ceramic slurries. This study introduces methodologies for the fabrication of porosity-graded ceramics with a controlled gradient in porosity and pore size distribution over the volume of a ceramic structure by the LCM method.

## Acknowledgements:

This work is part of the project entitled "GraCerLit - Development of Functionally Graded Ceramics by Lithography-based Ceramic Manufacturing (LCM)" that has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Individual Fellowship (H2020-MSCA-IF-2020) with Grant Agreement No. 101020104.

# Understanding the flash sintering mechanisms through the electric current parameterization.

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## Abstract:

Flash Sintering (FS) has been demonstrated as an energy-efficient sintering technique to obtain well-densified materials. The typical FS experiment applies an electric field to the green sample while heating it at a constant rate. At some specific temperature, the electric current flows through the sample producing a flash event. The flash event is characterized by a nonlinear increase in the electrical conductivity followed by increased sample temperature. The increase in the sample temperature lowers the electrical resistance, leading to the rise of the electric current, and as a consequence, the sample temperature continues increasing until reaching the electric current limit of the experiment. Despite the vast number of parameters implied in the FS technique, these experiments have proven relatively easy to reproduce. Nonetheless, the physics behind the flash event remains controversial, and there is no universal acceptance of the physical mechanism driving the process. Various mechanisms have been proposed, such as local heating of grain boundaries, nucleation of avalanches of lattice defects, the thermal runaway of Joule heating, among others. This work analyzes possible FS mechanisms by studying the electric current dependence with the sample temperature. Different parameterizations have been used to obtain the activation energy of the involved process. The non-Arrhenius parameterization shows the best accurate statistical fit parameters, opening the door to divergent temperature mechanisms as the principal mechanisms of the FS process. Barium Titanate has been used as a study case due to the vast knowledge about the processes ruling the sintering mechanisms. Nevertheless, the results of this work could benefit as a reference for other types of materials.

## Acknowledgements:

This work is supported by the AEI (Spanish Government) projectPGC2018-099158-B-I00.

# Optimization of Si3N4-based feedstock for direct ink writing

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## Abstract:

Silicon nitride ($Si_3N_4$) based ceramics have been prime materials explored for several structural applications due to their combination of properties, such as mechanical strength, resistance to thermal shock, high hardness, and good wear resistance. Additive manufacturing (AM) technologies could be a promising solution to fabricate $Si_3N_4$ components, due to their ability to form complex forms and high details. However, several difficulties have been reported in the development of $Si_3N_4$ components with high densities and proper mechanical performance, as a consequence of feedstock' properties. Direct ink writing (or robocasting) is an AM technique with high potential for ceramics, since it uses lower amounts of additives in feedstock when compared to other suspension-based technologies, as for example vat photopolymerization.

In this work, silicon nitride suspensions (containing $Y_2O_3$ and $Al_2O_3$ as oxide sintering aids), with different amounts of solids were prepared for robocasting process. Due to the shear-thickening behavior of silicon nitride aqueous-based suspensions, the adjustment of the rheological properties was crucial and challenging. Different types and amounts of dispersants and binders were studied to attain the required shear-thinning characteristics. After printing, the parts were carefully dried and submitted to isostatic pressing as a post processing method to reduce porosity. Structural and mechanical properties were evaluated in samples sintered at 1750 °C, being achieved 98 % average relative density and 1414 HV micro-hardness.

## Acknowledgements:

This work was developed within the scope of the 3DCompCer project, POCI-01-0247-FEDER-047060 and of project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PID-DAC).

# Effect of printing variables on the voids elimination for manufacturing highly dense bulk mullite-based ceramics via Fused Filament Fabrication

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## Abstract:

Manufacturing bulk, highly dense ceramic parts using Fused Filament Fabrication (FFF) is still one of the most critical challenges of this technology. Unexpected internal voids created during 3D printing and defects such as pores or cracks formed during binder removal negatively influence ceramics' final densification and thus physical and mechanical properties. This study deals with the influence of selected printing variables on the green bulk density and porosity, primarily on the origin of voids formation and their elimination. For the fabrication process, an in-house developed composite mullite-based filament was used. Results showed that with a proper selection and combination of selected variables, relative green densities up to 99 % of the theoretical value could be achieved for regular, cylindrical and anisotropic shapes such as prismatic bars or pillars.

## Acknowledgements:

This work was supported by the Slovak Research and Development Agency under Contracts no. APVV-16-0341, PP-COVID-20-0025 and APVV-14-0719. The financial support of the Slovak Grant Agency for Science VEGA grant No. 1/0342/21, by the Austrian FFG Funded Project "Filament 3D Printing under contract no. 15137992. The authors would like to thank for a financial contribution from the STU Grant scheme for Support of Excellent Teams of Young Researchers ADIKOMAT. This work was also created thanks to the support of the Operational Programme Integrated infrastructure for the project: Advancing University Capacity and Competence in Research, Development and Innovation ("ACCORD") ITMS2014 +: 313021X329, co-financed by resources of the European Regional Development Fund.

# Effect of feedstock properties and process parameters on the quality of parts prepared with thermoplastic 3D printing

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## Abstract:

Thermoplastic 3D printing (T3DP) is a cartridge-based material jetting method, which can also be used for preparing multi-material parts, with a multi-material jetting (MMJ) system. In these systems, the feedstock`s thermoplasticity, i.e., the ability to melt/flow, deposit and resolidify, is exploited for material deposition and shaping. Feedstock`s binder system is often wax-based allowing for the colloidal processing of ceramic particles, where powder dispersibility, as well as appropriate surfactants govern the stabilization of the particles in the slurry. It follows that the understanding and altering the interparticle forces and rheological behaviour of such feedstocks slurries is of utmost importance for achieving good printability and high quality of the final part.

The present paper will report on the effect of powder loading and chain length of carboxylic acids on the printability of thermoplastic feedstocks. The behaviour of the thermoplastic slurries was thoroughly characterized by rheology. Then, these suspensions were printed with T3DP method. The size and roundness of the droplets which are primary building units were evaluated. Surface quality of the green parts was evaluated by stereomicroscopy. Furthermore, the effect of process parameters on the properties of sintered parts was studied in terms of density, fractography, and Weibull analysis, while microstructural properties were evaluated with SEM.

## Acknowledgements:

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# Fabrication of complex Silicon Carbide architectures by a novel hybrid additive manufacturing process

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## Abstract:

The fabrication of Silicon Carbide components by a novel hybrid additive manufacturing process was investigated. Selective laser sintering of polyamide powders was used to 3D print a polymeric preform with controlled relative density, which allows manufacturing very complex parts with small features, such as cellular architectures. Preceramic polymer infiltration with a silicon carbide precursor followed by pyrolysis was used to convert the preform into an amorphous SiC ceramic. Five PIP cycles were performed to increase the relative density of the part. The final densification was achieved via liquid silicon infiltration at 1500°C, obtaining a SiSiC ceramic component without change of size and shape distortion. The crystallization of the previously generated SiC phase into δ-SiC, with associated volume change, allowed to fully infiltrating the part leading to an almost fully dense material. The advantage of this approach is the possibility of manufacturing SiC ceramics directly from the preceramic precursor, without the need of adding ceramic powder to the infiltrating solution. This can be seen as an alternative AM approach to Binder Jetting and Direct Ink Writing for the production of templates to be further processed by silicon infiltration.

# Fabrication of dense SiC ceramics by a novel hybrid additive manufacturing process

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## Abstract:

The fabrication of Silicon Carbide (SiC) components by a novel hybrid additive manufacturing process was investigated. Selective laser sintering of polyamide powders was used to 3D print a polymeric preform with controlled relative density, which allows manufacturing geometrically complex parts with small features, such as cellular architectures. Preceramic polymer infiltration with a silicon carbide precursor followed by pyrolysis (PIP) was used to convert the preform into an amorphous SiC ceramic, and six PIP cycles were performed to increase the relative density of the part. The final densification was achieved via liquid silicon infiltration (LSI) at 1500°C, obtaining a SiSiC ceramic component without change of size and shape distortion. The crystallization of the previously generated SiC phase, with associated volume change, allowed to fully infiltrate the part leading to an almost fully dense material consisting of $\beta$-SiC and Si in the volume fraction of 45% and 55% respectively. The advantage of this approach is the possibility of manufacturing SiSiC ceramics directly from the preceramic precursor, without the need of adding ceramic powder to the infiltrating solution. This can be seen as an alternative AM approach to Binder Jetting and Direct Ink Writing for the production of templates to be further processed by silicon infiltration.

# Digital Light Processing of Carbides

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## Abstract:

There is increasing industrial interest in complex parts of silicon carbide and boron carbide. Additive manufacturing (AM) offers a promising alternative to traditional forming processes which, require expensive moulds and struggle with complex geometries. AM has had success with ceramic oxides however, carbides remain challenging because of their high melting points and unfavourable optical properties. Among the available AM methods digital light processing (DLP), where 3D parts are sliced into layers which are sequentially cured by selectively illuminating each layer's pattern, offers superior resolution and surface finish.

Carbide's high refractive indices as well as absorption in the near UV spectrum limits the photocurable resin's cure depth. To overcome this, larger particle sizes are required which, creates a compromise between curing and sintering (liquid phase). As a result, most of the previous research focuses only on the forming process or requires additional infiltration steps. In this work presented, high solid loading (40 vol%), photocurable resins containing silicon carbide and sintering aids (alumina and yttria) have been formulated and optimised. The cure depths of the resins are sufficient to print using a 50 micron layer thickness with a relatively low light intensity (1.8 mW/cm$^3$). This presents the opportunity for low cost, tabletop DLP of silicon carbide. The microstructure and mechanical properties of the final sintered samples have been analysed and related to the processing parameters.

## Acknowledgements:

I'd like to thank MTC and Photocentric for their help and expertise during this work.

# Synthesis and characterization of La2Ce2O7 powder and mechanical properties of La2Ce2O7/YSZ composites

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## Abstract:

Lanthanum cerium oxide, $La_2Ce_2O_7$ (LC), has attracted increasing interest as a promising material for TBCs because of its high phase stability and potential capability to be operated above 1250 °C. Moreover, LC exhibits lower thermal conductivity and higher coefficient of thermal expansion than the conventional yttria-stabilized zirconia (YSZ) material [1]. However, TBCs based on LC/YSZ showed a better thermal cycling behavior than single LC or YSZ coating [2]. Therefore, a coating structure and its composition should be rationally designed to utilize the advantages of LC. In this work, LC powder was synthesized by solid-state reaction and investigated as a material for TBC application. Moreover, LC/YSZ composites with different weight fractions of YSZ (40 – 70 wt. %) were prepared by conventional mixing of LC and YSZ powders, followed by sintering of the powders via hot pressing at 1400 °C for 1 h. The effect of YSZ addition on the microstructure and mechanical properties, i. e. Vickers hardness and indentation fracture resistance, was investigated.

Scanning electron microscopy (SEM) of the prepared LC powder revealed agglomerated structure consisting of finely and uniformly distributed grains with size up to 10 µm. The fluorite structure of the LC powder after annealing at 1400 °C was confirmed by X-Ray diffraction (XRD). The thermal behavior of the LC powder was analyzed by differential scanning calorimetry (DSC) in the temperature range of 25 °C-1350 °C. Result shows high phase stability of the LC powder and its suitability for TBC applications.The hardness value of LC/YSZ composites increased with increasing mass fraction of YSZ particles. The LC/70YSZ composite material reached the highest hardness (12 GPa), while the hardness of LC/40YSZ was only 10 GPa.

## Acknowledgements:

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# DLP-based stereolithography of composites in the alumina-zirconia system: processing, microstructural development and mechanical properties

Barbara Inserra[1], Bartolomeo Coppola[1], Tanguy Lacondemine[2], Caroline Tardivat[2], Jean-Marc Tulliani[1], Laura Montanaro[1], Paola Palmero[1]

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## Abstract:

The traditional shaping of ceramics presents limitations in terms of geometries, and always require a post-production machining, such as cutting and surface polishing. Nowadays, these issues can be overcome by new 3D printing technologies, such as stereolithography, successfully used to produce technical ceramics such as alumina and zirconia. However, only few studies investigated the development of alumina-zirconia composites, which join the excellent hardness and wear resistance of a-alumina with the very high bending strength and fracture toughness of zirconia. Therefore, in this research, alumina-zirconia composites are fabricated by Digital Light Processing (DLP)-based stereolithography.

Alumina-zirconia composites slurries are prepared through three different approaches, characterized by growing degree of complexity.

First, composite samples at 15, 50 and 85 vol% $ZrO_2$ are prepared by mixing ready-to-use alumina and zirconia slurries. Mechanical properties were determined and compared to those of reference alumina and zirconia samples, while providing a comprehensive study on composition-microstructure-properties relationships.

Second, slurries are prepared starting from mechanically mixed alumina and zirconia powders. The role of solid loading on the rheological behaviour, sinterability and microstructural development is illustrated.

Finally, preliminary results achieved by exploiting a new patented technology to develop tri-phasic composites are presented, in which in-situ crystallization of second-phases occurs during the high-temperature treatment of the printed materials.

## Acknowledgements:

The researches leading to some of these results have received funding from the European project AMITIE (Marie Skłodowska Curie Grant Agreement n°734342).

# Additive manufacturing of feldspar for tooth implants by layerwise slurry deposition

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## Abstract:

Our ongoing project aims at producing individualized ceramic front teeth replacements by additive manufacturing. The layerwise slurry deposition (LSD) will be presented in this context as a promising technology to manufacture ceramic green bodies with a high packing density. We sintered the green bodies to produce parts with properties comparable to those achieved in traditional manufacturing technologies. The combination of LSD and binder jetting (LSD print) enables the additive manufacturing of personalized fitting teeth for each customer. This process also allows using a common ceramic product that is already commercialized for applications by subtractive manufacturing. In our research, we used this feedstock to develop a water-based slurry containing under 5 wt. % additives. It consists of dispersant to stabilize the suspension, as well as of a network building polymer. The polymer works as a binder, and it adjusts the rheological properties. In this publication, we show the rheological investigation along our feedstock development. Additionally, we present the microstructure analyses of the green and sintered material. Furthermore, we determine mechanical properties by biaxial strength measurements, comparing them to those of the same material produced by subtractive manufacturing. In conclusion, our research aims at revolutionizing the dental processing industry by individualizing the geometry and the coloring of artificial teeth through additive manufacturing.

## Acknowledgements:

This Project is supported by the Federal Ministry for Economic Affairs and Climate Action (BMWK) on the basis of a decision by the German Bundestag.

# Production of complex shaped MoSi2 heating elements using additive manufacturing methods and injection molding

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## Abstract:

Molybdenum disilicide ($MoSi_2$) heating elements are used as standard in large quantities as electrical resistance heating elements for the high temperature range. $MoSi_2$ is an excellent high-temperature material, but is subject to a destructive oxidation reaction, so called pest oxidation, in the temperature range of 350 - 700 °C. This situation requires special protective measures during production. Therefore, currently only very simple shapes, based on round profiles, are offered by the industry. The final product is protected from further oxidation over the entire temperature range by a dense layer of in situ formed $SiO_2$.

In order to avoid pest oxidation already during first firing, the addition of glass phase former was investigated. In this way, pest oxidation can be effectively prevented. This approach opens up new possibilities for processing. Examples of the fabrication and high temperature performance of complex shaped heating elements using thermoplastic injection molding or 3D printing as well as use of additively manufactured water soluble sacrificial molds are shown. In parallel, a coupled electrical-thermal-mechanical finite element model was developed to simulate the complex physical behavior in a spatially resolved manner.

# Conventional and high-speed microwave sintering of robocast porcelain

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## Abstract:

The combination of additive manufacturing technologies and microwave (MW) sintering offers new perspectives for the minimization of material, energy and time waste. This study aimed at investigating the thermal behaviour of robocast porcelain during conventional and microwave (MW) sintering.

Porcelain was chosen as a model material to investigate MW sintering processes because (i) its rheological behaviour can be modified by simple water addition (only a drying is required but not a debinding step) and (ii) its dielectrical properties evolve during the firing process (and hence the ability to interact with microwaves). Indeed, several transformations occur during porcelain firing: clay dihydroxylation (~450-600°C), alpha-beta quartz phase transformation (~573°C), mullite formation (>940°C), glass formation (~950-1050°C), quartz dissolution (> 1200°C).

Small cylinders were robocast and sagging corrected by sample design. Effect of heating rate (1-100°C/min), dwell temperature (1200-1300°C) and dwell duration (5-120 min) on sample density, shrinkage and microstructure was investigated. With conventional heating, a density of 2.36 g/cm$^3$ was achieved with a 2 hr dwell at 1250°C, independent of the heating rate (1-20°C/min). The same density was reached with MW hybrid heating with an optimized thermal cycle (100°C/min, 1300°C for 30 min). Without susceptor, the same density was obtained using a long heating phase at low temperature and a high heating rate (50°C/min) above 800°C. The thermal cycle influenced the types of mullite formed: type III mullite was only observed in samples sintered at high-speed MW heating with a 30 min dwell. This study provides seeding data for the development of efficient processes for the manufacturing of prototypes and small series.

# Effect of microwave heating on spinel formation

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## Abstract:

$MgAl_2O_4$ and $ZnAl_2O_4$ spinels can be obtained by a reactive heating between alumina and another ceramic oxide at high temperature. While resistive furnaces allow high accuracy of the heating process, a long stage is carried out at high temperature. Thus, in order to reduce reaction time and energy costs, new advanced processes are being developed, such as microwave (MW) heating whereby samples are quickly and directly heated by absorption of the electromagnetic field. The aim of this work was to obtain two pure $MgAl_2O_4$ and $ZnAl_2O_4$ spinels starting from raw oxide powders by MW heating.

The comparison of the reactivity under conventional (CV) and MW heating showed that the temperature of spinel formation and the amount of spinel formed was the same, but it was possible to achieve a 2-time higher heating rate with MW. A study was conducted without SiC susceptor to investigate the coupling between $MgO/Al_2O_3$ and $ZnO/Al_2O_3$ mixtures and microwaves. It was found that the mixture with $ZnO/Al_2O_3$ coupled better with microwaves than the $MgO/Al_2O_3$ mixture (due to a difference in dielectric properties), but was insufficient to initiate the heating. Hence, a SiC susceptor was needed to start the heating of both $MgO/Al_2O_3$ and $ZnO/Al_2O_3$ mixtures. Furthermore, two different alumina powders (a-$Al_2O_3$ and g-$Al_2O_3$) were investigated for the $MgAl_2O_4$ spinel formation. It was found that spinel was formed at lower temperatures with g-$Al_2O_3$ compared to a-$Al_2O_3$, probably due to a higher the specific surface area for g-$Al_2O_3$ than for a-$Al_2O_3$. This study shows that it is possible to obtain $MgAl_2O_4$ and $ZnAl_2O_4$ spinels using fast hybrid MW heating.

# Development of a New Range of Large Ceramic Tiles in Bla-group Stoneware Technology conforming to EN 14411, with Unique Full-body Ornaments Resembling the Patterns of Natural Materials, Including e.g. Stone or Wood

Anna Poddębniak

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**Abstract:**

Development of a New Range of Large Ceramic Tiles in Bla-group Stoneware Technology conforming to EN 14411, with Unique Full-body Ornaments Resembling the Patterns of Natural Materials, Including e.g. Stone or Wood".

# Comparative study of Hot-pressing and Spark Plasma Sintering of cerium oxide doped aluminium nitride: influence of the process on ceramics electrical behaviour.

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## Abstract:

Aluminium nitride (AlN) has been mainly studied thanks to its good electric and thermal properties making it suitable for use in advances electronic devices.

The densification of polycrystalline AlN has been investigated in order to reach thermal conductivity as close as possible to the one of the single crystal. Literature focused on both the use of sintering additives and the implementation of processes to promote the densification kinetic. This later is mostly pointed out in final properties improvement.

The goal of this work is to understand well the role of the secondary phases on the sintering and on the microstructure features. First, a fine characterization of the AlN raw concluded to the presence of an amorphous oxide layer around AlN particles, reacting with additive, to form secondary phases. Samples were then obtained with 1wt.% of $CeO_2$ and 3wt.% of $CeO_2$. Each composition has been sintered by both Hot-Pressing and Spark Plasma Sintering in order to underline the influence of these pressure-assisted methods. Formation of transient liquid phase appeared to promote the mechanisms of the mass transfer by diffusion and finally enhanced densification for both technics.

During sintering, added $CeO_2$ is reduced into $Ce_2O_3$ and, by reaction with AlN oxide layer, led to the formation of $CeAlO_3$, main secondary phase identified. The samples having similar additive amount appeared to be equivalent in density, grain size and secondary phase composition. However, secondary phase appeared located at the triple points from HP samples while it has been distributed along grain boundaries from SPS samples.

Finally, electrical conductivity of the samples was measured and appeared to be more dependent of secondary phase distribution rather than their amount or their relative density.

# Versatility of direct-ink writing for the manufacturing of lattice ceramic truss

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## Abstract:

Complex porous architectures, such as truss, honeycombs or foams, were widely investigated for many years due to their tunable multifunctional properties. A truss is defined as a periodic arrangement of a unit-cell made up of cylindrical struts whose properties are governed by the cell morphology and by the material it is made of. Trusses with the same internal design but different constituent materials will exhibit distinct functional properties making them compatible with different applications. For instance, a SiC truss can be used as an efficient heat exchanger while the same architecture made in CaP will find applications as bone substitute.

Despite competition (most notably with SLA-stereolithography), direct ink writing still remains one of the most interesting additive manufacturing technology to produce such architectures. It is very affordable, printed parts can be cleaned easily and DIW is not limited in terms of compatible materials contrarily to SLA for which SiC processing remains highly challenging.

In the present work, this versatility is highlighted by considering the manufacturing of trusses made with Silicon carbide (SiC) and doped-beta tricalcium phosphate (TCP). As the resolution was not a critical requirement for the targeted applications, DIW was considered as the most relevant technological choice. After a careful optimization of the inks/pastes, macro-porous scaffolds with dense struts were successfully manufactured showing sintered densities up to 95% of the theoretical density for both materials. One of the main DIW challenges is the drying step which is often the cause of cracks if it is not rigorously controlled. In this study, osmotic drying was demonstrated as a more efficient and faster alternative to conventional climatic drying.

# Reactive sprak plasma sintering of B4C composites using B4C-Ti-B powder mixtures

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**Abstract:**

High temperature ceramics have wide range of structural, aerospace and energy applications due to their thermal stability, corrosion resistance and superior mechanical properties. $B_4C$ is one of the high temperature ceramics having superior hardness (>35 GPa) along with low density (2.52 $g.cm^{-3}$), high melting point (2763 °C), good wear resistance, corrosion resistance, ballistic efficiency and neutron absorption capacity. Due to its superior properties, it is widely used in wear resistant, neutron absorption and body armor applications in nuclear and defense sectors. However poor sinterability and low fracture toughness ($\approx$ 3 MPa $m^{1/2}$) are the major limitations of $B_4C$ applications. Due to the strong B-C covalent bonding, it is extremely difficult to sinter it below 2000 °C using conventional sintering techniques. Spark Plasma Sintering (SPS) is one of the most promising techniques to sinter the high temperature ceramics at relatively lower temperatures with the advantages of shorter sintering time and limited grain growth.

In the present study, dense Boron carbide was prepared using mechanically activated Ti-B reactive mixture as sintering aid. Ti and B elemental powders were ball milled for 8 h. This Ti-B powder was mixed with Boron carbide in the proportions of 5, 10, 20 wt.% and milled for another 4 h for good dispersion. Spark plasma sintering was carried out at 1400°C, at 50 MPa pressure with 100 °C/min heating rate. Archimedes water immersion method confirmed the samples were dense. X-Ray diffraction studies showed that some amount of WC was picked up during milling. (Ti,W)C, $(Ti,W)B_2$ phases were observed in XRD. Scanning electron microscopy revealed the distribution and morphology of these phases. EDS studies confirmed the formed phases. Mercury intrusion porosimetry revealed the nano pores with mean pore diameter of 15.4 nm. The $B_4C$-5 wt.% $TiB_2$ composition showed highest hardness of 32.2 ± 2.2 GPa.

# FLASH sintering applied to porcelain production: Development of Processing Maps

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## Abstract:

Sustainability is a concern of every industry, especially those related with high temperature processes, as for traditional ceramics. Costa Verde, a ceramic company from Portugal, put the concern into practice and investigated the application of a new and sustainable sintering process, the FLASH sintering, to produce porcelain-based materials. FLASH is a Field Assisted Sintering Technique that allows the densification of ceramics at significantly lower temperature and time (less than 60s). The decrease in sintering temperature and time has a direct impact on sustainability and an indirect impact on the increase of production rate. However, FLASH sintering is not easily implemented in the industry and cannot be used for all types of ceramics. Therefore, it is fundamental to establish and define the FLASH sintering conditions for each case. Within this framework, in this work, we established FLASH processing maps for the Porcelain of Costa Verde by studying the effects of electric field and current on densification and microstructure development.

## Acknowledgements:

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# Sol-Gel and reactive-SPS: a route towards toughening of alumina with low dimensionality carbon nanophases

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## Abstract:

Low dimensionality carbon nanophases have attracted the attention as outstanding candidates for the reinforcement of advanced ceramic matrix composites (CMCs). Nevertheless, and despite several decades of effort, the use of graphene or carbon nanotubes as toughening agents in CMCs is still an open source of debate and researching. The lack of dispersion, the inter/intragranular location within the ceramic matrix, or the type of bonding matrix-reinforcing phase, are experimental issues that hinder the achievement of irrefutable and compelling mechanical reinforcements.

In this work, fully-dense alumina matrix with graphene oxide flakes are obtained by a new fabrication procedure based on a sol-gel route and reactive-SPS. This alternative methodology improves the dispersion of the graphene flakes within the composite, and is intended to induce the intragranular location of the flakes, and promote the formation of strong bonds between graphene flakes and ceramic matrix (Al-O-C oxygen bridges). The micro- and nanostructure of these composites are researched by techniques such as nitrogen physisorption or SEM and XPS. The high specific surface of the sol-gel precursor powder revealed as an interesting characteristic for enhancing faster and total sintering. Exhaustive SEM inspections of the precursor powder have revealed the absence of intergranular graphene agglomerations, and micro-Raman mapping was used for the first time to confirm the more homogeneous dispersion of graphene.

Besides, the mechanical properties have been studied by Vickers and Berkovich indentations. Features such as hardness, Young's modulus, and indentation fracture toughness are measured for different graphene contents. Finally, results are compared with those from conventional alumina-graphene CMCs.

## Acknowledgements:

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# Optimization of inks formulations for processing dense lithium disilicate glass-ceramics by Robocasting

Manuel Fellipe Rodrigues Pais Alves[1], Claudinei Santos[2], Susana Maria Henriques Olhero[1], Maria Helena Figueira Vaz Fernandes[1]

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## Abstract:

Additive manufacturing has attracted attention in the ceramic's fabrication, mostly because it is efficient on the manufacture of complex structures with reduced material waste, when compared to traditional methods. Among all the additive manufacturing technologies, the Robocasting technique stands out for its low processing costs, water-based inks, and the use of low amounts of polymeric additives. However, for the development of dense glass and glass-ceramic materials by robocasting, the thermal compatibility between the polymeric additives and glass system must be considered. Some high-end glasses systems present a low glass transition temperature, and if all the polymeric additives used in the ink formulation are not burned out until this point, there is a tendency of the polymeric material to be trapped due to the glass viscous behavior, inducing high levels of porosity. In this work, a high-end glass-ceramic based on lithium disilicate, which has great appeal in dentistry, has been chosen as subject of the study. The glass was melted, poured on water, and milled for up to 5 hours to achieve an optimized particle size distribution. The inks were optimized with a single additive route, employing different concentrations of carboxymethyl cellulose (CMC35 or CMC500) or a hydrogel (Pluronic F127). The glass powder and all polymeric additives were characterized by X-ray diffraction, FTIR, thermogravimetry and differential thermal analysis. All developed inks were characterized by their rheological properties (viscosity and viscoelastic properties). The impact of the polymeric additives on the rheological behavior of the inks and on the residual porosity of the glass ceramics are discussed, aiming to define the most suitable formulations for an efficient robocasting.

## Acknowledgements:

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# Laser surface modification of Inconel 625 by molybdenum and titanium carbides

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## Abstract:

This research concerns laser modification of Inconel 625 surface by transition metal carbides and possibility of carbide layer formation by the laser on alloy surface. Titanium carbide and molybdenum carbide powders were mixed together and sprayed on the polished nickel alloy substrate. The process was conducted in argon atmosphere in the reaction chamber by JK200FL fibre laser equipped with laser scanner. Laser treatment was performed using pulse wave mode with power up to 50W and 40 microns laser beam spot. Results shows that it is possible to obtain undissolved titanium carbide in Inconel 625 substrate fixed by molybdenum rich metallic matrix. Presented results include optical and scanning microscopy observations, EDS analysis and Raman spectroscopy which confirmed TiC presence in final samples. The obtained layer was crack free.

# Spark plasma sintering of Inconel 625 – Ti/Zr mixed carbides

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## Abstract:

The research concerns Inconel 625 modification by fine particles of laboratory synthesized $(Ti,Zr)C_{0.85}$ transition metal mixed carbides. The composites containing from 0 – 20 wt. % were homogenised with dextrin in rotary mill and spark plasma sintered at 1000°C in vacuum $2 \cdot 10^{-2}$ mbar under 45 MPa uniaxial pressure for 20 minutes. The heating rate was 100°C/min. In the first step such obtained samples were characterised in means of: densification, phase composition (XRD) and microstructural computer analysis of microscopic observations. Afterwards composites were subjected into differential scanning calorimetry with thermogravimetry analysis of oxidation process up to 800°C. The samples were also oxidized at 800°C in tube furnace from 2 – 24 hours. Such treated composited were taken into mass control investigations, SEM observations with EDS mapping and confocal microscopy analysis.

## Acknowledgements:

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# The microhardness improvement of titanium alloy by ZrO2 particles addition

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## Abstract:

One of the most common titanium alloys present in the industry and laboratory studies is Ti6Al4V. The main goal of this research was to improve material hardness by introducing of $ZrO_2$ particles into its surface. From the technological point of view alloy surface modification was made by zirconia particles melting in metal by use of fibre laser in continues wave mode. The used power density was up to 6.4 $MW/cm^2$. The $1000^oC$ melting point difference between ceramic particles and metal alloy together with density difference allowed to incorporate $ZrO_2$ into alloy surface. It improved microhardness in most cases by 3-4 times from about 300HV even up to 950 – 1200HV depending on laser process condition. The microstructural and chemical analysis were made on laser processed material surface and its cross-section by use of SEM-EDS.

# Novel hybrid method to additively manufacture graphite structures by Binder Jetting

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## Abstract:

Our study introduces two hybrid processes integrating an additive manufacturing technique with post-processing treatments, resulting in higher density and reduced defects/porosities of the parts. Various characterization methods were used to investigate the microstructure and mechanical properties which confirmed the fabrication of graphite parts with near theoretical density (without waste). This method of green (as printed) body densification is expected to create a new avalanche of industrial applications that are hitherto unexplored in hybrid additive manufacturing using BJP.

## Acknowledgements:

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# Development of printing resolution for binder jet 3D printing of cement-based inorganic materials: Implementing in-situ control of binder flow rate during printing

Farid Salari, Paolo Bosetti, Vincenzo Sglavo

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## Abstract:

Particles bed binding by selective cement activation -known as binder jetting technology- is an additive manufacturing (AM) process for producing cement-based inorganic materials. The features are created through the printhead movement over the powder bed at a given feed rate which forms a designed cross-section of the part from the coalescence of successive droplets. AM technologies such as binder jetting are based on physical principles of process parameters. But, current binder jetting operations rely on low fidelity data transmission between powder–binder interaction and the computer numerical control machine. Binder flow rate is the most critical printing characteristic. It has a significant influence on the mechanical properties and shapes accuracy of the printed parts. We suggest a new computing core that collects information from powder-binder interaction and binder flow rate and transmits processed data to the system's pressure control unit. As a result, various infill patterns can be adopted. The used system in this study is based on designing a rate of voxel ($r_v$), and accordingly calculating the correlated amount of binder which is a function of powder bed density and $r_v$. The required flow rate for the printing process is automatically adjusted by a proportional pressure regulator. In the present study, benchmarks of magnesium oxychloride cement parts have printed to evaluate the effect of in-situ pressure control on the printing resolution. The initial flow rate is updated based on actual printing speed (feed rate). The printed benchmark artifact are characterized by high geometrical accuracy depending on various infill strategies. The results show that the developed NC controller can satisfactorily improve printing resolution for cementitious materials.

# Effect of binder flow rate on the product quality of binder jet 3D printed magnesium oxychloride cementitious materials

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*University of Trento, Trento, Italy*

## Abstract:

This research studies a framework for binder jetting of cementitious material with inorganic binder. The printing process includes iterative steps of deposition of powder blend layers and jetting of binder liquid. Rheological properties of the binder fluid, technological properties of the powder feedstock and powder-binder interaction (PBI) were studied to depict an overall framework. Binder flow rate is a significant process factor that for cementitious materials is identified via the stoichiometry of the chemical reaction, "rate of voxel" ($r_v$), and powder bed density ($rho_{pbd}$). Demanded amount of binder should be adjusted either by pressure or signal frequency of the dispensing valve. PBI determines the product quality depending on set pressure for required flow rates. In this study,$r_v$ , $rho_{pbd}$, and particle sizes have been identified as the variables to study the effect of binder flow rate on density and flexural strength of the product. Smaller $r_v$ leads to more numerous cementitious bonds among aggregates and, therefore, higher densities with a better modulus of rupture were recorded. The influence of infill pattern was tested through designed specimens with 100% infill and rectilinear 0°, 45° and 90°, grid 0°-90° and 45°-45°. Samples with the deposition droplets' direction parallel to the x-axis demonstrated a higher modulus of rupture. Due to the droplets migration within particles, fabricated parts have a high level of residual porosities in a solid voxel and this critical issue limits this technology to be currently used in concrete 3D printing. Outcome results aid engineers in having a solid framework for further studies to develop the technology.

# Fabrication of Polymer Derived Mullite Ceramics Made by Pellet Extrusion 3D Printer

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## Abstract:

Thermoplastic behavior of preceramic polymers (PCPs) along with their low processing temperature has made fused deposition modeling (FDM) a favorable shaping method for fabrication of polymer derived ceramics (PDCs). Pyrolysis of Si-based preceramic precursors at elevated temperatures results in elimination of organic groups and leaves a ceramic residue that is an amorphous $SiO_2$. Despite all the advantages, fabrication of bulk polymer derived ceramics is critical due to gas evolution during pyrolysis and large shrinkage. Shrinkage can be reduced using an inert or active filler, however, production of dense PDCs by FDM has remained a challenge because of intensive gas release during crosslinking and pyrolysis. Investigated ceramic composition in this study is a thermoplastic polysiloxane and alumina powder (active filler) to achieve 3:2 mullite. Dense ceramic could be achieved by the addition of MgO sintering additive at 1600°C for 5h. Thermoplastic Ethylene vinyl alcohol (EVA) and polyvinyl alcohol (PVA) were used to achieve sufficient thermoplastic properties for pellet extrusion 3D printing, and the PVA was removed by solvent debinding process. The water-soluble binder additive generated an interconnected porous network by leaching out the soluble binder after shaping and building pathways for gaseous products escape. The effect of different EVA grades and PVA content on printability and debinding behavior was studied. EVA with a lower melt flow index (MFI) showed better compatibility with PVA additive in terms of mixing and printing process steps. Above 80% PVA removal is necessary to provide interconnected channels for efficient gas removal during crosslinking and therefore closed spherical pore structure could be avoided in the sintered structures.

# Processing of Rh-doped perovskite protective filters for selective gas sensing

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## Abstract:

Owing to its excellent properties, $BaTiO_3$ is used for manufacturing of thermistors and dielectric ceramic capacitors, photocatalysis, and in gas sensing. The incorporation of precious metals into the perovskite structure enables the stabilization of $BaTiO_3$ catalysts due to the self-healing mechanisms: the formation of well-dispersed metal nanoparticles under reducing conditions and re-incorporation of metal nanoparticles into the crystal lattice under oxidizing environments. This concept is successfully proven for gas sensing/monitoring of reformate products (CO and $H_2$) and during hydrogen separation and purification. Significant decomposition of traditional $SnO_2$ sensors under such reducing conditions necessitates the use of protective coatings to improve the performance as well as avoidance of sensing layer degradation. In this sense, the perovskite group of materials display several advantages such as: ease removal of oxygen, oxygen vacancies, electron mobility, and valence control that could improve gas sensing. This work reports on the synthesis of Rh-incorporated $BaTiO_3$ by oxalate-assisted co-precipitation method and processing into microgranules for better application of protective filters on to gas sensors. The synthesis process was performed in two steps: (1) preparation of precursor solutions with following mixing; (2) co-precipitation by pouring an oxalic acid ethanol solution in the cationic precursor solution with subsequent precipitate filtration, drying and calcination. The micro-granulation process is carried out in a laboratory spray-dryer. Soluble organic polymers are added as processing-aids as well as sacrificial pore-formers that lead to a structural porosity that enhances gas diffusion within the Rh-incorporated $BaTiO_3$ granulates.

# Lithography-based Ceramic Manufacturing of Precise Multi-Material Components

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## Abstract:

Combining different materials in 3D printing is garnering widespread attention due to the wide range of possibilities that it provides to produce parts, with enhanced functionality and/or improved mechanical properties. This paper presents the combination of lithography-based ceramic manufacturing, a technology capable of realizing high resolution 3D printing for ceramics with the mentioned multi-material approach. The presented approach not only enables the combination of different ceramics in different layers of the printed component, but also the spatially resolved combination within the same layer and hence, paves the way to the realization of complex bi-phasic ceramic components. First successful trials that will be presented include the combination of alumina and zirconia-toughened alumina (ZTA), alumina and zirconia, as well as zirconia and hydroxyapatite, respectively. For the combination of alumina and ZTA in a multilayer architecture an exceptional strength of >1 GPa could be demonstrated. The paper will present the actual multi-material 3D printing process, but also focus on the results and current challenges in terms of co-sintering of different ceramic materials. The initial results show that this technological approach holds great potential to path the way from classical single material structures to bi-material components and subsequently multi-material and functionally-graded ceramics.

# Shrinkage-free sintering of tin oxide ceramics – Monitoring microstructure and elastic property changes by temperature-dependent impulse excitation

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## Abstract:

Tin oxide ($SnO_2$) exhibits a quite rare and unusual sintering behavior: it sinters without shrinkage, i.e. without densification. The reason is the prevalence of non-densifying sintering mechanisms such as surface diffusion and evaporation-condensation. Therefore, it is an exceptional model system that allows one to study property changes due to microstructural parameters different from porosity, which would otherwise completely overshadow the other parameters in affecting the properties (including grain size). In this contribution we present experimental findings for pure tin oxide ceramics prepared by uniaxial pressing (at 50 MPa) and partial sintering to temperatures in the range 600–1400 °C with different dwell times (up to 6 hours) at a heating rate of 2 °C/min. Using scanning electron microscopy, mercury porosimetry and gas adsorption it is shown that during sintering the geometry and topology of the pore space changes, although the porosity, i.e. the pore volume fraction, remains essentially constant. Despite the constant porosity, the elastic properties, in particular Young's modulus and other elastic moduli, as measured by temperature-dependent impulse excitation, undergo significant changes, when the original sintering temperature is exceeded and the sintering process continues. Combining results from stereology-based image analysis and other methods with numerical modeling on computer-generated microstructures it is shown that these changes are related primarily to changes in the pore surface curvature.

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## Acknowledgements:

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# Fabrication of doped β-tricalcium phosphate bioceramics by robocasting for bone repair applications

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## Abstract:

β-tricalcium phosphate (β-TCP, β-$Ca_3(PO_4)_2$) is one of the most attractive biomaterials for bone repair since it shows an excellent biological compatibility, osteoconductivity, and resorbability. It is already commercialized under granules or preforms for bone filling but there are still some issues for β-TCP porous scaffolds fabrication. Indeed, β-TCP cannot be used as scaffolds in large bone defects or in load-bearing areas due to its weak mechanical properties related to insufficient densification level. Indeed, the sintering temperature is limited because of the occurrence of a phase transition b to α-TCP at 1150°C with a large lattice expansion causing microcracks and reducing shrinkage during sintering. The thermal stability can be increased by the incorporation of dopants inside the β-TCP lattice. Indeed, such dopants like cations can replace the calcium inside the structure and stabilize the b phase reaching higher densities. Moreover, dopants can also improve biological properties of β-TCP as bone implant like the osteoconductivity or the antibacterial behaviour.

In this work, doped β-TCP powders are synthetized by coprecipitation of $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ solutions in presence of magnesium, strontium, silver and copper cations in order to prevent the phase transformation, increase the sintering temperature as well as the mechanical properties and bring an antibacterial behaviour. Rapid microwave sintering can then be successfully applied with a limited grain growth and compared with conventional sintering. Cytotoxicity and antibacterial evaluation are conducted to assess the potential of the doped β-TCP.

Finally, 3D-printable suspensions are prepared from optimized doped powder to manufacture porous scaffolds by robocasting using water-based inks.

## Acknowledgements:

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# Mass customization, with additive manufacturing

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## Abstract:

## Introduction:

3D printing is the iconic technology of the fourth industrial revolution, characterized by a merger of diverse technologies that is blurring the boundaries between physics, digital technology and biology. Technical ceramics also take benefit of this breakthrough: 3D printing enables new innovative development in various market field. To open up this technology, 3DCERAM develops large range of printers along with high quality materials.

## Experimental:

3DCERAM worked with the C900 printer since 2010 which is designed with high viscosity materials. In 2019 3DCERAM focused its research on the development of lower viscosity and higher reactivity materials with same loading content (>52% vol). Thanks to this loading, we can ensure high quality sintered parts (microstructure, density and accuracy). The use of low viscosity slurries allows the automatization of the process and reduction of the printing time.

To reach the industrial scale, the development steps are dramatically crucial. That is why, 2 new printers have also been developed: the C100 (100x100x150mm) to build knowledge and the C3600 (600x600x300mm) for large production.

## Conclusion:

Thus far, ceramic additive manufacturing was mostly associated with prototyping only but thanks to these recent developments, this technology can now meet industrial needs by offering a wide range of quality ceramic materials and large-scale processes.

## Acknowledgements:

I have read and acknowledge the above paragraph

# Challenges in designing of advanced ceramics and composites obtained by colloidal processing

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## Abstract:

Colloidal chemistry is recently used in processing of high-quality advanced ceramics and in different types of composites (e.g. ceramic-ceramic, ceramic-metal, ceramic-polymer composites). Among these we can distinguish the preparation of powders for die pressing, tape casting, gelcasting, etc. These methods are commonly used in fabrication of ceramic materials for different applications, e.g. ceramic engineering, electronics, biomaterials.

Colloidal processing of ceramics and composites requires new, effectively working processing agents like deflocculants, binders, organic monomers, etc. The results of the studies on the synthesis and application of new water-thinnable binders and new monomers for die pressing, tape casting and gelcasting of advanced ceramics and composites will be presented. The authors will also present the synthesis and application of new organic compounds based on glycerol and saccharides. The synthesized compounds are glycerol monoacrylate, 3-O-acryloyl-D-glucose, 1-O-acryloyl-D-fructose and 6-O-acryloyl-D-galactose. These substances are low-toxic, water-soluble, inexpensive and renewable. The research showed that these compounds could play multifunctional role in colloidal processing of ceramic powders and composites.

The lecture will also concern ceramic-metal and ceramic-polymer composites. Metal particles can be incorporated from metallic powder or precursor. The authors elaborated the composition of suspensions based on ceramic and metallic powders like nickel, tungsten and molybdenum in the preparation of ceramic-metal composites. The key role of the colloidal chemistry in processing of advanced ceramics will be discussed on the basis of BST-polymer composites designed for the electronic devices working at the sub-THz frequencies.

## Acknowledgements:

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# Cathode ink formulation for inkjet printing technology

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## Abstract:

Since their commercialization by Sony in 1991, lithium-ion batteries (LIBs) have been the pioneering technology used as a power source for a wide range of applications, including portable electronics and electric vehicles. Though current-day LIBs are highly developed, there are still many engineering strategies that can be used to increase their performance. Design of well-defined three-dimensional electrode structures make a significant contribution to the advancement of the field. In order to enhance the energy density, the amount of active material must be increased, thereby enlarging the electrode thickness. This, in turn, restricts ion and electron transport, resulting in poor power output. A 3D electrode structure, as an alternative, enables the electrolyte to infiltrate through the electrode volume, and hence reducing ion diffusion lengths. Inkjet printing (IJP) is an auspicious additive manufacturing method that allows for the fast deposition of thin films or patterns with high precision. It brings many advantages over other thin film fabrication methods, but the development of a suitable ink is one of the most challenging tasks for researchers. In the present work, drop-on-demand piezoelectric IJP is suggested for the fabrication of the cathode structure. The cathode ink consisting of the active material (NMC), the conductive agent (Carbon Black), the binder (NEOFLON), a dispersing agent, and a solvent was formulated and characterized (viscosity, surface tension, dispersivity, and stability). The sedimentation test demonstrated excellent stability, with no observed powders settling for up to 1 month. Several inks were formulated by varying the solid to solvent ratio, showing the range of parameters within which, the ink is theoretically printable ($1<Z<10$).

# Nanometer structured yttria stabilized zirconia via two-photon-polymerization for powder processing

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## Abstract:

Additive manufacturing of ceramics is of huge scientific interest. It might bring ceramic properties into applications, where conventional ceramic manufacturing hits its borders. One of those is high resolution and lightweight object. Those parameters are addressed by two-photon-polymerization, a light inducing machine to solidify a liquid resin within the illuminated spot via a polymerization reaction.

In this study yttria stabilized zirconia was structured with this technology, for which needs to meet three main requirements. First, the resin must be transparent at 800 nm wavelength, to prevent the pulsed laser from scattering and therefore intensity loss. Second, its viscosity should not be too low or too high to ensure an ongoing photo-polymerization reaction. Third, the resin needs to be photo-curable despite its ceramic powder fraction. The development leaded to a resin with suitable transmittance, viscosity and a powder fraction of 70wt%. The outcome of the prints and several post-processing steps are sintered structures with a positive resolution down to 400 nm, which is unique for ceramic manufacturing.

# Densification behaviour and optical properties of nano-Y2O3 ceramics doped with bivalent transition metals

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## Abstract:

Transparent yttrium oxide ceramics can be fabricated using Spark Plasma Sintering (SPS). Doping yttria with bivalent ions promotes the diffusion of ions and densification. Bivalent transition metal ions provide double benefits: they assist the densification and, at the same time, introduce optically active elements into $Y_2O_3$ bodies. The present work investigates the effect of doping nano-yttria ceramics with $Mn^{2+}$, $Ni^{2+}$, or $Zn^{2+}$ on sintering and optical properties of nano $Y_2O_3$. A commercial nano $Y_2O_3$ was mixed with acetate sources of dopants and, afterward, consolidated using SPS at a temperature between 1200 and 1500°C depending on the dopant. The samples were then characterised in terms of the final density, microstructure, optical transparency, and photoluminescence. Bivalent transition metals ions dramatically reduce the sintering temperature of $Y_2O_3$ despite the limited solubility in $Y_2O_3$ crystal structure. The influences of the incorporation of dopants into $Y_2O_3$ crystal structure, charge compensation, and defects formation mechanism on the sintering behaviour and optical properties of fine-grained yttria ceramics were critically discussed.

## Acknowledgements:

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# Structure and optical properties of Mn and Cr doped MgAl2O4 transparent ceramics with LiOH as sintering aid

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## Abstract:

Magnesium aluminate spinel is transparent in a broad wavelength range, from 0.2 to 5.5 µm. It is also capable of hosting a variety of optically active ions. Transparent polycrystalline spinel can be produced using spark plasma sintering; however, carbon contamination is an inevitable drawback of SPS. Thus, lithium fluoride is often used to promote densification, reduce carbon contamination, and improve the transparency of sintered bodies. Lithium hydroxide is an alternative to LiF, with a similar impact on densification but employing a different mechanism. However, the effects of LiOH on spinel structure, dopants, and optical properties are unclear. In this work, we report on the influences of LiOH on the photoluminescence properties of Mn and Cr doped $MgAl_2O_4$. Limited amounts of LiOH between 0.0 and 0.6 wt% were added to a commercial $MgAl_2O_4$ powder. Afterwards, the powders were doped with various amounts of manganese and chromium, up to 1 mol%. The samples were densified using spark plasma sintering at 1300°C for 5 min. The samples were characterised in terms of densification behaviour, the crystal structure of spinel, the distribution of additives, optical transparency, photoluminescence (PL) spectra and decay. The results showed that incorporating lithium into $MgAl_2O_4$ increases the structural disorder, e.g. spinel inversion, promoting the densification. Also, lithium significantly enhances the PL intensity of samples doped with Mn and Co. The impacts of structural changes and charge compensation induced by the addition of $Li^+$ in spinel lattice on PL activity were critically discussed.

## Acknowledgements:

This paper is a part of dissemination activities of project FunGlass. This project has received funding from the European Union´s Horizon 2020, research and innovation programme under grant agreement No 739,566. The financial support of this work by the projects APVV-19-0010 and VEGA 2/0028/21 is gratefully acknowledged.

# ZrO2-Mo composites fabricated by aqueous colloidal processing with the use of metallic precursor

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## Abstract:

Metal reinforced ceramics are willingly used in many industries, for example as thermal and anti-corrosion coatings, piezoelectric actuators and anode materials in solid oxide fuel cells. The high interest in ceramic-metal composites is caused by outstanding properties of these materials. Reinforcement of ceramics with metallic particles can increase fracture toughness, abrasive wear resistance or bending strength of the materials while maintaining the key advantages of ceramics, such as resistance to high temperatures and aggressive chemical environment as well as high hardness. Manufacturing of composites with the use of metallic powders has some disadvantages, for example the use of micron-size metallic particles prevents preparation of nanocomposites, whereas the use of metallic nanopowders requires special conditions for storage and handling. A good solution to overcome these problems is a replacement of the metallic powders with suitable precursors.

The aim of research was to obtain ceramic-metal composites in which the matrix was $ZrO_2$, and the reinforcement was Mo added in the form of molybdenyl acetylacetonate. Composites have been obtained with the use of two colloidal processing methods: slip casting and gelcasting. The prepared suspensions contained 45 vol% of zirconia powder and different content of the metallic phase. The rheological properties of ceramic suspensions with metallic precursor were determined, and the properties of the obtained composites (density, Vickers hardness, fracture toughness) were examined. The microstructure of the obtained composites was analyzed by using scanning electron microscope, followed by EDS and XRD analyses.

## Acknowledgements:

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# SLA printed part exhibiting biomimetic nacre like structure

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## Abstract:

Ceramics are among the best materials for structural, thermal or technical applications thanks to their excellent properties such as a high hardness, good strength, tremendous abrasive resistance, remarkable biocompatibility. However, they are still handicapped by a brittle fracture mode which restricts their use in many applications for which the ductility of metals is reassuring. To improve the mechanical behaviour of ceramics, one usual industrial approach is to develop composite materials such as ceramic matrix composites reinforced with a ductile metallic or polymeric phase along with embedded fibres. In the nature, such organized materials have long been identified and characterized, one of the most studied and best-known examples being mother of pearl. Although nacre is mainly made of $CaCO_3$ (intrinsically brittle), its toughness is nearly 3000 times greater than that of its main constituent.

The aim of this work is to verify the compatibility of processing parts with a structure similar to mother-of-pearl by stereolithography (SLA/DLP). According to the literature, it is possible to shape, by tape casting, pastes comprising alumina plates. A tape casting-based SLA technique has been used for processing simple shapes. The study was also focused on the identification of the parameters and characteristics of the paste as well as the SLA printing settings in order to enhance the mechanical properties of manufactured parts and to determine which sets of parameters make it possible to obtain a mother of pearl structure.

# Structural, Morphological and Optical Studies of Nd/Er-co-doped Y2O3 Ceramics

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## Abstract:

Sesquioxide ceramics such as $Y_2O_3$, $Lu_2O_3$, and $Sc_2O_3$ are growing in popularity due to their excellent thermal conductivity and low phonon energy, and have been extensively researched as host materials for solid-state lasers. These ceramics with high transparency can be manufactured at around two-thirds of the melting temperature by the use of sintering additives. For this, sintering additives like $ThO_2$ $La_2O_3$, $HfO_2$, $ZrO_2$, etc., have been commonly used. Recently the researchers have studied the doping effect of rare earth elements on sesquioxide ceramics along with sintering additives for their improved microstructural, Physico-chemical, opto-electrical properties, and upconversion phenomenon. In the present work, rare earth elements (Nd/Er) doped $Y_2O_3$ ceramics have been synthesized using the vacuum sintering technique at a temperature of 1700 °C. $La_2O_3/ZrO_2$ has been simultaneously used as sintering additives. Structural, morphological, and opto-electrical properties have been thoroughly studied for all the synthesized samples.

# Defect-free drying of large fine-particle ceramic bodies prepared by gelcasting method

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## Abstract:

Drying defects represent the most serious limitation of wall thickness in gelcasting of large fine-particle ceramic bodies. In this investigation, we developed a defect-free drying process for bodies with large cross-sections prepared from fine zirconia particles. First, we identified the typical drying defects and relevant mechanisms of their generation. We studied not only the drying step but also the following steps of thermal treatment (pre-sintering and sintering) to identify also those defects that originate from drying but appear only in the later processing stages. Then, we focused on reducing the pressure gradient and differential strain during drying by varying the monomer content and choosing appropriate non-volatile cosolvents. Polyethylene glycols with different molecular weights and glycerol were used as non-volatile cosolvents dissolved in water as the primary solvent. The effect of the cosolvents was complex because they influenced the whole gelcasting process. The most important effect of the cosolvents in preventing the formation of drying defects consisted in decreasing inhomogeneous shrinkage during evaporation of the primary solvent. During drying, the non-volatile cosolvents remained in the ceramic structure and were homogeneously removed later along with the polymer gel and other organic species during pre-sintering. The effect of the individual cosolvents on the gelcasting process was assessed and the optimal cosolvents for particular applications were discussed.

## Acknowledgements:

This research was financially supported by the Czech Science Foundation under the grant 20-20175S.

# Analysis of ceramic sintering at the particle length scale by in-situ and post-mortem synchrotron X-ray nano-tomography

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## Abstract:

Ultra-high-resolution capabilities at the ID16B nano-analysis beamline of the upgraded ESRF synchrotron facility have made investigation of ceramic powders at the individual particle length-scale feasible. These features were taken advantage of to investigate and improve the understanding of sintering in ceramic powder systems. Complete 3D images were obtained with a voxel size as low as 25nm to depict particles and pores with enough details for subsequent quantitative analyses. Post-mortem analyses were initially carried out on a set of representative micron-sized alumina powders sintered separately at 1500°C for various time periods. The phase contrast X-ray holotomography technique employed at the beamline allowed us to include large volumes of interests and analyse various stages of sintering corresponding to the time periods. Furthermore, to monitor the evolution of sintering in real time, nano-tomography experiments were attempted in-situ inside the beamline experimental hutch. A compact high-temperature furnace was designed and developed for the same, providing us with images in the course of sintering at nano-scale for the first time. Several sintering phenomena contributing to the collective behaviour of the particles were accurately observed at the local scale. The subsequent quantitative investigations served as a validation to the results obtained from the post-mortem analyses as well as offered novel insights into sintering mechanisms. Data resulting from quantitative image analyses were used to explore both densification and grain growth phenomena throughout the sintering cycle. The experimental results were also subjected to a DEM simulation to further compare and validate key sintering parameters.

## Acknowledgements:

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# Upcycling of waste glass in development of FFF ceramic material

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## Abstract:

Waste reuse and management is becoming an increasingly important part of the industrial applications of materials. Although glass recycling is commonly accepted as the main route to re-utilize the materials and energy spent during its production, use of glass as the sintering additive in ceramic production process can also decrease the amount of new raw materials required in the whole technology.

In this work, we created a new modified version of our Fused Filament Fabrication (FFF) feedstock material previously published elsewhere [1]. The new formula consists partially of recycled glass powder (RGP), similarly to the one used in production of foamed glass that replaces originally used sintering agents.

The original material is sintered at a temperature around 1350°C, while the new formulation allows for further decrease in the processing temperature, thus decreasing the environmental impact of the material production in multiple ways – not only by reusing of the glass material, but to also decrease energy consumption needed to produce the new products.

Modified filament printability was not influenced by the substitution of the sintering agent. In addition, decrease of sintering temperature to about 1200°C resulted in bodies with comparable mechanical properties.

[1] VETEŠKA, P., Z. HAJDÚCHOVÁ, J. FERANC, K. TOMANOVÁ, J. MILDE, M. KRITIKOS, Ľ. BAČA a M. JANEK. Novel composite filament usable in low-cost 3D printers for fabrication of complex ceramic shapes. Applied Materials Today [online]. 2021, 22. ISSN 23529407. Available from: doi:10.1016/j.apmt.2021.100949

## Acknowledgements:

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# Multi-material printing of reaction bonded carbides by robocasting

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## Abstract:

In the present work, reaction bonded boron carbide (RBBC) and reaction bonded silicon carbide (BRSC) composites were fabricated using multi-material robocasting followed by liquid silicon infiltration (LSI). The fabrication of carbide based materials using LSI is of great technological interest because it avoids the need for the relatively high temperatures and pressures required in traditional fabrication. Multi-material robocasting offers the possibility of combining materials and thus their properties, as demonstrated in this work with silicon carbide (SiC) and boron carbide ($B_4C$).

The feasibility of combining RBSC and RBBC was demonstrated by printing multilayer bending bars. The microstructure of the samples was investigated and, in particular, the interfaces at each processing step were studied. After LSI, cracks were observed in the $B_4C$ layers due to differences in thermal expansion, but the interfaces showed no delamination and good interfacial bonding between the layers was evident. Hardness measurements were performed to investigate the interfacial bonding and residual stresses in the materials used. The manufactured RBSC and RBBC samples showed a hardness of 18.3 GPa and 17.1 GPa, respectively. The residual stresses in the layers were calculated theoretically and also based on the crack pattern generated by Vickers indentation. Tensile stresses in RBBC and compressive stresses in RBSC were determined and can explain the cracking in the laminated structures.

# Improving the properties of ceramic materials by doping combined with colloidal processing

Piotr Wiecinski, Michał Kukielski, Radosław Żurowski, Anna Więcław-Midor, Justyna Zygmuntowicz, Artur Kasprzak

*Warsaw University of Technology, Warsaw, Poland*

## Abstract:

The intense development of ceramic materials is related to their excellent and interesting properties like: high corrosion, heat and wear resistance, high hardness but also n-type and p-type conductivity, piezoelectric and ferroelectric properties or light transparency. However, in order utilize these properties it is necessary to obtain materials o high quality and defect free microstructure. Moreover, shaping methods should give the possibility to adjust the properties of materials e.g. by doping. Colloidal processing methods meet these both requirements. Within the research wet forming methods were applied to obtain high density ceramic materials (ZnO, $Al_2O_3$) modified by metallic and graphen oxide additions in order to increase the mechanical properties and electrical conductivity. In case of metal addition, metal salts were used as water-soluble precursors. DCC method (Direct Coagulation Casting) was used to obtain Co and Cu doped ZnO-based materials. Such approach allows to distribute homogenously even small quantities of compounds. The influence of sintering parameters as well as the amount and type of metal precursor on the microstructure and properties of ZnO-based ceramic was analysed. Ceramic-graphene composites are also intensively developed during last 10 years. Due to almost two-dimensional shape of graphene and its high tendency to agglomeration it is difficult to obtain homogeneous composite by wet forming method. However, within our research, by using functionalized graphene oxide it was possible to achieve high solid loading of $Al_2O_3$ and graphene in the suspension of low viscosity. The effect of the graphene oxide modification and sintering conditions on the microstructure, electric and mechanical properties of $Al_2O_3$-based materials was investigated.

## Acknowledgements:

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# Photocurable ceramic dispersions of different compositions for additive manufacturing techniques

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## Abstract:

The increasing interest in complex-shaped ceramic elements cause dynamic development of additive manufacturing techniques also known as rapid prototyping or 3D printing. Ceramics of complex shape are more often desirable in many fields, such as medicine, dentistry, electronic or space industry. By using additive manufacturing methods, objects are built from CAD projects from many thin liquid layers of a powder dispersed in a monomer. Single layers are solidified by the photopolymerization in a UV light. The generated polymeric network holds ceramic particles in its matrix to shape up the 3D structure of the green body. The key stages in the fabrication of complex ceramics by these techniques are the preparation of stable and photocurable ceramic dispersions and the selection of favourable curing mechanism. For this reason, there is a big interest in the development of compositions of such suspensions. In this research, the various curing systems containing the monomer (e.g, acrylates, oxetanes), the photoinitiator (e.g. onium salts), the ceramic powder (e.g. $ZrO_2$, $Al_2O_3$, $SiO_2$) and other organic additives (e.g. dispersing agents) have been prepared. The influence of the type of powder, solid loadings, the concentration of the photoinitiator, the type of the used monomers on the rheological properties of the dispersions and a cure depth were examined. The complex ceramic parts were fabricated by using selected ceramic dispersions by stereolithography and robocasting methods.

## Acknowledgements:

This work has been financially supported by Warsaw University of Technology (project number: IDUB TM-1).

# Fused Deposition Melting of Carbon Fibre Reinforced Ultra-High Temperature Ceramics Matrix Composites

Jon Binner, Daorong Ye

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## Abstract:

Ultra-high temperature ceramics matrix composites, UHTCMCs, can be used for applications such as heat shields and jet vanes operating in harsh environments. The carbon fibre reinforced ceramic composite has a higher toughness compared to the monolithic UHT ceramics, and the ceramic matrix protects the carbon fibre from degrading in extreme operating environments.

This work focuses on an additive manufacturing method for the fabrication of carbon fibre reinforced ceramics, allowing the simultaneous fabrication of continuous carbon fibre and ceramic matrix. The fused deposition melting (FDM) technique allows flexibility in the carbon fibre reinforcement structure, whilst being capable of producing parts of complex shapes and good surface finish, potentially without a need for final machining. The influences of the FDM parameters are currently being investigated and the research aims to increase the ceramic loading and minimise the porosity to improve the thermo-mechanical properties of the samples after FDM and pyrolysis, reducing the demand for subsequent chemical vapour infiltration to densify the parts.

# Novel materials and fabrication routes for target components for radioactive ion beams

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## Abstract:

Radioactive ion beams have attracted a great deal of attention due to their applications in nuclear physics, material science and astrophysics. Moreover, the development of ISOL (Isotope Separation On-Line) facilities has led to fundamental advances in the field of nuclear medicine, with particular interest in the production and release of radioisotopes. Further advantages are linked to the appropriate choice of the ISOL target material and titanium carbide perfectly meets the demands in terms of thermal and mechanical properties. However, the release of isotopes strictly relies on the presence of open porous structures, thus enhancing the diffusion from the target material. To fulfil this requirement, additive manufacturing has proved to be an appealing technique and enables the production of three-dimensional parts with high-order controlled architecture. Direct ink writing process has been successfully employed for the fabrication of complex structures based on TiC commercial powders, even though this route does not allow for customization of the material properties. The sol-gel method offers a versatile approach to overcome this shortcoming, providing a powerful tool to obtain tailor-made materials. Research is still underway to investigate fine-tuning of the properties; nevertheless, mesoporous titanium carbide exhibiting exquisite textural properties has recently been synthesised by means of a sol-gel route involving a titanium alkoxide and phenolic resin, which was later substituted by the more environmentally friendly sucrose. Ongoing efforts are thus devoted to the coupling between additive manufacturing processing and sol-gel chemistry, offering tremendous possibilities and new perspectives for the design of advanced materials with novel properties.

# Additive Manufacturing of advanced ceramics by layerwise slurry deposition and binder jetting (LSDprint)

Andrea Zocca, Nils Hendrik Schubert, Jens Günster

*Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany*

## Abstract:

Powder bed technologies are amongst the most successful Additive Manufacturing (AM) techniques. Powder bed fusion and binder jetting especially are leading AM technologies for metals and polymers, thanks to their high productivity and scalability.

The application of these techniques to most ceramics has been difficult so far, because of the challenges related to the deposition of homogeneous powder layers when using fine powders.

In this context, the "layerwise slurry deposition" (LSD) has been developed as a layer deposition method which enables the use of powder bed AM technologies also for advanced ceramic materials. The layerwise slurry deposition consists of the layer-by-layer deposition of a ceramic slurry by means of a doctor blade, in which the slurry is deposited and dried to achieve a highly packed powder layer. This offers high flexibility in the ceramic feedstock used, especially concerning material and particle size.

The LSD technology can be combined with binder jetting to develop the so-called "LSDprint" process for the additive manufacturing of ceramics.

The LSDprint technology combines the high-speed printing of binder jetting with the possibility of producing a variety of high-quality ceramics with properties comparable to those achieved by traditional processing.

In this presentation, the LSD process will be introduced and several examples of application ranging from silicate to high-performance ceramics will be shown.

Recent developments towards the scale-up and industrialization of this process will be discussed, alongside future perspectives for the multi-material additive manufacturing.

# Structural Investigation of 3D Printed Reaction Bonded Silicone Carbide

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## Abstract:

Silicon compounds including silicon carbides (SiC) are used in many critical fields such as aerospace components, high temperature applications and thermal management systems. SiC can be produced by number of techniques, such as chemical vapor deposition (CVD), reaction-sintering, polymer impregnation and pyrolysis, or sintering with various additives, mainly, for simple geometries. But for production of components of higher complexity (eg, heat exchangers, flanges, turbines) may not be readily produced using current technologies. That can be done by Additive Manufacturing.

Fabrication process of Reaction Bonded Silicone Carbides (RBSC) including Binder Jet (BJ) 3D-Printing, additional carbonization and Capillary Liquid Silicon Infiltration (CLSI) has been examined. This method allows to produce significant RBSC based on SiC matrix with inclusions of residual Si less than 10-15%. The obtained structure was analyzed by means of high-resolution SEM (scanning electron microscopy) and TEM (transmission electron microscopy) for better understanding of mechanisms of secondary SiC phase formation, it's microstructural properties. The results showed there are four main phases: primary a-SiC particles, secondary (reaction-bonded) a-SiC phase having the same orientation as the primary SiC particles it grew from, leftover silicon that did not react with the excess carbon, and a SiB3-type Si-B-C ternary phase.

# Effects of Eu, Y, Mg doping on the sintering and microstructural development of MgAl2O4

Paulina Zubrzycka[1], Dariusz Zientara[2], Anita Trenczek-Zając[2], Marta Radecka[2], Thomas Graule[1], Michael Stuer[1]

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## Abstract:

In order to obtain high-performance – small grained and optically transparent – spinel, the control of density versus grain growth during sintering is key. In addition to appropriate sintering cycles, the use of dopants that segregate towards grain boundaries modifying diffusion mechanics and grain boundary energies are efficient means to control and modify the final microstructure. For some dopants, complexion transitions may occur modifying the structure and properties of grain boundaries. Such complexion transition has been previously reported in Eu-doped $MgAl_2O_4$ [1][2]. Direct observation of complexion transitions is labor intensive, but efforts can be reduced by identifying potential fingerprints during master sinter curve or microstructural observations.

In this work, the effects of single- and co-doping strategies of $MgAl_2O_4$ with Eu, Mg, Y at a constant total cationic doping level ratio of 500 ppm on the microstructural development is investigated (equi-molar concentration for co-doping). Dilatometry studies are used to determine the apparent activation energies at various density states and identify through the master sintering concept fingerprints that might be associated to complexion transitions. Selected doping strategies and pre-sintering conditions are used to evaluate optimal processing routes towards high performance transparent $MgAl_2O_4$ after a post-HIP treatment. The study offers new insights into microstructural development of spinel for optimal doping and sintering strategy selection for transparent $MgAl_2O_4$ applications.

1. Schumacher, Marvel et al. 2016

2. Krause, Kundu et al. 2020

# Rheological aspects in designing the functional properties of ceramic-matrix-composites

Radosław Żurowski[1], Paweł Falkowski[1], Michał Kukielski[1], Anna Więcław-Midor[1], Artur Kasprzak[1], Justyna Zygmuntowicz[2], Mikołaj Szafran[1], Piotr Wieciński[1]

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## Abstract:

The huge expectations of society in almost every area of human life have become a reason for the impressive progress in science. The interdisciplinary approach of scientists worldwide, and therefore the synergy of many knowledge fields, has contributed to the establishment and the continuous development of a new scientific area - composite materials. Unusual features of these materials are the result of combining the properties of various constituent components (two or more). Nowadays, composite materials are present in almost every aspect of human lives, particularly in application areas where their smart and innovative character dominates. This work is devoted to smart ceramic-matrix-composites based on oxide nanopowders. The authors present the results concerning the influence of the utilized components on the rheological properties of colloidal suspensions. The rheological characteristics include both dynamic viscosity tests as a function of shear rate and oscillatory measurements. The main focus was put on the influence of the particles morphology and volume fraction of ceramic powders on the rheological behaviour of the suspensions. The results obtained in this area allowed to determine how the key rheological parameters translate into the functional properties of the final composites.

## Acknowledgements:

The studies were funded by Materials Technologies project granted by Warsaw University of Technology under the program Excellence Initiative: Research University (ID-UB) - Agreement number: 1820/3/Z01/POB5/2021.

# Symposium C: Modelling, Simulation, characterization and digitalization of materials and processes

## Invited presentation:

# Fracture behaviour in the vicinity of Curie temperature of BaTiO3 piezoceramic

Zdeněk Chlup[1], Hynek Hadraba[1], Daniel Drdlik[2], Oldrich Sevecek[3], Filip Siska[1], Karel Maca[2]

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[3] *FME, Brno University of Technology, Brno, Czech Republic*

## Abstract:

Barium titanate is the most studied ferroelectric material serving as a lead-free alternative to nowadays commercially used piezoceramics. The drawback of all alternative materials is their relatively low piezoelectricity accompanied by brittleness and low strength. The contribution is focused on the phenomenon that occurred in the vicinity of the Curie temperature where a dramatic change in elastic properties is reported, but the fracture behaviour was not examined in detail. According to experimental data obtained, the fracture toughness of the BTO based material can suffer by step like change. The microstructure and elastic behaviour can be related to this change in fracture behaviour. The presented study is aiming to clarify such behaviour observed in the vicinity of Curie temperature and offer an explanation based on numerical simulations of the model of real microstructure. The fracture toughness change observed will be related to the kinetics transformation of individual grains dependent on their size generating local residual stresses.

## Acknowledgements:

This work was financially supported by the Czech Science Foundation project 21-24805S.

## Invited presentation:

# Are disclination dipoles responsible for high temperature superplasticity in ceramics?

Diego Gomez-Garcia, Jose Antonio Bejarano-Palma, Bibi Malmal Moshtaghioun

*Departement of Condensed Matter Physics, University of Seville, Spain, Sevilla, Spain*

### Abstract:

A model for high-temperature plasticity of polycrystals controlled by disclination dipoles is proposed that predict a parabolic dependence of the strain rate versus the applied stress. The presence of a precise stationary disclination density explains the origin of plasticity without microstructural invariance, commonly known as superplasticity. The disclination mechanism is universal, although other processes, such as dislocation glide, are superposed to this one in many systems such as metals or metallic alloys. While, in ceramics it is likely to be the only operative mechanism. Activation of disclination dipoles is a necessary condition for plasticity and sufficient one for superplastic yielding.

### Acknowledgements:

All the authors are grateful to the Ministerio de Ciencia y Innovacion de España for the research funding through the project PID2019-103847RJ- I00 financiado por MCIN/ AEI /10.13039/501100011033 and 'Junta de Andalucía' through the project P18-RTJ-1972.

## Invited presentation:

# The Ball-on-Three-Balls-test: Improving accuracy while simplifying stress evaluation

Maximilian Staudacher, Tanja Lube, Peter Supancic

*Montanuniversitaet Leoben, Department of Material Science, Leoben, Austria*

## Abstract:

The Ball-on-Three-Balls-test has proven to be an accurate and easy-to-use option for strength testing. However, the maximum stress must be calculated based on Finite-Element-Analysis (FEA) results. For this purpose, a fitted function was provided by Börger et al. in 2002. This function is based on results which were generated under the assumption of punctiform load introductions, a condition that is valid for most specimens in practice. Deviations from these ideal conditions occur through large specimen deformations, plastic deformation of the balls, friction, or an increase in contact-area between the balls and the specimen.

In this work, these non-linear effects are investigated by FEA for a wide range of specimens (with respect to the relative thickness or overhang, the applied load, and the elastic properties of both the balls and the specimen). It is shown that the maximum stress of both exceptionally thin and thick (relative to the support-radius) specimens is sensitive to the area of contact between the loading ball and the specimen. Furthermore, thin specimens are subject to large deformations which significantly decrease the maximum stress. Based on these findings, characteristic specimen geometries and properties have been defined to limit the applicable range of the function for punctiform load introductions. To further increase usability, a shorter fitted function for this case is presented. For specimens that do not fulfil these specifications, non-linear effects will be considered with adjustment factors added to the new fit function.

Therefore, an easy-to-use stress determination is provided for most practical specimens while also allowing stress determination for exceptionally thin or thick specimens with increased accuracy.

## Invited presentation:

# Digital twin of sintering using artificial neural network as constitutive law

Jingzhe Pan[1], Venkat Ghantasalaa[1], Shuihua Wang[2]

[1] *School of Engineering, University of Leicester, Leicester, United Kingdom*

[2] *School of Computing and Mathematical Sciences, University of Leicester, Leicester, United Kingdom*

## Abstract:

A digital twin refers to a pair of physical process (such as sintering) and its digital representation (such as a finite element model of sintering). It is a natural extension to computer modelling but a key difference is that the computer model in a digital twin is frequently updated using data collected from the physical process. The final shape and dimensions as well as the state of microstructure of sintered ceramics can be predicted using the finite element method. The prediction is however subject to uncertainty in the actual manufacturing process. The use of digital twin can reduce the uncertainty in the computer models. A constitutive law connects strain rates to stresses is at the core of the finite element analysis. A digital twin for the sintering process requires a constitutive law that can be updated using data collected from the manufacturing process. The updating is better dealt with using deep machine learning techniques. An artificial neural network (ANN) can learn the effects of manufacturing variables on the sintering process directly from collected data. However, training and validating an ANN requires huge amount of data which are unavailable or incomplete in a real manufacturing process. To overcome this problem, this talk presents a transfer learning technique. It is demonstrated that the data requirement can be reduced by employing a two-step learning technique. In the first step the ANN is made to learn an existing analytical constitutive law. Secondly the weights and bias of the ANN are transferred to an expanded ANN. The ANN is trained again using only limited experimental data. It is shown that such an approach can successfully capture the constitutive behaviour of fine-grained alumina without demanding for extra experimental data.

A research grant from the UKRI’s Strength in Places Fund (grant number 82148) is gratefully acknowledged.

## Invited presentation:

# Rigid body motion of multiple particles in solid-state sintering

Fumihiro Wakai[1], Gaku Okuma[2]

[1] *Tokyo Institute of Technology, Yokohama, Japan*
[2] *National Institute for Materials Science, Tsukuba, Japan*

## Abstract:

The prediction of complicated microstructural evolution during sintering requires the deep understanding on rigid body motion and shape change of multiple particles for manufacturing products with tailored properties. The densification takes place as a result of relative motion of particles that is driven by the sintering force. A rigorous simulation of sintering by coupled grain boundary diffusion and surface diffusion is presented to investigate the fundamental processes in complex evolution of pore structures; the growth of contact area, the pinch-off of a pore channel, and the shrinkage and elimination of a closed pore. The present simulation result in three dimensions was used as a bench mark for checking to what extent large-scale multi-particles simulations, such as discrete element method, kinetic Monte Carlo method, and phase field method, can approximate the rigid body motion of particles in sintering accurately.

## Acknowledgements:

This work was supported by JSPS KAKENHI (Grant Number JP19K15289, JP19K05093).

# High temperature dielectric properties of different SiCf/SiC samples at various infiltration levels

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[3] *Department of Civil and Industrial Engineering, University of Pisa, Via Diotisalvi 2, 56122 Pisa, Italy, Pisa, Italy*

## Abstract:

In the microwave (MW) processing of ceramics at high temperatures, it is important to know the dielectric response of the materials as a function of the temperature T, given the large variations with the temperature expected for the dielectric permittivity. This knowledge is essential both in the design of the reactor and in the optimization of the energy efficiency of the process [1].

For SiC-based monolithic ceramics and composites, at high T the dielectric losses can be as high as of the order or higher than the real part of the permittivity. Thus, an accurate measurement of the dielectric parameters of these materials requires a method as much rigorous as possible.

In this contribution, the method of measurement of the complex permittivity (the apparatus, the measurement technique and the data analysis) is briefly described. Then, the results obtained in the dielectric characterization of $SiC_f$/SiC samples, having different interphases and prepared at various levels of densification by conventional Chemical Vapor Infiltration (CVI) process, are presented and discussed in detail.

The valence of the obtained results is assessed in the context of the pilot-scale MW-CVI plant operating at IPCF-CNR in Pisa, providing a detailed analysis of the energy efficiency of the reactor loaded by the investigated $SiC_f$/SiC ceramics, in a typical process involving heating and infiltration stages.

[1] R. D'Ambrosio, A. Cintio, A. Lazzeri, G. Annino, Design of an overmoded resonant cavity-based reactor for the ceramic matrix composites production, Chem. Eng. J, 405 (2021) 126608

# Dark-Field X-ray microscopy for the determination of oxygen vacancies

Antonella Gayoso Padula, Trygve Magnus Ræder, Hugh Simons, Urko Petralanda Holguin

*Technical University of Denmark, Lyngby, Denmark*

## Abstract:

Oxygen vacancies play an important role in the physical functionalities of ceramics. In view of this fact, we propose to study their nature, distribution and concentration by using Dark-Field X-ray microscopy (DF-XRM), which has been used in the past to obtain the domain structure embedded within a bulk single crystal of barium titanate. This technique seeks to overcome the surface-scale and indirect limitations usually found in advanced spectroscopy and microscopy methods (transmission electron microscopy or X-ray photoelectric spectroscopy) and classical chemical characterization (impedance spectroscopy or $O^{18}$ exchange), by probing directly the elastic deformation caused by buried point defects in oxide materials.

We carry out the analysis of the experimental results through a comparison with simulated 3D multiscale models. This method consists of a combination of atomistic simulations from DFT and finite elemental analysis in COMSOL Multiphysics. This approach allows us to recreate 3D maps of the local strain produced by the oxygen vacancies down to the resolution of our instrument. We then use the obtained strain field to simulate DF-XRM images pixel by pixel. The support of simulations allows us to quantify and characterize oxygen vacancy distributions in experimental data.

In future experiments, we plan to study the behavior of the point defects under the effects of an external electric field and determine the interaction with other defects, such as domain walls, deep within the bulk of the crystal. This is the first time that a multiscale method is used to simulate a Dark-Field X-ray microscopy image, and more importantly, it signifies a revolutionary milestone in determining the density of embedded oxygen vacancies within prototypical perovskites.

## Acknowledgements:

This work is financially supported by ERC 3D-PXM starting grant. The authors are greatful to Thomas Olsen for the scientific discussion and atomistic simulations.

# Can indentation cracks describe residual/internal stresses in Al2O3/ZrO2 laminates?

Zdeněk Chlup[1], Filip Šiška[1], Daniel Drdlík[2], Lenka Novotná[2], Hynek Hadraba[1]

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## Abstract:

The strongly bonded laminates typically alumina/zirconia ($Al_2O_3/ZrO_2$) layers can form relatively high residual/internal stresses reaching in some cases the strength of materials. The effective management of residual stresses via proper design/architecture can result in a combination of high fracture resistance with high strength and stiffness. The presence of compressive residual stresses formed in $Al_2O_3$ layers can suppress and deflect cracks propagating through the layers. The easy to use and very common method how to estimate fracture behaviour in ceramic materials is the indentation technique. The residual stresses are in literature also commonly investigated by this method. In the case of laminates with strongly bonded layers is the crack path in the vicinity of the interface governed by both the elastic properties and the internal stress field of individual layers. The laminates alternating $Al_2O_3$ and $ZrO_2$ layers with various layer-thickness ratios ranging from 0.1 to 3 were used to investigate the effect of residual stresses and influence of crack formation pattern on the crack path development. The indentation surface cracks observed in various alumina-zirconia laminates exhibit the same crack deflection at the interface independently of the level of internal stresses. This finding was explored in more detail and compared with the crack deflection observed on the fracture surfaces of bending specimens. The observed complicated crack path was explained experimentally by 3D reconstruction with the support of numerical simulations.

## Acknowledgements:

This work was financially supported by the Czech Science Foundation project 21-24805S.

# Light scattering predictions for transparent ceramics with birefringent grains

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## Abstract:

Light scattering is a general problem that has to be overcome to achieve high transparency in transparent ceramics. The typical sources of light scattering are pores, impurities (secondary phases) or randomly oriented birefringent grains. While predicting transmittance based on light scattering by pores is quite straightforward, predictions for ceramics with birefringent grains are still a mystery to some extent. The reason for that is the most popular models (Apetz and van Bruggen and Pecharromán) include some shortcomings that have only recently been corrected by the authors and that the reasoning behind choosing some of the parameters in these models might seem not too clear. Moreover, real ceramics exhibit grain size distributions, which have to be adequately implemented into the light scattering models. In this contribution, corrected models which take the grain size distribution into account will be presented and light scattering model predictions based on mean grain sizes will be compared to results based on the whole size distributions. Based on the comparison of these results we will discuss the key question whether there is a certain mean grain size that is able to represent the whole grain size distribution for light scattering predictions and if there is actually any simple, yet reliable way for ceramists to predict transmittance in transparent ceramics with birefringent grains.

[1] Apetz R., van Bruggen M.P.B., J. Am. Ceram. Soc. 86(3) (2003) 480–486.

[2] Pecharroman C. et al., Opt. Express 17(8) (2009) 6899–6912.

[3] Pabst W., Hříbalová S., J. Eur. Ceram. Soc. 41(3) (2021) 2058-2075.

[4] Hříbalová S., Pabst W.: Transmittance predictions of transparent alumina ceramics based on the complete grain size distribution and a simple way to circumvent it (submitted).

## Acknowledgements:

This work was supported from the grant of Specific university research – grant No A1_FCHT_2022_002.

# Structural changes of Al2TiO5 - MgTi2O5 solid solutions resulting from heterogeneous nucleation

Kamil Kornaus[1], Agnieszka Gubernat[1], Radosław Lach[1], Izabela Czekaj[2], Natalia Sobuś[2]

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[2] *Cracow University of Technology, Faculty of Chemical Engineering and Technology, Krakow, Poland, Kraków, Poland*

## Abstract:

The aim of the following work was to determine the structural changes occurring in tialite through the formation of magnesium titanate-aluminum titanate solid solutions. For this purpose, a dft simulation of the structural changes occurring in tialite was performed. The simulation proposed a number of possible atomic substitutions occurring in the elementary cell of tialite along with calculations of the lattice parameter changes in this material. Then, the actual changes occurring in the structure of tialite due to the formation of solid solutions were investigated. Comparing the obtained results, it is possible to confirm the mechanism of tialite solid solutions formation claiming that 1 magnesium atom together with 1 titanium atom substituted two aluminum atoms simultaneously. The results of experimental work have been confirmed by theoretical calculations, where changes in lattice parameters with Mg and Ti substitution is observed.

## Acknowledgements:

This work was supported by the statutory project no 16.16.160.557 of AGH University of Science and Technology in Krakow, Faculty of Materials Science and Ceramics. The theoretical work was supported by the PL-Grid Infrastructure (grant plgzeodesign2021).

# Optical characterisation of shrinkage for modelling of drying 3D printed green body ceramics

Nicolas Lauro, Benoit Nait-Ali, David Smith, Arnaud Alzina

*IRCER, Limoges, France*

## Abstract:

While the drying of a green body made using a traditional process can be viewed as an independent step, for robocasting the drying of the product starts during the fabrication itself and the position of the extruder should take into account the associated dimensional variations. It is thus necessary to precisely anticipate the dimensional shrinkage to improve the process of 3D printing. With this objective, we have developed methods to measure dimensional changes at different scales based on optical images, and a numerical model of drying which is able to simulate dimensional changes.

A first method using markers and a camera to record experimental data on the drying shrinkage of a green body was developed. It has shown the anisotropic nature of the drying shrinkage for a kaolin green body. Despite very good results, this method is not completely transferable to the study of a cord due its reliance on markers and the small radius of the extruded cords (1mm).

A new, non destructive, method was developed to measure the drying shrinkage of an extruded cord and a 3D printed green body using a camera. It relies on image processing, using the openCV python library, to identify the borders of the cords. Consequently, useful data can be obtained without having to interact with the drying sample.

We present how the drying shrinkage varies between a non-extruded green body sample, an extruded cord and a printed green body using experimental data collected from drying experiments conducted in a controlled environment, along with the method used for the image processing. An example of these results being used as input data in a multi-physics drying model combining heat and mass transfers with shrinkage will be presented.

# Grain morphology and microstructural evolution during high temperature and high-pressure deformation of a potential optical ceramic: comparison to simulated microstructures.

Katharina Marquardt

Imperial College London, London, United Kingdom

## Abstract:

Microstructure evolution is highly relevant for the structural stability and performance of modern materials. Grain boundaries impact material properties not only through grain size but also through the expression in their 5 macroscopic degrees of freedom and because they can exist in multiple stable/metastable structures or complexions. Often, textured poly-crystalline microstructures cannot be accurately characterized from just one single planar slice. Therefore a method is required to derive 3 dimensional (3D) microstructural data such as 3D synchrotron-based or X-ray tomography methods. Yet a 2D method, accessible in most laboratories would facilitate wider and less expensive access to 3D microstructural characterization. Thus we test the applicability of stereological approaches to a textured poly-crystalline sample synthetically generated using Dream3D. The simulated microstructure serves as the ground truth and is subsequently analyzed on 3 orthogonal sides as if using EBSD orientation mapping. We observe that combining grain morphology information from 3 orthogonal sides provides the average 3D GBPD for cubic, textured samples. We present a grain boundary character distribution study evaluating the evolution of grain boundaries during dislocation-assisted grain boundary sliding (disGBS) during experimental deformation. Our results suggest that the rate of deformation is controlled by the assimilation of dislocations into grain boundaries and controllers the specific type of grain boundaries formed, we will place this in context with our simulation-based study.

# Damage propagation in Silicon Nitride ceramics under cyclic indentation

Mehdi Mazaheri, Yuri Kadin, Stefan Geerts

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## Abstract:

Due to limited ductility of ceramics, standard fatigue tests are hardly available. However, in bearing applications it is crucially important to know the material resistance to crack propagation under repeated loading. Sharp indentation (e.g., Vickers) is broadly used to evaluate ceramics hardness and crack propagation resistance. With repeated indentation method, proposed in the current research, we can assess the cyclic response of Si3N4 in terms of crack propagation. With available automated Vickers indentation equipment, this method is easy to implement and potentially can be used for the distinction (in terms of fatigue performance) between different grades of silicon nitride. In this work, the cyclic indentations test was used for several grades of fully densified silicon nitride material. Our results shows that crack propagation occurs when performing cyclic indentations at 10 kg loading, which can indicate the low cycle fatigue behaviour of this material simulates fatigue results. For example, after 1000 cycles of indentations on a bearing grade silicon nitride materials, the tip to tip crack dimension grow from 248 to 335 µm. Our investigations also shows that failure can occur after certain number of indentations, in terms of material chipping. That is probably due to the fact that plastically deformed zone, around and beneath the Vickers indent, is full of nano- and micro-metric cracks. When the nano-cracks join together, the material cannot anymore bear the indentation load, and this will results to an spall. Finally, for the interpretation of the experimental observations the Finite Elements (FE) modeling was developed. This model was used for the analysis of tensile stresses which are responsible for the initiation ad propagation of Vickers intonation cracks.

# Numerical study of electric field distribution in breakdown strength testing of ceramics

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## Abstract:

Dielectric breakdown of insulators is a combined electrical, thermal, and mechanical failure. The exact breakdown mechanism in ceramics and the formulation of useful models are still subject of investigation. Recent studies highlighted that several experimental aspects of dielectric breakdown strength testing affect the test results, and thus impede the recognition of fundamental principles.

Excess field strength near the electrode can lead to premature breakdown in the insulating liquid. This would cause superficial damage to the test specimen and thus falsify the measurement results.

The field strength distribution is influenced by the ratio of permittivity of the sample and the surrounding insulating liquid. Premature breakdown depends on the breakdown strength of the liquid and the actual test voltage. The test voltage again depends on the specimen thickness.

To systematically investigate these relations, a numerical simulation study (FEM) of the electric field distribution in a typical testing rig with cylindrical electrodes was performed. The permittivity of the sample and the insulating liquid was parameterized, as well as the sample thickness. The electric field distribution was calculated for increasing test voltage. Field strength maxima are compared to experimental breakdown strength of typical insulating liquids and experimental breakdown locations on alumina. Strategies are discussed to adjust the insulation liquid and the sample thickness to reduce the influence of the testing setup on the dielectric breakdown strength results.

# Response surface methodological (RSM) model for optimizing erosion response of WC reinforced SiC ceramics

Divyansh Mittal[1], Shriya E[1], Surya Yadav[2], Rajiv Kumar[1], Sandan Sharma[1]

[1] Punjab Engineering College (Deemed to be University), Chandigarh, India
[2] Indian Institute of Technology (Banaras Hindu University), Varanasi, India

## Abstract:

Response surface methodology (RSM) method was used for the optimization of the process parameters and recognizing the optimal conditions for the erosion wear of SiC-WC composites. The reinforcement of 10, 30, and 50 wt% WC led to change in hardness to fracture toughness ratio ($H/K_{1c}$) from 3.63 for 50 wt% to 4.07 for 30 wt% (~12% improvement). Erosion behavior was analyzed against SiC erodent in environmental conditions. Erosion resistance was found to increase with $H/K_{1c}$ ratio. The experimentally obtained response of composites were further validated using central-composite experimental design (CCD) coupled with response surface optimization method. Variables considered were $H/K_{1c}$, impingement angle (IA) for the first design, and WC percentage and impingement angle for the second design. Furthermore, statistical analysis of variance (ANOVA) was also used to determine the CCD's suitability and showed a reasonable degree of agreement between the experimental data and the output of the suggested model for SiC-WC composites. Various statistical parameters were used to verify the experimentally generated RSM model and were significant. The model predicted that, 27.36 wt% WC reinforcement provides minimum wear at 30° impingement angle of erodent. As a result, it was concluded that the proposed method and models may be used effectively to predict the wear response of SiC-WC composites.

# Processing variables influencing the relative density of Alumina-Zirconia ceramic materials: statistical evidence learned from the literature

Sónia Gouveia[1], Ana Carvalho[1], Daniel Castro[1], Joaquim Pinho-da-Cruz[2], Susana Olhero[3]

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## Abstract:

Reliable methods for predicting material properties constitute a useful tool to avoid excessive burden in laboratory experimentation. The first step in the development of such models is the identification of variables that influence the target property under analysis. Different statistical modelling techniques can be used for such purposes and, among those highly explainable and interpretable, multivariate linear regression (MLR) models play a central role.

This work describes the development of MLR models to identify processing variables influencing the properties of ceramic materials. The ceramics studied here are composed of Alumina (A, vol%), Zirconia (Z, vol%) and their mixtures, and the (target) property is the relative density (RD, %) attained for the produced material. The analysis is based on data collected in a large systematic review [1] covering 344 literature papers with 1313 different experiments reporting the RD of ceramics produced with different processing settings, e.g. the manufacturing method (Conventional Powder Pressing – CPP, Conventional Colloidal Technologies – CCT and Additive Manufacturing – AM), the relative content of A and Z, the use of HIP, the use of dopants (e.g. $Y_2O_3$ and $CeO_2$), temperature and time of sintering among others.

The MLR models were constructed using different stepwise procedures with coefficients estimated by maximum likelihood. The standard errors and p-values were used to inspect statistical significance. Variables were also compared via standardized coefficients to compare the strength of their effect on RD. The results show that MLR models are statistically significant ($p<0.01$) with adjusted R2 above 20%. Among the significant variables, suspension-based technologies and those using HIP tend to increase RD ($p<0.01$) whereas the use of AM leads to ceramic materials with lower RD when compared to conventional manufacturing methods (CPP and CCT, $p<0.01$).

## References

[1] Olhero, S.; Torres, P.; Mesquita-Guimarães, J.; Baltazar, J.; Pinho-da-Cruz, J.; Gouveia, S. Conventional versus additive manufacturing in the structural performance of dense alumina-zirconia ceramics: 20 years of research, challenges and future perspectives. Journal of Manufacturing Processes 2022, 77, 838–879. doi:10.1016/j.jmapro.2022.02.041.

## Acknowledgements:

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# Modeling of the dielectric properties in ferroelectric-based composites by a new dynamic finite element method

Leontin Padurariu[1], Lavinia Curecheriu[2], Mirela Airimioaei[3], Vlad-Alexandru Lukacs[4], Radu-Stefan Stirbu[1], Liliana Mitoseriu[4]

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## Abstract:

Since single-phase ferroelectric materials cannot accomplish all the technological requirements in applications, developing composite materials that combine the properties of the ferroelectrics with other constituent phases (linear dielectrics, magnetic materials or other conductive/semiconductor components) is a commonly proposed solution. Recently, it has been shown by Finite Element Method simulations that a major factor that influences the effective properties of composite materials is the local electric field inhomogeneity introduced by the interfaces. Based on this effect, we proposed the original concept local field engineering which involves the design of materials with controlled microstructures and, implicitly, an optimum inhomogeneity of the electric field to improve the functional properties [1,2].

Another important factor that influences the functional properties of composites is the accumulation of free charges at interfaces, but this has been neglected so far because it involves important computational difficulties. In this work we propose a new modelling dynamic approach based on finite element method able to describe the complex impedance at any frequency in the range from 1Hz to 1MHz. The approach allows us to explore the influence of free electric charges on the effective dielectric properties of real composite systems. To demonstrate its generality, the new dynamic approach was implemented in this work to describe different types of ferroelectric-based composites: with conductive inclusions, magnetoelectric composites and porous ceramics.

## References:

[1] L. Padurariu et. al., Appl. Phys. Lett. 100, 252905 (2012)

[2] L. Padurariu et. al, Acta Mater. 103, 724 (2016)

## Acknowledgements:

This work was supported by the UEFISCDI Romanian project PN-III-P1-1.1-TE-2019-1929.

# Modelling of Hertzian crack initiation in brittle materials using a stress-energy criterion

Roman Papšík[1], Oldřich Ševeček[2], Raul Bermejo[1]

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## Abstract:

Study of indentation-induced fracture of brittle ceramics has been motivated by characterisation of material hardness, indentation strength and specific fracture energy. When a hard spherical indenter (a ball) is pushed onto a flat surface of brittle ceramic material, a ring crack develops, which can further extend into a cone crack. Fracture force required for crack initiation is linearly or quadratically proportional to the small or large ball radius respective. This size effect is commonly explained by two approaches: the flaw statistics or the energy balance.

Classical linear elastic fracture mechanics assumes that a crack present in the material propagates when the Griffith's criterion is fulfilled ($G >= G_c$). However, it does not allow prediction of crack initiation or to determine the critical force and the location of macroscopic crack. An alternative approach, called the finite fracture mechanics (FFM), does not require presence of a crack. Instead, FFM can predict the formation of a new crack of finite length $a_0$, which initiates when both stress and energy conditions (a coupled criterion) are simultaneously fulfilled:

1) Stress must overcome tensile strength all along the prospective crack path.
2) There must be enough available energy to create a crack ($G_{inc} := -[E_p(a_0)-E_p(0)]/a_0 >= G_c$).

In this work, we developed computational model to predict fracture forces and crack locations based on elastic properties, fracture toughness and strength of a brittle material without any further assumptions about the flaw distribution on the surface. Predictive ability of the model is demonstrated by comparing experimental data available in the literature with calculations. The model can explain, why decreasing maximum radial stress with increasing ball radius is not a paradox.

## Acknowledgements:

Research was funded by the European Research Council (ERC) through the Consolidator Grant (program Horizon 2020) for the project "Tailoring Microstructure and Architecture to Build Ceramic Components with Unprecedented Damage Tolerance" (project CeraText 817615).

# Computational ceramics engineering utilizing microstructure-based simulation of material properties

Simon Pirkelmann, Gerhard Seifert, Friedrich Raether

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**Abstract:**

Microstructure-based simulation of ceramic material properties can be a very valuable tool to support selection of raw materials and thermal processing parameters for a tailored, application-specific material performance. Ideally, the numerical tools enable a top-down approach for material design.

In this work, recent progress in this field is reported: A methodology for the top-down design of ceramic materials composed of two or more phases has been developed. It is demonstrated on the example of the well-known alumina / zirconia (AZ) material system. Core of the method is an automated simulation chain based on representative volume elements for generating a database of microstructure-property relations. The database emanating from this simulation chain was used to train machine learning models for enabling fast predictions of material microstructure according to preset material properties. A gradient boosting algorithm provided reliable and fast calculations for the exemplary chosen thermal and mechanical properties of the AZ material system. This enables reverse identification of selected microstructural parameters needed to obtain a specific value of a material property of interest, or briefly: top-down ceramic material design.

# Raman spectra of ceramic materials from first principles

Maxim Popov[1], Jürgen Spitaler[1], Vignaswaran Veerapandiyan[1], Eric Bousquet[2], Jiri Hlinka[3], Marco Deluca[1]

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[2] *Physique Théorique des Matériaux, QMAT, CESAM, Universite de Liège, Liege, Belgium*

[3] *Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic*

## Abstract:

Raman spectroscopy is an indispensable tool for investigating the properties of ceramic materials. It provides rich information about the chemical composition, local atomic structure, defects, phases and phase transitions, strain state, and many other properties. In addition, Raman spectroscopy is a non-destructive technique allowing for fast data acquisition, thus making it suitable for online, on-the-fly testing at the production site. Interpreting the measured spectra is facilitated by the existence of databases and theoretical methods, most notably, by symmetry analysis and ab-initio modeling. The theory and modeling of Raman spectra are rather well developed, however, they primarily concentrate on the single-crystalline material form. Ceramics have received significantly less attention and they require averaging the signals coming from each individual grain. In the standard approach, this is accomplished by resorting to the so-called Placzek invariants. In our recent paper [1], we show the deficiencies of this method and introduce the new spherical averaging method that significantly improves the ability of the theory to predict the Raman spectra of ceramic materials. We illustrate here the performance of the new method by calculating the spectra of polycrystalline $BaTiO_3$, AlN, and $LiNbO_3$ from first principles. The calculated spectra are not only able to predict peak positions and intensities with high accuracy, but also allow to obtain the asymmetric peak shape–characteristic for oblique phonons–in an unprecedented way.

[1] Popov, M.N., Spitaler, J., Veerapandiyan, V.K. et al. Raman spectra of fine-grained materials from first principles. npj Comput Mater 6, 121 (2020)

# The dispersion and aggregation problems of the carbon nanotubes as reinforcing phase assessed by computer simulation

Laura Garrido-Regife, Pedro Rivero-Antúnez, Víctor Morales-Flórez

*University of Seville, Seville, Spain*

## Abstract:

Although numerous efforts have been made to improve the properties of ceramic materials by adding a nanostructured phase like carbon nanotubes (CNT), the appearance of aggregates during manufacturing processes continues to be a problem, hindering the achievement of unquestionable and consistent mechanical improvements. Given the size of CNT (nm - μm), techniques such as small angle scattering (SAS) can be a remarkable tool to study the formation of aggregates and to quantify the degree of homogenization of the nanophase in the matrix. In this work, a series of simulations have been performed to study how the aggregates of CNT can be revealed in SAS experiments. Systems with different concentrations of CNT were simulated in different states of aggregation, starting from a perfectly homogeneous dispersion of individualized CNT, which was progressively aggregated through a Monte Carlo algorithm. The obtained results show that a Guinier regime appears in the scattering signal in the range of "low q" values (high sizes) and the well-defined fractal regime rapidly disappears when the CNT start to agglomerate. Consistently, the position of this regime shifts according to the size of the CNT aggregate. The intensity curves have been analysed and two parameters have been considered as probes for revealing the appearance of the aggregates and to quantify the quality of the dispersion of the nanophase in the ceramic matrix: the first derivative of the intensity at "low q" and the ratio of the intensity at the minimum of q with respect to the intensity $I_0$ obtained from the fitting to the Guinier model in the region associated to the diameter of the CNT.

## Acknowledgements:

Project PGC2018-094952-B-I00 (INTRACER) financed by FEDER/Ministerio de Ciencia e Innovación - Agencia Estatal de Investigación. Project P20_01121 (FRAC) financed by Consejería de Transformación Económica, Industria, Conocimiento y Universidades (Junta de Andalucía).

# Thermal shock characterization of refractories and ceramics using improved in-situ methods

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## Abstract:

Refractories are a key element for energy efficient thermal processes, contributing to cost, $CO_2$-footprint and quality of the products. Refractories are used as insulating and structural elements in the furnace and product support. Exact knowledge of the material properties under application conditions is necessary for their successful selection. A particularly important topic is their resistance to thermal cycling and shock. Even though many techniques have been described for testing, most of these are based on fast, usually undefined temperature changes between high temperatures and room temperature e.g. by quenching. However, in most applications the more realistic stress occurs between levels of high temperature; for refractories used in melting metallurgy hot thermal shock is more relevant than quenching. In order to investigate these conditions with more accuracy, a new ThermoOptical Measuring device has been developed and is being constantly improved. It is a unique combination of a high-temperature furnace, a $CO_2$-laser and specific in-situ sensors. The furnace establishes a base temperature in a controlled atmosphere. The laser is used for short-term heating (thermal shock or cycling) of samples. To be representative for coarse microstructures like refractories, samples with a volume of about 20 $mm^3$ are investigated. Special laser cycles, one- or two-sided irradiation, variable spot size and pulse rate are used to create well-defined temperature gradients in the samples. To improve the efficiency a software has been developed which allows pre-estimation of thermal stresses for material adapted testing conditions, minimizing tedious pre-testing. The benefits of these developments will be presented based on recent tests on standard refractory materials.

# Comparative analysis of BaTiO3 ceramics produced from cuboidal and spherical nanoparticles: the role of nanopowders assembly during the pressing step

Radu-Stefan Stirbu[1], Lavinia Petronela Curecheriu[1], Leontin Padurariu[1], Vlad Alexandru Lukacs[1], Gabriel Caruntu[2], Maria Teresa Buscaglia[3], Oana Condurache[4], Liliana Mitoseriu[1]

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## Abstract:

The functional properties of $BaTiO_3$ ceramics produced by using the same strategy for pressing and two-steps sintering method from different starting nanopowders are comparatively investigated. Hydrothermally syntesised nanopowders with two types of morphologies (cube-like and spherical particles) and similar particle size of ~10-16 nm have been employed. For various sintering temperatures, the starting particle morphology is lost in the sintered ceramic body [1]. Higher density of ceramics is always reached when using cube-like nanoparticles, e.g. a relative density of 95% vs. 88% and grain size of 290nm vs. 335nm, when sintering by fast heating at 1250°C, cooling & sitting for t=24h at 800°C, followed by slow cooling down to 20°C. The functional properties are enhanced in cube-like ceramics: higher permittivity, polarisation and tunability values are found. Both types of ceramics show a tetragonal-orthorhombic phase superposition around room temperature and have extremely stable dielectric properties vs. frequency. HRTEM analysis indicated clean grain boundaries and epitaxial growth of ceramic grains mostly for cubic-like starting particles. The major difference is described in terms of the nanoparticle assembly during the pressing step. The compactisation process of cubic and spherical nanoparticles were numerically simulated and the resulted local clusterisation of powders and the resulted density of the green ceramics were derived and their role on the densification during sintering and on the functional properties have been comparatively discussed.

## Acknowledgements:

This work is supported by PN-III-P4-ID-PCCF-2016-0175 (HighKDevice) grant.

## References:

[1] V.A. Lukacs et al., Ceramics International, 47, 18105 (2021)

# Mesoscale models for strain-stress distributions in anisotropic porous BaTiO3 ceramics

Radu-Stefan Stirbu, Leontin Padurariu, Vlad Alexandru Lukacs, Liliana Mitoseriu

*"Alexandru Ioan Cuza" University, Iasi, Romania*

## Abstract:

Finding the relationship between functional properties of electroceramics at different scales is a challenging problem and multiscale analyses are necessary to complete the composition-nano/microstructure-properties picture. Among the microstructural factors, ceramic density is important because: (i) porosity is unavoidable during the processing and (ii) specific porosity distribution may provide superior properties (tunability and piezo/pyroelectric FOMs) [1,2].

The role of pressing (i.e. uniaxial vs. hydrostatic) on the formation of anisotropic pores in $BaTiO_3$ ceramics obtained from spherical sacrificial templates and their impact on the dielectric and piezo/ferroelectric properties of the resulted porous ceramics are reported. Firstly, FEM-based models were elaborated to describe strain-stress distributions originating the formation of anisotropic polymeric fillers during the pressing step in the green bodies. Further, a FEM model was designed for deriving the local electric field and potential distributions in the porous sintered ceramics [3] and to compute the effective permittivity along various pressing directions, which were compared with the experimental ones of $BaTiO_3$ ceramics with relative porosity levels from 5% to 26%. The results were discussed in terms of microstructural variations as pore level and connectivity, which changes from a (0,3) one at low porosity to a more complex one at higher porosity levels.

## References

[1] C. Padurariu et al., Ceram. Int. 43, 5767-5773 (2017); [2] Y. Zhang et al., Acta Mater. 154, 100-112 (2018); [3] L. Padurariu et al., Appl. Phys. Lett. 100, 252905 (2012).

## Acknowledgements:

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# Development of a 3D model for prediction of curing dimensions, conversion rate, temperature and homogeneity of ceramic systems in stereolithography

Dylan Vallet, Vincent Pateloup, Philippe Michaud, Thierry Chartier

*Ircer, Limoges, France*

## Abstract:

To meet industry's ongoing and future expectations in terms of ceramic additive manufacturing, a better comprehension of the stereolithography process and laser scattering through the ceramic slurry is mandatory. This knowledge could allow to master green part dimensions and conversion rates in order to optimize subsequent post-sintering mechanical properties, to reduce production time and to reach better resolutions. This work focuses on the development of a new 3D polymerization modeling for stereolithography process able to predict curing mechanisms occurring during printing. First, new equations relative to pulsed lasers are integrated in the model in order to consider the real energy source. Then, a design of experiments is carried out to identify material-dependent parameters, calibrate and validate the model. The calibrated model makes it possible to predict conversion rates and dimensions of any printed green part depending on manufacturing parameters. Finally, temperature prediction during process and evaluation of homogeneity in exposure have been developed and open the way to analysis of potential variations of shrinkage and mechanical properties. This 3D model showed a really good ability to predict curing dimensions and conversion rates.

# Mid-IR OCT imaging as a method for studying additive manufactured ceramics

Ivan Zorin[1], Dominik Brouczek[2], Julia Eichelseder[2], Martin Schwentenwein[2], Bettina Heise[1]

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## Abstract:

Additive manufacturing (AM) of ceramics is an emerging technology of great industrial and research interest. Various methods for producing dense high-precision ceramic parts find application in many fields. Ceramic materials used for AM are being advanced and optimized to meet high requirements on e.g. resolution, mechanical properties and surface quality. Thus, it is of particular importance to assess the quality of materials and manufactured parts and get insights into the printing processes.

Various quality control methods are used to address these problems. Among them are optical methods that are simple and provide reasonable spatial resolution. To obtain sub-surface structural information, an axial ranging technique based on coherence gating, called optical coherence tomography (OCT), can be used.

OCT is a high-sensitivity non-destructive testing method that enables 3D structural imaging of complex samples with a resolution in the order of several to tens of micrometers. However, standard OCT systems (operating in the near-infrared range) have limited capabilities for imaging porous ceramic materials because of strong scattering. Thus, adequate probing depth cannot be ensured in practice; structures can be hidden and masked by multiple scattering gradients. Due to rapid advances in mid-infrared technology, OCT has recently moved further towards longer wavelengths. The emerged mid-IR OCT has increased the resistance of the technique to scattering. Thus, OCT imaging scenarios that were previously infeasible have become possible. In this contribution, we demonstrate the capabilities of mid-IR OCT for non-destructive testing of lithography-based manufactured ceramic samples. We show structural imaging of green, sintered and multi-material parts.

## Acknowledgements:

This work was supported by the Austrian research funding association (FFG) under the DIQACAM Project (contract 877481).

# Symposium D: Structural Ceramics / Ceramic Coatings / Porous Ceramics

Invited presentation:

# Exploring new concepts to design damage tolerant ceramics using additive manufacturing

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## Abstract:

The combination of ceramics with other materials (metals, polymers or other ceramics) has enabled the fabrication of hybrid systems with exceptional structural and functional properties. However, a critical issue affecting the functionality, lifetime and reliability of these systems is the initiation and uncontrolled propagation of cracks in the brittle ceramic parts, yielding in some cases very high rejection rates of component production. In previous work, design concepts that combine different approaches used in current ceramics engineering have proved successful in obtaining highly reliable ceramic materials with enhanced fracture resistance. For instance tuning the location of "protective" layers within a ceramic multilayer architecture can significantly increase its fracture resistance, while retaining high strength. The use of tailored residual stresses in embedded layers can act as an effective barrier to the propagation of cracks from surface flaws, providing the material with a minimum design strength, below which no failure occurs. Moreover, by orienting (texturing) the grain structure, similar to the organized microstructure found in natural systems such as nacre, crack propagation can be controlled within the textured ceramic layers. In this contribution, the potential of employing lithography-based ceramic manufacturing (LCM) process to design multi-phase layered architectures is presented, which can contribute to the fabrication of future 3D ceramic components with enhanced damage tolerance.

## Invited presentation:

# Mesoporous Si3N4(C,O) Encapsulated Co or Ni nanocatalysts: from design to application in catalyst-assisted reactions in alkaline media

Marwan Ben Miled[1], Roberta Morais[1], Maira Mallmann[1], Rafael Nishihora[1], Ricardo Machado[2], Umit Demirci[3], Stéphane Célérier[4], Aurélien Habrioux[4], Samuel Bernard[1]

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### Abstract:

The scientific and technological challenges of energy-related fields are mainly associated with the emergence of new, advanced knowledge and fundamental understanding of materials. In the different categories of materials, ceramics offer a unique combination of physical and chemical properties making them key contributors for energy production/conversion and storage applications. The Polymer-Derived Ceramics (PDC) route enables the synthesis of such materials with an excellent control of the porosity at mesoscopic length offering potentialities as support materials to anchor and disperse active metals or for a direct use as catalysts if the metal (= the catalyst) grows directly in the matrix (= the support). The main topic reviewed in this presentation is related to the chemical modification of preformed polymeric precursors, namely polysilazanes, with metal-containing species and their transformation into mesoporous components in which the catalytically active phase (Co or Ni) is homogeneously distributed in a matrix designed in the Si-C-N-O system. These fully characterized materials are then used in two catalyst-assisted reactions known to produce $H_2$: hydrolysis of hydrides and water electrolysis.

### Acknowledgements:

Dr. Samuel Bernard, Prof. Umit B. Demirci and Prof. Ricardo Machado acknowledge the CNPq for providing financial support for the PhD thesis of Maira Mallmann and Campus France and CAPES through the COFECUB project N°Ph-C 956/19 entitled Design of monolithic polymer-derived ceramics nanocomposites with tuned micro-/mesoporosity for energy-related fields for financially support the PhD thesis of Roberta Morais and the postdoc fellowship to Dr. Rafael Kenji Nishihora Dr. Samuel Bernard, Dr. Stéphane Célérier et Dr. Aurélien Habrioux would like to thank The Nouvelle-Aquitaine region and IRCER who financially supported the PhD thesis of Marwan Ben Miled.

## Invited presentation:

# Diamond-SiC composites with excellent wear resistance and thermal properties

Mathias Herrmann[1], Björn Matthey[2], Steffen Kunze[1], Andreas Kailer[3]

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### Abstract:

SiC-bonded diamond ceramics with extremely hardness and wear resistance can be manufactured by reaction bonding of diamond by silicon infiltration like the SiSiC process. Using this technology, components can be produced cost-effectively in large sizes and with complex shapes. Diamond contents of up to 60-65 vol.% and Si content less than 5 vol.% can be achieved in the composite materials. The materials exhibit high wear-resistance and low friction coefficients.

These composites also exhibit excellent thermal conductivity with values of up to 600 W/m*K. Systematic experiments show the correlation of microstructure, diamond distribution and thermal properties.

A key factor for the excellent behavior are the strong interfaces between diamond and SiC caused by epitaxial growth of the SiC on the diamond particles. The influence of the interface on the thermal and mechanical properties will be discussed.

### Acknowledgements:

The research was supported partially by the Federal Ministry for Economic Affairs and Energy in the maritime research program under the project SUBSEASLIDE (contract number 03SX508F) and partially by the Army Research Office under Cooperative Agreement Number W911NF-20-2-0115.

## Invited presentation:

# Multilayer ceramic as a novel functional material for lightning and sensing platform

Anna Kozłowska[1], Helena Węglarz[1], Agnieszka Szysiak[1], Oskar Bogucki[1], Joanna Kowalko[1], Kamila Leśniewska-Matys[2], Romain Trihan[3], Anne Aimable[3], Fabrice Rossignol[3], Bartosz Fetliński[4], Bartosz Janaszek[4], Marcin Kieliszczyk[4], Paweł Szczepański[4], Michał Malinowski[4], Marcin Kaczkan[4], Martin Ihle[5], Steffen Ziesche[5], Piotr Giemza[6], Marcin Szczypa[6]

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### Abstract:

Our work is focused on development of layered ceramic which will serve as the luminescent substrate in novel lightning/sensing device. Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) doped with various rare earth ions ($RE^{3+}$) is used as a phosphor material. The layered construction of the ceramic, that is proposed in this work, allows to tailor spectral and spatial characteristics of the light source under LED excitation. The composition of ceramics (active dopants, scattering phase material, etc.) is modified in order to obtain the desired color rendering index and a high efficiency of the resulting source.

Two different synthesis routes of the layered ceramics are considered in this work, i.e., 1. granulate pressing and 2. tape casting, followed by sintering under vacuum conditions. Pros and cons of both techniques are discussed, with special emphasis on feasibility study in industrial environment. Results of spectroscopic measurements for exemplary $Ce^{3+}$:YAG/$RE^{3+}$:YAG substrates, performed with use of nanosecond tunable laser as well as LED excitation, are presented. Comparison of optical properties of layered ceramics with the bulk counterparts (co-doped samples) is demonstrated. Thorough microstructural analysis of the samples (SEM, TEM) proves high quality of the elaborated ceramics.

### Acknowledgements:

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## Invited presentation:

# Mechanical properties and thermal stability of High Target Utilization Sputtered TiNbVTaZrHf based nitride and carbide coatings

Frantisek Lofaj[1], Lenka Kvetkova[2], Tomas Roch[3], Margita Kabatova[2], Petra Hviscova[2], Marian Mikula[3]

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## Abstract:

High entropy ceramics, particularly bulk carbides, are promising candidates for ultrahigh temperature applications. In the case of analogous high entropy-based carbide and nitride coatings, improved thermal stability at temperatures exceeding 1000°C can be expected due to the presence of refractory elements. The aim of the current work was to optimize deposition conditions of multicomponent TiNbVTaZrHf-N and TiNbVTaZrHf-C(:H) coatings prepared by reactive High Target Utilization Sputtering (HiTUS) from the viewpoint of improvement of mechanical properties (hardness and elastic modulus) at room temperature and then investigate their structural stability and mechanical properties after thermal annealing.

The microstructure and subsequent X-ray diffraction observations showed that the coating structures vary from practically amorphous in pure metallic state to textured nanolamelar when stoichiometry of the content of nitrogen in the coating increased with the increase of the flow of in the sputtering atmosphere. Their hardness and indentation moduli increased from around 15 GPa in metallic state to over 30 GPa when nitrogen content reached stoichiometric composition. In the case of carbide coatings, their structure and properties were controlled by the amount of excess carbon. The highest hardness of carbide coatings was around 40 GPa. The annealing of the nitride coatings in vacuum at 1000°C and 1200°C for 5 min resulted in the growth of crystallite size, relaxation of microstrains and only a small degradation of mechanical properties.

## Acknowledgements:

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## Invited presentation:

# Boride hierarchical composites for ultra-high temperature applications

Laura Silvestroni[1], Nicola Gilli[1], Diletta Sciti[1], Jeremy Watts[2], William Fahrenholtz[2]

[1] *CNR - ISTEC, Faenza, Italy*
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## Abstract:

Here we present a simple method to obtain highly refractory boride-based ceramic nano-composites.

Fundamental requirement for the development of a hierarchical boride composite is the formation of a solid solution around the native $MB_2$ boride grain during the densification stage. This can be obtained upon addition of soluble transition metal compounds.

In the present case, introduction of W- or Ta-based compounds enabled to form $(M,W)B_2$ or $(M,Ta)B_2$ shells around the original $MB_2$ cores. Subsequent annealing at high temperature further developed the nano-texturing in the shell, where metallic W or TaC nano-particles precipitated within $MB_2$ grains and displayed unprecedented refractoriness.

Here we show the microstructural features of different diboride composite and show how these microstructural change impact on local properties measured by nanoindentation and on the ultra-high temperature strength.

The unique microstructural findings reported open vast opportunities for nano-composite ceramic development, manufacturing and applications.

## Acknowledgements:

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# Reticulated porous perovskite structures for implementation of cyclic redox-based thermochemical gas-solid reactions

Mathias Pein, Christos Agrafiotis, Martin Roeb, Christian Sattler

*DLR-German Aerospace Center, Cologne, Germany*

## Abstract:

Redox-oxides-based solar-driven thermochemical $H_2O$ and $CO_2$ splitting cycles, air separation and heat storage are promising approaches to address challenges of sustainable energy supply climate change and receding fossil energy reserves. This work, based on prior studies on composition optimization with respect to critical properties of interest, presents the manufacturing and application-specific testing relevant to the fields above, of reticulated porous redox perovskite structures made entirely of Ca-Mn-based, earth-abundant, low-cost, environmentally-benign raw materials. Mechanical stress and multi-cycle tests demonstrate structural integrity, resilience and sufficient durability for the use of such porous monoliths in non-moving modular reactor systems. Long-term cyclic reduction-oxidation conditions reveal that such structures are characterized by fully reversible thermochemical expansion/contraction and thus dimensional stability during such operation, an attribute in contrast to other redox oxides targeted for similar applications. The performance of all-reticulated-porous-ceramics (RPCs) cascades in application-relevant tests is evaluated and compared to that of non-porous, compact and particle-based configurations. Benefits and drawbacks of porous monolithic structures of redox active perovskites are discussed together with operational strategies to maximize their performance. An outlook to future use cases of such all-perovskite-made RPCs in a variety of cyclic thermochemical processes is presented, either directly coupled to concentrated solar irradiation or to high-temperature industrial gas-solid processes handling high pressure gaseous streams, due to the well-known advantageous pressure drop characteristics of RPCs relevant to particle packed beds.

# Improvements to the performance of alumina-based ceramics through the reaction sintering of alumina-mullite nanocomposites

Douglas Andrews, Richard Todd

*University of Oxford, Oxford, United Kingdom*

## Abstract:

Improving the ballistic performance of alumina through the production of alumina-mullite nanocomposites would allow for more financially accessible forms of armour as the method of forming alumina-mullite nanocomposites is less expensive than alumina-SiC nanocomposites, which requires inert gas and high sintering temperatures. The mullite nanoparticles are formed through a cheaper method, in which SiC particles are oxidised and reacted with the alumina matrix during sintering. The microstructure and crack propagation routes in alumina-mullite nanocomposites with dopants were analysed. This was achieved via scanning electron microscopy and energy dispersive x-ray spectroscopy (EDX) of the areas surrounding Vickers hardness testing sites and undeformed areas of the bulk material. The additives caused microstructural changes including significant abnormal grain growth with the addition of $Y_2O_3$, $Nd_2O_3$ and CaO. Samples with this microstructure showed an increase in Vickers hardness of up to 27% over alumina-mullite composites without the addition of dopants. The doped samples also showed a shift in failure mode in the cracks surrounding the impact site; in the presence of dopants, cracks followed a transgranular failure path whereas without doping, failure followed an intergranular failure path. The improvements in hardness, and abnormal grain based microstructure, are only visible in samples sintered at over 1500 $^0$C. EDX showed that the improved samples contained larger groupings of the mullite particles than in the undoped samples. The reasons for the property improvements are discussed.

## Acknowledgements:

University of OxfordDSTL

# Fly ash-based porous geopolymer: A review

Chengying Bai, Xinyu Li, Yingjie Qiao, Paolo Colombo

*Harbin Engineering University, Harbin, China*

## Abstract:

Geopolymer, possessing a semi-crystalline 3D inorganic network generated by the dissolution and reaction of a solid alumino-silicate source with an activating solution, have attracted increasing attention from both academia and industry because of their unique and favorable characteristics . Porous geopolymers (PGs) is one of the fastest growing research field in porous inorganic non-metallic materials according to the good global starting materials availability, sintering-free process, and their promising properties (high mechanical strength, low thermal conductivity, great chemical stability etc.).

Fly ash is a large amount of solid waste generated from coal combustion, which efficient resource utilization and high value-added utilization problems remains to be solved. Among many ways of waste resource utilization, the preparation of porous geopolymer is one of the effective ways to improve the high added value of fly ash. A variety of processing techniques (direct foaming method, replica route, sacrificial template method, additive manufacturing method, fast microwave foaming method, combined route, etc.) are available to fabricate PGs over the last decade. Fly ash-based porous geopolymer were synthesized by direct foaming (using various surfactants/stabilizing agents with or without chemical pore-forming agent), additive manufacturing, reactive emulsion templating combined with peroxide route Additionally, the performance and influencing factors of fly ash-based porous geopolymers are reviewed, as well as the applications on heat insulation, filtration, sound absorption, pH buffering, expounds the current development status of fly ash based porous geopolymer, and looks forward to the future development prospect of this field.

# Atmospheric plasma sprayed bioactive glass coatings containing strontium and magnesium

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## Abstract:

Bioactive coatings are studied for their use on orthopaedic implants with the aim of conferring biocompatibility and protecting them against corrosion and degradation promoted by biological fluids. Usually, these coatings can be deposited by different techniques such as enamelling, sol-gel or dipping. However, atmospheric plasma spraying (APS) is one of the most studied and used method to obtain this type of coatings.

Therefore, the aim of the present work is to prepare bioactive coatings by APS employing, for the first time, the novel glass composition BGMS10 (2.3% $Na_2O$, 2.3% $K_2O$, 25.6% CaO, 10.0% MgO, 10.0% SrO, 2.6% $P_2O_5$ and 47.2% $SiO_2$, in wt%). First, thermal characterisation of the glass was carried out and then, after mixing it with a fluidiser, different coatings were manufactured by varying both the spraying distance and the argon flow rate. Then, the resulting coatings were microstructurally characterised by means of scanning electron microscopy, energy dispersive X-ray analysis and X-ray diffraction. Finally, the bioactivity was assessed by in vitro tests in Simulated Body Fluid (SBF) up to 7 days.

Different porosities, thicknesses and surface roughness were achieved when the spraying distance and the argon flow rate are modified. However, all coatings display a better microstructure (denser with less inner porosity) than an analogous one deposited with the same spraying parameters employing the 45S5 bioglass. Finally, even though all coatings display good bioactivity, those deposited with lower argon flow rate are the most bioactive probably due to their surface topography.

## Acknowledgements:

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# Modification of the nozzle geometry to improve HA deposition efficiency in cold gas spraying

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## Abstract:

Cold spray is based on the acceleration at a supersonic velocity (up to 1200 $m.s^{-1}$) of unmelted powder particles through a de Laval nozzle by a high-pressure gas (e.g. $N_2$). As the powder is not molten in the gas, the deposit is mostly generated by the powder plastic deformation and/or brittle fragmentation and its mechanical anchorage when impacting the substrate at high kinetic energy.

Up to date, cold spray has been mostly dedicated to ductile materials (i.e. metals). However, cold spray of brittle materials (i.e. ceramics) has recently gained attention. In the specific case of ceramics, the challenge consists mostly in controlling the powder fragmentation at the impact to optimize the coating quality (i.e. low porosity and good mechanical adhesion) and its construction rate.

In thermal spraying, usually axial injection is chosen at the expense of the radial one. Indeed, the particles injection in the stream is more homogeneous and chance of clogging are lower. However, in Low Pressure Cold Spray, axial injection is not possible, since it takes place in the diverging part of the nozzle. In the specific case of brittle material, there is also a problem of fragmentation inside the nozzle. Thus, the idea of this work is to create a nozzle where the powder will be injected with an angle lower than 90°.

This angle permit at the same time to limit the powder fragmentation mentioned before, to increase the precision in the velocity measurement, and to improve the deposition efficiency.

# Influence of porosity on dielectric, ferroelectric and pyro-, piezoelectric properties for Ba0.85Ca0.15Ti0.90Zr0.10O3 porous ceramics

Cristina Elena Ciomaga[1], Lavinia Petronela Curecheriu[2], Leontin Padurariu[3], Alexandru Lukacs[3], Nadejda Horchidan[3], George Stoian[4], Liliana Mitoseriu[3]

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## Abstract:

Porous $Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O_3$ (BCTZ) lead-free ceramics were fabricated via burn polymer spheres (BURPS) method by introducing poly(methyl methacrylate) (PMMA) particles as the pore-forming agent. The inflence of porosity on the structural, microstructure, dielectric, and pyro-, piezoelectric properties of the porous materials were investigated. The structural analysis has shown that the porosity induced phase transition from orthorhombic to tetragonal phase. The low and high field dielectric properties have been studied for the obtained BCTZ ceramics with various porosity levels (from 4 to 31% of porosity). The maximum permittivity decreases with increasing porosity, from around 6000 (ceramic with 92% density) down to 3000 (ceramic with 69% density), and a shift with a decrease of Curie temperature from 70°C to 65°C due to the possible structural and strain modifications is occur. All the investigated ceramics preserve a high level of tunability as in the BCTZ dense material. The piezoelectric measurements have confirmed that by increasing porosity in the BCTZ system led to an enhancement of piezoelectric response ($d_{33}$). Therefore, we have obtained porous BCTZ ceramics with reduced dielectric constant and enhanced piezoelectric FOM, which are leading to the idea for using them as materials for energy harvesting applications. By using Finite Element Method (FEM) was calculated and simulated realistic porous microstructures, and it was demonstrated that the porosity influences the permittivity response: for a relative porosity of ceramics of 10% leads to a decrease of the permittivity compared to that of dense ceramics to 80%, and for a relative porosity of 30%, the decrease of permittivity reaches 55% compared to that corresponding to the dense material.

## Acknowledgements:

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# Investigation of energy harvesting properties in porous Ba0.85Ca0.15Ti0.90Zr0.10O3 ceramics with enhanced piezoelectric figure of merits

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## Abstract:

In the last years, piezoelectric materials have attracted growing attention for energy harvesting due to their excellent electromechanical conversion properties. The first approach of this study was to prepare a Pb-free material with high piezoelectricity which possesses a combination of physical (figures of merit (FOM)) properties. The challenge in obtaining these types of materials with enhanced FOM is to reduced dielectric constant while keeping high the piezoelectric performances. The recent studies demonstrated the benefits of introducing porosity in ceramics for various purposes and improving piezoelectric FOM for energy harvesting applications. In order to increase the piezoelectric performances, solid solutions of $BaTiO_3$ close to the morphotropic phase boundary like in $Ba_{0.85}Ca_{0.15}Zr_{0.10}Ti_{0.90}O_3$ (BCTZ) was proposed. Porous BCTZ ceramics have been fabricated via the burn polymer spheres technique by using poly(methyl methacrylate) (PMMA) microspheres as a sacrificial template. The obtained materials have been tested for their piezoelectric energy harvesting capabilities by using mechanical stimuli at different frequencies. The piezoelectric measurements have confirmed that increasing porosity in the BCTZ system led to an enhancement of piezoelectric response ($d_{33}$). The experimental set-up realised for measuring and testing the piezoelectric response has demonstrated and confirmed the beneficial effect of porosity for increasing the collected signal over a certain frequency range and finding the range of interest for energy conversion as f= 6 ÷ 10 kHz. Therefore, we have obtained porous BCTZ ceramics for which the permittivity decreases and piezoelectric FOM increases, requirements important for considering them as materials for energy harvesting applications.

## Acknowledgements:

This work was supported by a grant of the Romanian Ministry of Education and Research, CNCS – UEFISCDI, project no PN-III-P4-ID-PCE-2020-1988, within PNCDI III.

# Strengthening and plasticity in a (Hf-Ta-Zr-Nb)C high-entropy carbide

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## Abstract:

Strengthening and plasticity are known in general as mutually exclusive properties of materials. This phenomenon has been investigated in grains of a recently developed (Hf-Ta-Zr-Nb)C high-entropy carbide and compared with the binary (Hf-Ta)C and constituent monocarbides of TaC and HfC subjected to nanoindentation and micropillar compression. The samples were prepared by spark plasma sintering and the crystallographic orientation of grains was determined by electron backscatter diffraction (EBSD). Micropillars and micro-cantilevers were milled out from grains of specific orientations using a focused ion beam (FIB) technique. Nanoindentation tests exhibited a significantly enhanced hardness (36.1±1.6 GPa,) compared to the hardest monocarbide (HfC, 31.5±1.3 GPa) and the binary (Hf-Ta)C (32.9±1.8 GPa). Micropillar compression test of near {001} oriented grains revealed that (Hf-Ta-Zr-Nb)C had a significantly enhanced yield (6.2 GPa) and failure strength compared to the corresponding base monocarbides (3.0-3.9 GPa) while maintaining a similar ductility to the least brittle monocarbide (TaC) during the operation of {110}<1-10> slip systems. Nanohardness anisotropy was correlated to the activate slip systems during nanoindentation determined by EBSD and TEM analyzes. The strength enhancement obtained in binary (Hf-Ta)C and high-entropy (Hf-Ta-Zr-Nb)C systems was explained by the increased Peierls stress of an a/2<1-10>{110} edge dislocation due to larger atomic randomness with the increasing number of elements at the dislocation core. This study revealed that the hardness and strength of high-entropy carbide ceramics could go beyond the constituent monocarbides while their plasticity could be also improved via the promotion of dislocation slip on the {111} planes.

## Acknowledgements:

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# Designing the pore morphology of SiOC freeze-cast structures using solvent mixtures

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## Abstract:

Designing macroporous SiOC via unidirectional solution-based freeze-casting of preceramic polymer creates pore morphologies with balanced mechanical and mass transport properties. In this work, cyclohexane (CH) and tert-butyl alcohol (TBA) were used as a novel template media in freeze-casting to create a permeable pore structure with high mechanical stability. Results show that using only CH or TBA generates dendritic or prismatic pore structures, respectively, while a mixture of these solvents creates honeycomb-like pore structures. Variations in the amount of TBA led to pore window sizes between 11-57 µm and consequently to water permeabilities of $4.4 \times 10^{-13}$ to $1.4 \times 10^{-11}$ m². The dendritic pore structure has the highest compressive strength (39 MPa) due to its smallest pore sizes (16-20 µm) and secondary dendrites. In wicking experiments, these structural properties and the lowest permeability resulted in the slowest wicking rate in contrast to prismatic pore structures with the biggest pore sizes (31-57 µm) and highest permeability. Honeycomb-like pore structures allow medium wicking rates with the pore size being the main influencing factor. Due to the highest mechanical strength and stability, the dendritic pore structure was selected to create crackless porous screens for air-hydrofluoroether phase separation and bubble point test. First results will be presented using samples with different pore sizes and porosities.

## Acknowledgements:

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# Lithography-based additive manufacturing of polymer-derived SiOC/SiC composites

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## Abstract:

Polymer-derived ceramics (PDCs) are a highly promising class of materials owing to a combination of excellent mechanical and thermal properties, and highly versatile processability. The use of preceramic systems such as polysiloxanes opens a wide variety of shaping options due to intrinsic polymer properties, a recent focus of interest in this field being lithography-based additive manufacturing (AM) of PDCs.

Typical challenges encountered during PDC processing include high shrinkage and mass loss during the heat-induced polymer-to-ceramic conversion, often resulting in cracks, and limiting the maximum feature size of components. This behavior can be mitigated by the introduction of particulate fillers such as SiC.

In this contribution, we report on a novel polymer-derived SiOC/SiC composite system suitable for advanced geometric designs achievable by lithography-based ceramic manufacturing (LCM). The SiC-filled photoreactive resin system developed exhibits suitable viscosity characteristics, adequate stability against sedimentation, and a fast photocuring behavior. After printing and pyrolytic conversion, SiC particulates were well-dispersed within the PDC matrix.

A direct comparison with the unfilled system showed that the addition of particulate SiC increases handleability, reduces shrinkage, and significantly increases critical wall thicknesses up to 5 mm. A biaxial ball-on-three-balls testing methodology yielded a characteristic strength of 325 MPa for SiOC/SiC composites, the material thus exhibiting mechanical properties comparable to other structural ceramics.

The results achieved in this work can be considered an important milestone on the path toward the development and implementation of high-performance SiC-based materials suitable for LCM.

# Disclosing residual thermal stresses in fiber-reinforced ceramic composites

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## Abstract:

In this work, residual thermal stress (RTS) of carbon fiber-reinforced ultra-high temperature $ZrB_2$-based ceramic were tailored through fiber anisotropy and fiber coating. Materials under study were two composites based on the same matrix and different carbon fiber reinforcement. Intermediate modulus PAN-derived fibers (tensile modulus and CTE according to the supplier are 294 GPa and $-0.4 \cdot 10^{-6}$ °$C^{-1}$, respectively) coated with pyrolytic carbon were used to fabricate slightly stressed composite. The level of RTSs was maximized by using uncoated ultra-high modulus pitch-based fibers (tensile modulus and CTE according to the supplier are 780 GPa and $-1.5 \cdot 10^{-6}$ °$C^{-1}$, respectively).

The materials were fabricated trough slurry infiltration and sintering of the unidirectional preforms stacked in 0/0° sequence. Further details of the process were reported in Ref.s [1,2].

A detailed microstructural analysis was performed. The different RTS level, among the composites, was investigated by comparing the stiffness-displacement curves of bending test and the curves of cycled dilatometry. The correlation between RTS level and thermomechanical behaviour was also confirmed through bending test at 1500°C and after thermal shock. The results showed that RTSs not only reduced the flexural strength, but also influenced the damage evolution and the linearity of the stiffness. As consequence, RTSs releasing can change not only the original shape but also the Young's modulus of the matrix and the failure onset of the investigated CMCs.

[1] Zoli L, et al. J Eur Ceram Soc 2020;40:2597–603.

[2] Sciti D, et al. J Eur Ceram Soc 2020;41:3045–50.

## Acknowledgements:

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# Alumina ceramics prepared by reactive pressureless sintering dip-coated with PDMS-TEOS hybrid material

Manuela González-Sánchez[1], Pedro Rivero-Antúnez[1], Rafael Cano-Crespo[1], José Carlos Almeida[2], Maria Helena Figueira Vaz Fernandez[2], Víctor Morales-Flórez[1]

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## Abstract:

The objective of this work is to obtain alumina constructs suitable for bone regeneration. Despite the outstanding and tuneable mechanical properties of the porous alumina, its major problem for tissue engineering is the lack of bioactivity. To bioactivate alumina, a coating based on a procedure for obtaining hybrid sol-gel material PDMS-TEOS [1] is applied to the samples by dip-coating. The alumina structures are fabricated by reactive pressureless sintering from boehmite with alpha alumina seeds [2]. In order to tune the mechanical properties, a specific porosity was created by carbon sacrificial template that is removed by calcination. The activation of the surface by soaking the structures in piranha solution was also considered. The samples were mechanically characterized by uniaxial compression tests. SEM-EDS, Hg porosimetry and XRD allowed to assess microstructural and crystalline features of the samples. In vitro bioactivity was studied by immersion tests in Kokubo's SBF. The first results are encouraging and suggest that the alumina structures achieved by this method may be the basis of a novel line of permanent scaffolds for bone regeneration.

[1] Almeida, J.C et al. A biocompatible hybrid material with simultaneous calcium and strontium release capability for bone tissue repair. Materials Science and Engineering C 2016, 62, 429-438

[2] Rivero-Antúnez, et al. Reactive SPS for sol–gel alumina samples: Structure, sintering behavior, and mechanical properties. Journal of the European Ceramic Society 2021, 41, 5548-5557

## Acknowledgements:

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# Taguchi's method applied to manufacture of porous alumina by reactive spark plasma sintering and sacrificial carbon template

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## Abstract:

The Taguchi's method allows to optimize the search for appropriate values of the parameters involved in a manufacturing process because resources (such as time and materials) are limited and a large number of experiments cannot be performed. Thus, in order to find the best combination of parameters for an optimized given result, this procedure proposes how many experiments have to be done and under what conditions. In this work, the Taguchi's method is used in the manufacture of porous alumina made by reactive spark plasma sintering and carbon sacrificial template. The process begins with the mixture of boehmite, $\alpha$-alumina seeds and carbon. During sintering, the phase change from boehmite to $\alpha$-alumina occurs. The carbon is removed from the sintered sample by calcination, and the resulting porous structure receives heat treatment to consolidate. For Taguchi's method the input variables are: type of carbon, wt% of carbon, time of plateau sintering, heating rate of calcination and heat treatment. The target is to obtain these porous structures with pore size that favor bone regeneration and a Young's modulus similar to the bone, 7 – 30 GPa. So these magnitudes are the "Taguchi's output" and are studied in all samples by Hg porosimetry and uniaxial compression.

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# Sputtered tungsten trioxide for scalable hydrogen modules with separate hydrogen and oxygen evolution

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## Abstract:

Sputtered tungsten trioxide for scalable hydrogen modules with separate hydrogen and oxygen evolution

Michael Arnold[1], Arno L. Görne[1], Stephan Ulrich[2], David Adner[3], Christian Hagendorf[3]

The photo-electrochemical generation of hydrogen requires scalable effective methods. In addition to cathode materials such as CGS, materials such as bismuth vanadate and tungsten trioxide are promising candidates as anode material. Because the onset potential of a pure photo-elechrochemical cell (PEC) is general low, PV-PEC tandem devices could be a way. Tungsten trioxide was deposited from a ceramic and from a metal target on glass/FTO surfaces of 25 cm2. RF sputtering and DC sputtering were used in both variants. Various temperatures of the substrate during sputtering deposition were used. This resulted in considerable differences in photocatalytic activity. In the XRD and in the microstructure, large differences could also be observed, which correlated with the photo-electrochemical activities more strongly than with the thickness of the deposited layers (500 to 1500 nm). But the most important is the substrate temperature. Photocurrents up to > 1 mAcm$^{-2}$ could be measured. The method is scalable and suitable for the construction of PV-PEV tandem module.

Figure: annealed and cold deposited tungsten trioxide by RF sputtering on glass/FTO (thickness ca. 1100 nm)

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## Acknowledgements:

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# Enhancing contact damage tolerance through microstructure tailoring and layered design

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## Abstract:

Surface contact damage is a major cause for rejection of structural and functional ceramic components. This work demonstrates strategies to enhance contact damage tolerance by impeding the propagation of contact cracks on the example of alumina-based ceramics. One strategy is bioinspired from the structure of nacre, which involves texturing the microstructure to deflect cracks along the elongated grains. Further improvement is achieved by embedding such textured layers in a multilayer architecture to induce compressive residual stresses, acting as a "protective shield" against crack propagation. Contact damage resistance of such layered alumina system has been investigated under Hertzian contact loading and compared to the corresponding monolithic equiaxed and textured alumina materials. Acoustic emission detection was used for "in-situ" monitoring of the materials response. It was found that a textured microstructure can accommodate the damage below the surface by shear-driven, quasi-plastic deformation instead of the classical Hertzian cone cracking observed in equiaxed alumina. In the multilayer system, a combination of both mechanisms, namely Hertzian cone cracking on the top surface layer and quasi-plastic deformation within the embedded textured layer, was identified. Further propagation of cone cracks at higher loads was hindered and/or deflected owed to the combined action of the textured microstructure and compressive residual stresses. These findings demonstrate the potential of embedding textured layers as a strategy to enhance the contact damage tolerance in alumina ceramics.

## Acknowledgements:

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# Prediction of crack propagation in honeycomb ceramics by polarimetry and digital image correlation.

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## Abstract:

The fracture behavior and crack propagation of ceramic components are characterized by their brittle performance and are difficult to predict for complex and cellular structures in particular. In addition, the production of ceramic prototypes is time-consuming, and many samples are required for reliable statements about the properties. For this reason, it is helpful to adopt alternative but established characterization methods from other fields like glasses or brittle polymers, like polarimetry. To predict the crack propagation of ceramic honeycombs, brittle polymer lattices were 3-D printed via stereolithography. The angle of the unit cell was varied from -35° to 35°, with negative angles forming an auxetic and positive hexagonal lattice. These were photoelastically characterized under mechanical loading, revealing regions of excess stress. For comparison, alumina unit cells were fabricated via a combination of ceramic transfer molding and 3D printing. Characterization using compression testing and Digital Image Correlation (DIC) showed a good agreement for crack propagation. The stress distribution is much more homogeneous for angles of smaller magnitude, which is reflected in highly increased compressive strengths. By identifying the stress peaks with polarimetry, it was also possible to predict crack propagation, which was moreover confirmed by digital image correlation.

# Porous metakaolin/slag-based geopolymer adsorbent synthesized by a water-soluble template method

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## Abstract:

This paper reports a novel and easy extraction water-soluble template (NaCl) for fabricating porous geopolymer through the sacrificial template method. Metakaolin and slag were used as raw mineral materials combined with sodium-based alkali activator and NaCl was used as the water-soluble template or pore-forming agent to obtain NaCl/geopolymer samples. A water-soluble template (NaCl) is easily extracted via hot water coupled with pore formation. XRD, FTIR, CT, SEM, and EDS were used to investigate the effect of NaCl content on the pore morphology, porosity, density, boiling water absorption, and mechanical and structural characteristics of the synthesized porous geopolymers. Porous geopolymers (PGs) with low bulk density ($0.51< \rho_b < 0.85$ g/cm$^3$), high porosity ($\sim 67.4 < \varepsilon < \sim 80.4$ vol%), high compression strength ($2.4 < \sigma < 7.0$ MPa) and high boiling water adsorption ($68.6< W < 127.1$ wt%) were successfully prepared. High adsorption capacity up to 19.7 mg/g for methylene blue was realized, which demonstrates the potential of applications in wastewater treatment systems. Furthermore, these monolithic adsorbents were successfully regenerated and reused for four cycles, and the MB uptake even increased after the first two regeneration cycles.

## Acknowledgements:

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# Dielectric strength analysis of Al2O3 anodic layer deposited on Al substrate

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## Abstract:

In this study, we present the results of the dielectric strength investigation of the fabricated aluminium oxide ($Al_2O_3$) layer for high-temperature electronics applications e.g., for thermoelectric energy converters. $Al_2O_3$ coatings were produced on aluminium (Al) alloys by the electrochemical anodization method and characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) analysis, and X-ray diffraction (XRD). Thermal conductivity of the anodic oxide layer was defined on the base of the thermal properties of $Al_2O_3$/Al heterostructure substrate measured by laser flash analysis (LFA) method. The temperature-dependent breakdown voltage of $Al_2O_3$ anodic layer was evaluated as a key parameter that defined the workability of high-temperature electronic devices. The analytical calculations of the breakdown voltage were performed using Fock theory of thermal breakdown of solid dielectrics, which takes into account the influence of temperature on dielectric properties of the insulation layer. The breakdown voltage $U_{bd}$ measurement was carried out over a temperature range of 300 K – 500 K by the developed testing setup. The estimated breakdown voltage $U_{bd}$ of around 250 V and 80 V were achieved for 10 μm layer thick at 300 K and 500 K, respectively. Moreover, the thermal resistance of the 1 mm thick Al substrate with 10 μm dielectric layer is more than 5 times lower than the corresponding value for polycrystalline commercial $Al_2O_3$ plate. Therefore, the application of $Al_2O_3$ anodic layer as a dielectric substrate is a promising solution for the improvement of heat transport in high-temperature electronics devices.

## Acknowledgements:

The work was supported by TECHMATSTRATEG2/408569/5/NCBR/2019 project"Development of a technology for the production of a new type of thermoelectric modules for the conversion of low-parameter waste heat into electricity", The National Centre of Research and Development.

# Interaction in cerium oxide (+3) and oxides of yttrium subgroup systems

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## Abstract:

The interaction in the systems of $Ce_2O_3$ and $(Tb–Lu,Y)_2O_3$ is of interest due to the prospect of using complex $ZrO_2$ stabilizers to create new high-temperature thermal barrier coatings. The interaction between lanthanide oxides consists in the formation of continuous solid solutions between the components, as well as areas of solid solutions with different (X, H, A, B and C) $Ln_2O_3$ structures. In addition, ordered phases with a $Ln^{I}Ln^{II}O_3$ perovskite-like structure appear in some of these systems.

Investigations of lanthanide oxides polymorphic transformations by the method of derivative thermal analysis lead to the conclusion that all lanthanide oxides are characterized by the formation of all structural forms (X, H, A, B and C). For lanthanides of the yttrium subgroup (Tb — Lu, Y), the temperature regions of X, A, and B structures are very narrow and do not exceed 5–10 °C (Fig. 1). For technological developments, the presence of such narrow homogeneity areas does not play a crucial role, but when constructing phase diagrams they should be taken into account.

Tentative phase diagrams of unexplored $Ce_2O_3$—$(Tb—Lu)_2O_3$ systems have been constructed on the basis of experimentally constructed phase diagrams and established regularities. The polymorphic transformations of lanthanide oxides established by derivative thermal analysis were taken into account.

# Valorisation of local residues, by-products and wastes into ceramic materials for civil engineer application

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## Abstract:

Sand is the primary substance needed in construction field. From today to 2030, global aggregates demand is estimated to rise from 50 to 60 billion tonnes per annum [1]. Overexploitation of the last few available deposits leads several negative impacts on environment such as beaches disappearance, marine biodiversity troubles and pollution increase [1].

To prepare for an upcoming shortage and reduce carbon footprint, building industries began to look for alternative materials such as industrial wastes and by-products. For example, glass wastes [2][3] and granite wastes [4] may be used to replace sand and enhance fired bricks properties such as water absorption and shrinkage, while improving firing conditions and lowering environmental impact.

The purpose of this work is to identify inorganic residues, by-products and wastes deposits available in Occitanie region (France) and evaluate their potential to replace sand in local building bricks production. Experimental parameters such as shrinkage, true density and compressive strength were studied on fired pressed clay bricks containing from 5 to 40 % of regional by-products: domestic glass, wood pellet combustion ash, granite powder and mud, blast furnace slag and foundry core sand. In addition, regional waste clays from rock carriers were also studied to get 100 %-recycled bricks.

Results showed that up to 20% of some by-products (alone or by two) can be integrated to bricks composition while maintaining satisfying properties. Compressive strength of some formulations including waste clays has exceeded the reference value. Complementary parameters such as freeze-thaw and leaching stabilities must still be investigated before beginning industrial-scale tests and evaluating environmental viability of the new formulations.

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# Microstructural features of plasma electrolytic oxidation ceramic coatings on titanium scaffolds

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## Abstract:

One of the most widespread applications of titanium is in the fabrication of implants due to its mechanical strength and biocompatibility. However, the thin natural titanium oxide layer is not bioactive and is susceptible to damage turning titanium chemically vulnerable. The production of thick ceramic coatings increases the corrosion resistance of titanium, and may improve the bonding strength and integration with bone. This work studies the microstructure of $TiO_2$ and $TiO_2$-hydroxyapatite coatings formed by plasma electrolytic oxidation on titanium scaffolds. The scaffolds produced by material extrusion additive manufacturing had surface roughness ($S_a$) of 13 μm, porosity of 50 % and some open pores in the strands remnant of the sintering process (2 %), with size between 40 and 60 μm. The deposition of $TiO_2$ coating hidden the sintering pores and reduced the surface roughness, but generated the formation of larger number of new open pores of smaller size due to the formation of discharge channels that transport oxides form the titanium surface to the coating surface to increase the coating thickness up to 100 μm. The coating composed of anatase and rutile increased the corrosion resistance and decreased the corrosion rate of the titanium scaffolds. The incorporation of hydroxyapatite nanoparticles in the electrolyte further reduced the porosity and pore size of the composite coating layer due to the particles adhered on the surface and penetrated in the pores. These ceramic coatings are envisaged not only as corrosion protective, biocompatible and bioactive, but also may increase the fatigue endurance of the titanium scaffolds by reducing the surface roughness inherent to the processing.

## Acknowledgements:

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic (LTAIN19112) and the Indian Department of Science and Technology (DST/INT/CZ/P-06/2019).

# High Shear Wet Granulation of Geopolymer and Geopolymer-Zeolite powders for CO2 adsorption

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## Abstract:

Being widely used by the pharmaceutical industry, granulation of powders is a very simple method requiring, however, a strict control of processing parameters. The purpose of this research was to produce geopolymer granules from the controlled agglomeration of geopolymer and zeolite powders, to be used inside a fixed-bed column system for testing $CO_2$ adsorption. Granules composed of pure geopolymer, geopolymer/zeolite, and geopolymer impregnated with APTES during/after granulation were successfully produced using a high shear wet granulation technique. Granules of different dimensions were tested by compression, and their main characteristics were assessed by SEM, BET, and porosity measurements.

The adsorption capacity was measured as grams of $CO_2$ per kilogram of sorbent. The breakthrough curves from continuous adsorption tests were obtained using different concentrations of $CO_2$ in air. The produced granules showed $CO_2$ adsorption capacity similar to other materials reported in the literature.

# Dependence of the tribological behavior of graphene-based ceramic composites on the graphene structure.

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## Abstract:

Spark Plasma Sintering (SPS) has been succesfully used to fabricate different graphene based ceramic composites using different graphene structures such as graphene nanoplatelets (GNP) or few layered graphene (FLG). The incorporation of GNP to the ceramic matrix has been reported to improve the tribological behavior of these composites due to the formation of a protective carbon-rich tribolayer [1].

The present work investigates the effect of the graphene structure on the tribological properties of these composites. Commercial nano 3 mol% yttria stabilized zirconia powders were mixed with different types of graphene (GNP and FLG) and, afterwards, consolidated using SPS at a temperature of 1250°C under uniaxial pressure of 75 MPa. Friction and wear tests were performed on a ball-on-disk tribometer to evaluate the tribological behavior of the fabricated samples. The tests were carried out using normal loads of 5, 10 and 20 N. The influence of the different types of graphene on the microstructure of the samples and on their tribological behavior were related and discussed.

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## Acknowledgements:

This research was supported by the Ministerio de Ciencia, Innovacion y Universidades (MCIU) under the project PGC 2018-101377-B-100 (MCIU/AEI/FEDER, UE) and by the Junta de Andalucía (Consejería de Economía, Conocimiento, Empresas y Universidad) under the project PAIDI 2020: P20_01024. C. Muñoz-Ferreiro acknowledges the financial support of a VI PPIT-US fellowship through the contract USE-18740-H.

# Developing zinc aluminate and zinc silicate ceramic films by a cost-efficient screen printing method assisted by a molten salt flux

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## Abstract:

Aluminate and silicate-based materials as $ZnAl_2O_4$ and $Zn_2SiO_4$ have been attracting numerous interest due to their wide optical band gap, excellent thermal and chemical stability, and radiation resistance. Moreover, these aluminate and silicate-based materials are promising luminescent hosts that can act as emitters without and with the incorporation of rare-earths from the UV to the NIR range. These color-tunable emissions make these materials a suitable host for a wide range of applications, e.g, bio-imaging, security markers, imaging devices, optical coatings and solar cells. Nowadays, simplified synthesis techniques to control the production of uniform films are highly desired. For this reason, taking the advantage of screen printing method assisted by a molten salt flux, submicron and continuous films based on $ZnAl_2O_4$ and $Zn_2SiO_4$ were obtained over alumina and fused silica substrates. The objective of this work is, therefore, a twofold: (i) a comprehensive study of the role of the paste formulation is and the drying and annealing process to densify the film, aimed at gaining a deep understanding of its real contribution to all the phases of the production of the film, and (ii) an assessment of the incorporation of dopants (rare earths) to tune the luminescence performance. By virtue of processing conditions and the development of dopant free and Ce and Nd doped films, it is possible to tune their functional response. Our results will help to understand and facilitate the development of luminescent films through a screen-printing technology that gives the possibility of producing ceramic layers with low cost and easily scalable process.

## Acknowledgements:

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# Creation of porous ceramics with hierarchical pores using capillary suspensions for bone tissue engineering

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## Abstract:

Bone fractures are a common health problem affecting millions of people worldwide each year. Although bone tissue has an exceptional ability to naturally regenerate when the fractures are small and uncomplicated, healing of more severe defects is usually a long process that is hindered by complications, such as infections, bone deformities and non-union fractures, necessitating the use of artificial fasteners. However, the presently used materials for bone tissue engineering poorly mimic natural bone, thereby increasing the risk of further fractures while also not stimulating bone reconstruction. Scaffolds possessing hierarchical structures increase bone development but are still difficult to fabricate. This paper will discuss the process of developing an easy, biodegradable implant to enhance natural bone growth via hierarchical morphology.

A novel method is used by introducing micro-porosity by creating a capillary suspension from tricalcium phosphate and alumina. Such capillary suspensions are 3-phase systems composed of a solid loading dispersed in a bulk phase where up to 5% of an immiscible liquid is added, which leads to the formation of secondary fluid bridges between particles, inducing the formation of a sample-spanning particle network. To add the second level of porosity, we further utilize either freeze-casting or 3D printing. These methodologies allow fabricating the desired materials in a simple yet robust and controllable way. The SEM analysis of the scaffolds successfully reveals the existence of a hierarchical interconnected pore structure: pores not exceeding 10 µm coming from the initial capillary suspension network and 30-80 µm pores from the secondary structuring. This material has the possibility to significantly increase bone tissue regeneration.

# Interface optimization of hybrid polymer-ceramic microdevices for transdermal applications.

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## Abstract:

The combination of different materials in a layered structure as hybrid components have been highly explored for several applications, since it allows the creation of devices with distinct and unique properties that, when made with only one material, would not be possible. The interface between the different materials are crucial for the final performance of the device, demanding a high research focus in the optimisation and characterisation of the adhesion between the different layers. Several studies confirm that it is possible to obtain a polymer-ceramic interface, strong enough to realize devices for transdermal application, using ceramic materials such as alumina and zirconia [1,2] and with a flexible substrate derived from polydimethylsiloxane [3].

In this study, the interface between a flexible polymeric component made of soft skin adhesives (SSA) and a porous self-setting ceramic-based component was analysed and optimized, in order to design a device for transdermal application. For that, different combinations of polymeric commercial SSA was evaluated by rheological measurements and mechanical properties. Similarly, several compositions of self-setting ceramic parts were developed and analyzed by density, porosity, and pore size distribution. The adhesion between both polymer and ceramic parts was studied by bonding strength tests. The interface of the most promising hybrid layered components were then characterized by scanning electron microscopy, energy dispersive X-ray and microcomputed tomography. The results obtained demonstrate a stable and strong enough surface adhesion at the interface of both materials, highly promising to go ahead with future developments of devices for transdermal applications.

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## Acknowledgements:

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# Influence of powder composition on the internal stresses and thermal annealing behavior of ceramic films formed by Powder Aerosol Co-Deposition

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## Abstract:

The Powder Aerosol Deposition (PAD) method is a novel method to produce ceramic films at room temperature. During the coating process, a ceramic powder forms an aerosol and is transferred to a vacuum deposition chamber. Particles are accelerated by a nozzle and subsequently impact on a substrate where a dense film is formed.

PAD films typically bear a high internal compressive stress in the range between 0.5 GPa and 2.5 GPa as an intrinsic feature. Firstly, this stress may lead to a film delamination in case of high film thicknesses, if the interface of film and substrate cannot withstand the occurring shear stress. Secondly, film stresses cause a significant deterioration of electric properties like the electronic or ionic conductivity. Thermal annealing diminishes the internal stress and regains high electrical properties, yet this treatment opposes to the advantage of PAD of ceramic room temperature processing.

In this work, the internal stress of PAD films consistent of different materials and their mixtures was determined. Furthermore, the mechanical annealing behavior was studied by XRD and substrate curvature measurements after thermal treatments. The results show different internal stresses depending on the powder composition.

# Calcium phosphate coatings on gel-cast ZrO2 foams

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## Abstract:

Gel-casting of foams method was used to produce $ZrO_2$ porous ceramics. The obtained foams with total porosity in the range of 66-89.5 vol% were composed of approximately spherical cells having the mean diameter in the range of 103 – 537 µm interconnected by circular cell windows having the mean diameter of 20 – 152 µm . The effect of foam porosity on selected mechanical properties (compressive strength, Young's modulus) and permeability was determined. Next, the $ZrO_2$ foams were coated with fluorapatite (FA) and hydroxyapatite (HA) layers by slurry infiltration. The intermediate fluorapatite (FA) layer was introduced to prevent the chemical reactions between $ZrO_2$ and HA at high temperatures during sintering process. The $ZrO_2$ samples containing only HA coatings, were also tested, for comparison. The obtained ceramic biomaterials were subjected to in vitro tests in the simulated body fluid (SBF) solution. The bioactivity and dissolution rate of the obtained ceramic biomaterials were evaluated.

## Acknowledgements:

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# Dislocation Toughening in Oxide Perovskites

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## Abstract:

Dislocation-tuned functionality in ceramic oxides is gaining serious research attention, with promising proofs-of-concept realized most recently including increased electrical conductivity (Muhammad, Q. K.et al., Nano Energy 2021, 85, 105944), ferroelectric properties (Höfling, M. et al., Science 2021, 372 (6545), 961) and superconductivity (Hameed, S. et al., Nature Materials 2022, 21, 54-61).

To improve the mechanical properties of ceramics in general and pave the road for dislocation-tuned functionality, and thus reaching higher reliability and lifetime of future dislocation-based devices, we studied dislocation-based crack initiation and propagation. In this talk, we demonstrate that by engineering high dislocation densities (up to $10^{14}$ $m^{-2}$) in single-crystal perovskite oxides such as $KNbO_3$ and $SrTiO_3$ (cf. Porz, L. et al., Mater. Horiz., 2021,8, 1528-1537), both damage tolerance (threshold for crack initiation) and fracture toughness (threshold for crack propagation) have been improved at room temperature.

We find that, under critical load, the crack initiation is fully suppressed and the fracture toughness is increased by a factor of 2-3. The interactions of crack tip and dislocations, as well as other microstructure (e.g., domain walls in KNbO3), are closely examined by optical microscopy, electron channelling contrast imaging and piezoresponse force microscopy methods to shed light on the toughening mechanisms.

Together with the dislocation-tuned functionality, our findings suggest a promising route of using dislocations as the single building block to engineer ceramics that are both functionally superior and mechanically robust.

# Mechanical Properties of Al2O3/Y2O3 Nanolaminate Films on Aluminum towards Protective Coatings

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## Abstract:

Atomic layer deposition is an appealing deposition technology for the fabrication of protective ceramic coatings for various applications, including semiconductor manufacturing chambers and related metallic parts with complex 3D topographies, where a key requirement is (thermo) mechanical robustness of the coatings. Here we study the mechanical properties of atomic layer deposited $Al_2O_3$, $Y_2O_3$ and their nanolaminate coatings on Al metal substrate. Tensile straining experiments accompanied with in-situ optical and scanning electron microscopy indicate that the fragmentation onset of 100-nm thick coatings can be tailored in the strain range of 1.3 – 2.1 % by controlling the layer structure and composition of the nanolaminates, such that a higher $Al_2O_3$ content, denser layer spacing and amorphisation favor higher crack onset strain. Although the fracture toughness of $Al_2O_3$ and $Y_2O_3$ are found to be similar, $K_{IC} = 1.3$ MPa·m$^{1/2}$, the (substantially tensile) intrinsic residual stress for $Y_2O_3$ is a disadvantage for applications where tensile applied stresses are to be expected. The films adhere well to the Al substrate as significant delamination of the films is not observed in the tensile experiments; the analysis of the fragmentation patterns indicates that insertion of an $Al_2O_3$ layer at the film/substrate interface can enhance interface toughness. High-temperature (425 °C) tensile experiments for the $Al_2O_3$ films indicate good temperature tolerance for the coatings, and in comparison to the room-temperature data, a significant difference is seen in the increase of saturation crack spacing. Moreover, structure and composition of the films are studied in detail through X-ray reflection and diffraction, transmission electron microscopy, Rutherford backscattering spectrometry, and elastic recoil detection analysis. The results are particularly interesting for protective ceramic coating applications.

## References:

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DOI: 10.1021/acsanm.2c00378

# Elaboration of yttria-stabilized zirconia coatings at room temperature by Aerosol Deposition Method (ADM)

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## Abstract:

Discovered and developed in the late 90s by J. Akedo et al., the « Aerosol Deposition Method » (ADM) is a dry coating process based on kinetic energy, almost analogous to the Cold Spray (CS) process. The unique deposition mechanisms of ADM make the ceramic coatings at room temperature possible. Indeed, adherent layers are achievable thanks to a phenomenon that combines plastic-elastic deformation and in-situ grain fragmentation of ceramic particles called « Room Temperature Impact Consolidation » (RTIC). Thus, resulting nanostructured coatings of the Aerosol Deposition process can be highly dense (>95%), with a thickness from few hundreds of nm to hundred of µm, in a low vacuum environment and at room temperature from a dry ceramic powder. This innovative technology allows to produce composite layers by mixing powders and spraying them on different types of substrates: polymers, ceramics, metals, from the most flexible to the hardest.

In this context, CTTC and IRCER work on different ceramic materials through the ADM since 2010s. This talk will focus on the fabrication of yttria-stabilized zirconia coatings (especially $ZrO_2$- 3% mol. $Y_2O_3$) at room temperature by Aerosol Deposition Method. To do so, a spotlight on the powders sprayed and their properties will be presented. Through various characterizations, a correlation between powders specifications and their ability to produce coatings by ADM will be highlighted. On a second part, the machine parameters used and the characterized coatings obtained (microstructure, adherence etc.) will be showed. Finally, the connection between the powder characteristics, the resulting coatings and their properties will be discussed.

## Acknowledgements:

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# β-TCP porous scaffolds with controllable macro-microporosity prepared by PU replication method assisted by vacuum

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## Abstract:

Nowadays, calcium phosphate (CaP) ceramics are the leading standard of bone grafting materials because of their many useful properties in bone tissue engineering. Their bioactivity can be assigned to their structural similarity to the mineral part of bone and when implanted they act as a suitable scaffold to enhance the growth of bone cells and direct deposition of bone for rapid bone regeneration, that is they are osteoconductive. Research also strongly suggests that the key parameters that play a role in a material's osteoinductivity, that is the property of a material to grow bone, are microstructural surface properties such as particle size, microporosity, specific surface area and surface roughness. Therefore, control of macro-microporosity is very beneficial.

In this study, we report on the influence on microstructure, porosity and compressive strength of the scaffold bodies prepared with vacuum assisted infiltration of polyurethane (PU) sponges as opposed to scaffolds fabricated without vacuum infiltration. Starting powders were synthesized through aqueous precipitation and characterized structurally (by FTIR and XRD) while shaped scaffolds were characterized microstructurally (by SEM and $N_2$ adsorption/desorption) and mechanical testing. The course of the synthesis proved promising for preparing osteoconductive scaffolds.

## Acknowledgements:

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# Understanding fracture of layered alumina-based ceramics with textured microstructures: from macro- to micro-scale

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## Abstract:

To improve the mechanical reliability as well as the resistance against crack propagation of advanced ceramics, mimicking the "damage tolerance" of biological materials (i.e. nacre) has been established as a remarkable approach to design multilayer ceramic architectures. It has been demonstrated that the use of tailored residual stresses in embedded layers can act as an effective barrier to crack propagation from surface flaw, providing a minimum threshold strength, below which no failure occurs. Moreover, orienting the microstructure (texturing) within the embedded layers may be exploited to further enhance the fracture resistance of layered ceramics. It is hypothesized that the exceptional damage tolerance in these materials is mainly attributed to crack deflection events along the weaker basal grain boundaries within the textured microstructure. To prove this hypothesis, the fracture toughness of individual textured alumina grains and grain boundaries has been measured through micro-cantilever bending tests. The benefits of embedding textured layers in alumina multilayers on the contact damage tolerance will be discussed. Furthermore, the temperature influence on mechanisms acting within the ceramic architectures with textured microstructures during high-temperature bending (up to 1200 °C) has been investigated.

## Acknowledgements:

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# Utilization of waste diatomaceous earth for cellular glass fabrication

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## Abstract:

With increasing concerns regarding fire safety and service life of polymer based thermal insulating materials, inorganic thermal insulating materials, such as foam glass, have been gaining significance in past decades. Coupled with environmental efforts and the potential scarcity of glass cullet in certain regions, finding suitable alternative raw materials for foam glass production, is a very relevant issue. In this study, low quality diatomaceous earth emerging as a by-product during production of diatomaceous earth for filtration purposes, was used as an alternative raw material for foam glass production. Waste diatomite was thoroughly characterized to assess its suitability for foam glass production. Conversion of this secondary resource to foamed product was achieved via hydrate mechanism, using NaOH solution as foaming agent. Different pre-treatment temperatures and firing regimes were investigated. Changes in high temperature behaviour and materials properties were studied using heating microscopy and TG-DTA analysis. Prepared foams were characterized in terms of their physical and mechanical properties. Microstucture and phase composition were studied using scanning electron microscope and X-ray diffraction analysis, respectively. Highly porous samples with bulk densities ranging from 150 kg/m$^3$ to 560 kg/m$^3$ and compressive strength 0,16–1,2 MPa were obtained using direct high temperature foaming of waste diatomaceous earth.

## Acknowledgements:

This work was supported under Internal Grant Agency of Brno University of Technology, specific junior research No. FAST/FCH-J-21-7280 with project name: Utilization of waste diatomite as a secondary raw material for production of inorganic insulation materials.

# Characterization of transparent conducting ITO-Al2O3 composite thin films deposited by aerosol deposition

Kazuki Shinozuka[1], Yuuki Sato[2], Shinzo Yoshikado[2]

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[2] *Doshisha University, Kyotanabe,KYOTO, Japan*

## Abstract:

Tin-doped indium oxide (ITO) thin films are widely used in flat panel displays and solar cells because of their high visible light transmittance and excellent conductivity. Aerosol deposition (AD) is a film fabrication method by colliding high-speed aerosol of crystal particles of a few microns onto the substrate at room temperature. It maintains the crystal structure of raw materials; mixture powders can be used as raw materials. ITO-$Al_2O_3$ composite thin films were fabricated using the AD method. Raw materials were prepared by mixing ITO with $Al_2O_3$ in different volume ratios. The aim is to reduce the consumption of ITO while maintaining its properties.

The ITO-$Al_2O_3$ composite thin films showed a constant resistivity of $5.0\times10^{-3}$ Ohm·cm with $Al_2O_3$ from 0 to 66 vol%. High resistivity of $1.0\times10^{-2}$ Ohm·cm was observed when added $Al_2O_3$ over 66 vol%. These values are a bit higher than commercial one due to the interface resistance. The resistivity of ITO thin films decreased as ITO raw particles' size decreased from 2.51 µm to 0.97 µm. Addition of $Al_2O_3$ to ITO particles up to 80 vol% did not produce any noticeable changes in resistivity, when ITO particle size was relatively small. The resistivity of the composite thin film increased while increasing $Al_2O_3$ amount, using relatively large ITO particles.

The crystallite size of ITO in composite film calculated by the Williamson-Hall method decreased as the gas flow rate increased. A dense composite film with a small crystal size showed high optical transmittance. ITO-$Al_2O_3$ composite thin films had almost the same transmittance and absorption coefficients as ITO thin films.

AD-deposited ITO and composite films showed a higher resistivity and a higher transmittance than sputter-deposited films due to the consisting of nano particles.

# Additive Manufactured Replica Foams

Swantje Simon[1], David Köllner[1], Jonas Biggemann[1], Ken-ichi Kakimoto[2], Tobias Fey[1]

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## Abstract:

The Replica technique is a well-established method for the fabrication of macroporous, stochastic foams with various pore sizes (5-100ppi), but is however limited in terms of pore shape, distribution by its natural or synthetic templates. The replica technique was therefore combined with additive manufactured (AM) templates to overcome this issue and produce foams with an individual periodic 3D-architecture and modified strut morphologies. Polymeric templates with rectangular/cuboid cells (size= 2.5 x 7.5 mm) were 3D-printed with triangular and circular struts (diameter 250/388 µm) using a stereolithographic 3D-printer and afterwards coated with an alumina slurry. After debinding and sintering the microstructural properties and mechanical performance were characterized by micro-computer tomography, SEM and compression tests in comparison to a stochastic 30 ppi foam with identical porosity. The AM-derived foams showed a superior compressive strength (>+15%) than the stochastic replica foams. The properties could be further improved by using a subsequent sol-gel coating process with a tetraethylorthosilicate (TEOS) gel, reaching struts strength of up to 291 MPa.

# Preparation and characterization of ZTA intended for structural ceramics

Joanna Szymanska[1], Teresa Rey Wojcik[1], Veronika Müller[1], Sarah Griesser[1], Daniela Jaschak-Arrich[1], Jasmin Koller[1], Angelika Priese[2]

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## Abstract:

Continuously rising quality requirements for the industrial materials induced a great interest in fabrication of zirconia toughened alumina (ZTA) composites that exhibit suitable room-temperature mechanical properties such as strength, toughness and wear resistance. The increasing need for production of such durable materials performing ultra-high strength and sufficient lifetime is becoming tremendous, especially in automotive (valves, fluid pressure sensors), biomedical (implants) and industrial applications (seal rings, marker, cutting tools, wear resistant parts, machine screws etc).

The current industrial production of ready to press ZTA implies manufacturing of granulated composite powder in a few basic operations:

- the mixture preparation (based on selected alumina, zirconia and chemical additives: dispersant, binder, plasticizer, defoaming agent);
- spray drying of the slurry into granules suitable for cold/hot isostatic/uniaxial pressing and further sintering.

This paper describes the use of Zeta potential measurements to develop slurries with optimized 88/12 ZTA based on different alumina and zirconia powders.

The ceramic properties of the received granules were further evaluated by pressing disks and analysis of the green and sintered density, shrinkage, hardness, MOR and sintered grain size. The granules were also characterized by flowability, bulk density, and SEM.

The conclusions showed the suitability to apply ZTA as a potential material for the structural ceramic market.

# Boron nitride nanosheets as a reinforcement for silicon nitride

Monika Tatarková[1], Peter Tatarko[1], Alexandra Kovalčíková[2], Ivo Dlouhý[3], Ján Dusza[2], Pavol Šajgalík[1]

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## Abstract:

Fully dense $Si_3N_4$ materials with 1.5 vol.% and 3.0 vol.% of h-BN nanosheets were prepared by spark plasma sintering at 1750°C with the dwell of 7 min under a pressure of 50 MPa in a vacuum. BN nanosheets with different dimensions were prepared by ultrasound-assisted liquid phase exfoliation of h-BN powder, followed by centrifugation at different speeds (1000 rpm and 3000 rpm). The addition of BN nanosheets hindered the particle rearrangement stage of sintering, which resulted in the delayed $\alpha \to \beta$ phase transformation of $Si_3N_4$. To study a direct effect of BN nanosheets on the mechanical properties of $Si_3N_4$, the results were compared to the monolithic $Si_3N_4$ with similar grain size and $\alpha/\beta$-$Si_3N_4$ ratio. The addition of 3 vol.% h-BN nanosheets (1000 rpm) increased both the fracture toughness (~ 26 %) and the strength (~ 45 %) of $Si_3N_4$, when compared to the monolithic $Si_3N_4$ with similar microstructure.

## Acknowledgements:

This work was supported by the Slovak Grant Agency APVV-18-0542 and VEGA Project No. 2/0116/22 .

# Filtration Performance of Highly Porous Glass Filters Made from Capillary Suspensions

Kevin Tedjokusuma

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## Abstract:

One of the most commonly employed processes to produce porous glass filter is sintering of glass powder, which typically results in low porosity and permeability of the filter. In this work, an innovative method to produce highly porous sintered glass filters by using capillary suspensions as precursor is presented. The so produced filters have substantially high open porosity of up to 60 % and the pore size can be tuned between 0.5 and 100 µm. Capillary suspensions are made by adding a trace amount of a suitable immiscible secondary liquid to a suspension. Under stirring, a self-organizing particle network is formed. Secondary fluid droplets are deposited between the particles and act as pendular bridges, which reinforce the network. This can considerably suppress shrinkage and crack formation during the subsequent debinding process. The structure of this network is essentially retained even after the final sintering. Accordingly, the properties of the pore structure of the sintered glass filter can be adjusted directly during the preparation of the capillary suspension. In this study, the pore structure is tuned by varying particle size and solids content. The connection between the pore structure and the filtration performance investigated via filtrations tests will also be discussed. The cut-off, the service life, and the backwash behavior are determined by permeability test and analysis of the turbidity and particle size distribution in the filtrate. Furthermore, asymmetric glass membranes consisting of a thin functional porous layer in the range of 200 µm and an underlying large-pore support layer will be presented. This combination permits a low cut-off and a low filtration resistance. The filtration performance will be compared with a symmetric glass filter.

# Photovoltaic Glass Waste Recycling In The Development Of Susbtrates For Photovoltaic Applications

Karina Trevino Rodríguez[1], Astrid Iriana Sánchez Vázquez[1], Juan Jacobo Ruiz Valdés[1], Jorge Ibarra Rodríguez[1], Manuel García Méndez[2], María Guadalupe Paredes Figueroa[3], Anabel Álvarez Méndez[1]

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[3] *Universidad de Monterrey, Monterrey, Mexico*

## Abstract:

In this research, a glass waste material with high volume generation forecast is proposed to be included in the photovoltaic field as substrate material. Soda-lime glass was produced using photovoltaic waste glass as main raw material and other waste materials such as quartz sand and dolomite waste, and the feasibility to use these materials as substrates for photovoltaic applications was tested.

For this work, poly-crystalline Si photovoltaic panels waste were treated to recover the photovoltaic waste glass (PVWG) by heat treatment, the different materials obtained from photovoltaic waste separation are the following: PVWG 80.23% weight, 2.93% correspond to crushed silicon cells, and 11.95% to the separated Tedlar® with silicon cells, EVA, and metal rods. X-Ray Fluorescence (XRF) results shown its main components of PVWG are $SiO_2$ (63.57%), $Na_2O$ (32.23%), CaO (2.77%), MgO(0.76) and $Al_2O_3$ (0.53%). To obtain a soda-lime glass substrate (wSLG) using PVWG and other industrial waste materials, rejected dolomite and quartz sand were incorporated to adjust the typical soda-lime glass formula. The wSLG was characterized by UV-VIS transmittance and compared to commercial soda-lime glass (cSLG) in the visible region (400-750 nm). The average transmittance in the visible region (400-750 nm) for wSLG and cSLG are 83.6% and 85% respectively. A 866 nm thickness of Aluminum doped Zinc Oxide (AZO) was deposited on wSLG by RF-Sputtering. The average transmittance in the visible-NIR range (350–1000 nm) is 75% and the optical band gap ($E_g$) is 3.53 eV.

This work presents and alternative process to recycle photovoltaic waste glass to be re-incorporated to the photovoltaic industry, in particular, in the production of photovoltaic windows using waste materials.

## Acknowledgements:

- K. Treviño-Rodríguez thanks to Consejo Nacional de Ciencia y Tecnología (CONACYT) for the PhD scholarship.
- All the authors thank to Dr. Antonio Zaldivar Cadena from Facultad de Ingeniería Civil, Universidad Autónoma de Nuevo León, for the help in photovoltaic waste glass characterization in this research.
- Thanks to Dr. Eduardo Sánchez from the Laboratorio de Materiales II of the Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, for the UV-VIS measurements.

# A new SPR-based sensor using transparent ceramics coated with gold-silica nanoparticles and mesoporous topcoat

Romain Trihan[1], Anne Aimable[1], Fabrice Rossignol[1], Joanna Kowalko[2], Helena Węglarz[2], Agnieszka Szysiak[2], Oskar Bogucki[2], Anna Kozlowska[2], Martin Ihle[3], Steffen Ziesche[3], Bartosz Fetliński[4], Bartosz Janaszek[4], Marcin Kieliszczyk[4], Paweł Szczepański[5], Michał Malinowski[4], Marcin Kaczkan[4], Piotr Giemza[6], Marcin Szczypa[6]

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## Abstract:

This research study focuses on the development of a new optical sensor platform. The device is based on a layered doped transparent ceramic pumped with a laser diode and coupled with a functionalized surface plasmon resonance (SPR) structure as an innovative photonic component for both lighting and sensing. Targeted areas are the detection of pollutants in water (Cu, Fe, etc.) or air (CO, NOx, etc.), as well as medical diagnosis.

The core of the lighting component is a doped YAG ceramic, adapted to the desired optical properties, under LED excitation. Light enhancement occurs at the device surface due to the SPR effect. On that purpose, the SPR effect is obtained by adding hybrid gold-silica or silver-silica nanoparticles. In addition, a functionalized mesoporous silica topcoat is also deposited according to the targeted chemical or biological compound.

The presentation will focus on surface functionalization (nanoparticles synthesis, deposition on the surface, mesoporous silica topcoat elaboration) and detection capabilities through optical measurements based upon a demonstrator.

## Acknowledgements:

Financial support of this work from the M-era.Net is gratefully acknowledged. The postdoctoral position granting was also possible thanks to the French National Centre for Scientific Research (CNRS).

# Quantifying local fracture toughness in nacre-like ceramics

Victoria Vilchez[1], Pedro I.B.G.B. Pelissari[2], Victor C. Pandolfelli[2], Florian Bouville[1]

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## Abstract:

Unlike synthetic ceramics which are brittle and prone to catastrophic failure, biological materials combine both stiffness and toughness. Nacre, for example, is composed of 95 vol% calcium carbonate yet exhibits a fracture energy 3 orders of magnitude higher than $CaCO_3$. This toughness amplification stems from nacre's brick-and-mortar architecture which provides multiple toughening mechanisms at different length scales. Consequently, nacre has become a blueprint for manufacturing tougher synthetic ceramics. We are now able to accurately reproduce at similar length-scale the architecture of nacre with processes like magnetically assisted slip casting (MASC). MASC enables the controlled alignment of anisotropic platelets decorated with superparamagnetic nanoparticles under low intensity magnetic field during slip casting. Using this process and others, nacre-like ceramics (NLCs) of various compositions have been developed. However, if the reinforcing mechanisms acting in biological nacre have been intensely studied, they are still not well understood in NLCs, in which the complexity of the highly deflected crack paths makes it difficult to evaluate fracture using the standard tools of fracture mechanics. We developed a formulation based on mixed-mode stress intensity factors to describe fracture at the crack tip, taking into account the angle of deflection and the presence of multiple cracks. This formulation was applied to experimental data obtained from in situ mechanical testing on NLCs of various compositions and its accuracy confirmed by finite element analysis. This new description of NLCs' fracture gives us a better understanding of the local mechanisms controlling crack propagation, a necessary condition to push their mechanical properties further in the future.

# FastCast – open porous ceramics

Moritz Weiß

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## Abstract:

Capillary suspensions can be used as stable precursors for the production of porous ceramics with high open-porosity. Capillary suspensions are ternary solid-liquid-liquid systems in which a small amount of an immiscible secondary liquid is added to a suspension. A particle network connected by capillary bridges is much stronger than one formed by van der Waals forces. It does not collapse during debinding or sintering and can therefore serve as precursor for sintered materials with high open-porosity.

This processing route enables manufacturing of highly open-porous ceramic bodies with tailored microstructure and mechanical properties. Due to the elasticity of the capillary-induced particle-network, drying stresses can be degraded without cracking. Here, we are applying this technique for shell building in investment casting, thus accelerating processing times from 10 to 2 days. We also simplify the production process by requiring only 1/3 of the current machinery. Our approach is a "drop-in" technology, meaning that no additional equipment in manufacturing is needed. These advantages motivate us to start our own company to revolutionize investment casting. Our future company will be based on a direct transfer of knowledge from science to industry.

# Combination of polymer derived ceramic and physical vapour deposition coating methods for new functional coatings

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*Chair of Ceramic Materials Engineering, University of Bayreuth, Bayreuth, Germany*

## Abstract:

Physical vapour deposition (PVD) is a coating method for thin and very hard coatings used for wear resistance applications. Due to low deposition rates coating thickness is limited to a few micrometres. Hence, PVD coatings are not suitable for applications like oxidation protection as the coating thickness is not sufficient. In contrast the polymer derived ceramic (PDC) route offers the possibility to produce thicker coatings up to 100 µm. PDC coatings based on polysilazanes possess excellent oxidation protection properties. Their disadvantage is the limited stability against abrasion. Due to the complementary properties of the mentioned methods regarding coating thickness, oxidation protection and mechanical properties a combination of PDC and PVD coatings could lead to a coating system with improved oxidation protection and enhanced mechanical properties.

Therefore, PDC coatings based on the commercially available silazanes Durazane 2250 and Durazane 1800 were coated additionally with titanium nitride (TiN) via PVD. The formation of a homogeneous TiN coating was successfully demonstrated on silazane coatings ceramised up to 700 °C prior to the PVD process. The scratch resistance of the combined coatings was increased from 2 N to 10 N compared to the silazane coating. Cross cut tests confirmed the good adhesion as the damage of the coating area was reduced by 32 % and coating was classified as Gt-1. Hence, the combination of PDC and PVD coating technique leads to coating systems with improved mechanical and excellent oxidation protection properties.

## Acknowledgements:

We like to thank Mr. Mucha from the MAT PlasMATec company, Germany for the preparation of the PVD coatings, Mrs. Tangermann-Gerk from the Bayerischen Laserzentrum GmbH, Germany for the preparation of the energy-dispersive X-ray spectroscopy measurements and Mr. Lenz Leite, Chair of Ceramic Materials Engineering, University of Bayreuth, Germany for the support at the conduction of the mechanical tests. We also like to acknowledge the Federal Ministry of Germany for Economic Affairs and Energy (BMWi) for the financial support in the frame of the ZIM cooperation program project number ZF4109903AG7.

# Mechanical properties and hydrothermal aging of ATZ composites prepared from zirconia powders with different yttria content

Marek Grabowy[1], Agnieszka Wilk[2], Zbigniew Pędzich[2]

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[2] *AGH-University of Science and Technology, Kraków, Poland*

## Abstract:

The submitted work presents the investigation of three different grades of $ZrO_2$ materials containing $Al_2O_3$ particles (ATZ ceramics with 2.3–20 vol.% of alumina). The zirconia powders containing 3 mol.% yttria were synthesized by a precipitation/calcination method and fabricated from two zirconia powders with different yttria content. The selected ATZ composites with increasing $Al_2O_3$ content (called ATZ-B, ATZ-10 and ATZ-20) were prepared by means of conventional mixing, compacting and sintering at 1450 °C for 1.5 h. The phase composition, microstructure and basic mechanical properties were determined. Uniform, fine microstructures with relative densities over 99%, hardness values between 12.0–13.8 GPa and flexural strength up to 1 GPa were obtained. The $K_{IC}$ parameter has reached extraordinary value of 12.7 $MPa \times m^{1/2}$ for ATZ-B. Mechanisms contributing to the increase in $K_{IC}$ were identified to explain the reason for such a large improvement in fracture toughness. The aging susceptibility of alumina toughened zirconia materials, because of hydrothermal treatment, was investigated. The aim of this study was to determine the influence of low temperature degradation on the tetragonal to monoclinic phase transitions and on the flexural strength of hydrothermally aged specimens. The lowest relative flexural strength decreases (about 10–20%) were observed for aging at 150°C (24h and 48h), suggesting that these materials are capable of operating under similar conditions for long periods of time without significant loss of strength.

This research shows that ATZ composites that have excellent mechanical properties and sufficient hydrothermal aging resistance can be later used in technical and biomedical applications.

# Microstructural evaluation of zinc oxide thin films deposited by aerosol deposition method

Yumeng Zheng, Shoki Toriyama, Yuuki Sato, Shinzo Yoshikado

*Doshisha University, Kyoto, Japan*

## Abstract:

Aerosol deposition (AD) is a novel technique for fabricating thin films of high melting point materials at room temperature, suitable for a wide range of materials such as metals, ceramics, and others. In this process, aerosol particles of sub-micro size are emitted at the speed of sound through a slit nozzle and impact on a substrate, pulverizing into nano-size grains and rebinding as a film.

Zinc oxide (ZnO) is a wide bandgap semiconducting material with many applications such as in transparent thin-film transistors, varistors, solar cells, etc. Many techniques have been used to produce ZnO thin films, including chemical vapour deposition, sol-gel, magnetron sputtering, laser ablation and so on. However, high energy is typically requited to form a dense ZnO film. In this study, a dense ZnO thin films were successfully prepared on different substrates, such as sapphire, glass, Ag, using AD at room temperature. Experimental conditions such as gas flow rate and scan count have been investigated. The crystal structure was analyzed by X-ray diffraction and characterized by Rietveld refinement. The microstructure of the thin films was observed by scanning electron microscopy and transmission electron microscopy. It was found that this ZnO thin film showed an interesting nonlinear voltage-current (V-I) characteristic. The mechanisms of these nonlinear properties will be further discussed.

# Influence of cost-efficient Si3N4 powders on the microstructure formation of alpha/beta Sialons prepared via an aqueous processing route

Eveline Zschippang, Fabian Loepthien, Anne-Kathrin Wolfrum, Björn Matthey, Kerstin Sempf, Mathias Herrmann

*Fraunhofer IKTS, Dresden, Germany*

## Abstract:

Alpha and alpha/beta sialons are known for their high chemical stability, excellent mechanical properties, and high wear resistance. They are used as components in chemical, mechanical and plant engineering or as cutting tools. The use of cost-efficient $Si_3N_4$ powders in combination with an aqueous processing route could make the production of sialons more economic and easier, making their use even more attractive.

High quality alpha/beta-Sialons with nominal composition $R_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$ and m=0.5 and n=1 and 4 wt% $Y_2O_3$ excess were reproducible prepared in the authors lab. The influence of the powder quality (SN-E10, Silzot HQ, SicoNide P95H) on sintering and phase formation was investigated.

Findings reveal that that the oxygen content of the $Si_3N_4$ starting powder plays a significant role, as it influences densification, phase formation and microstructure formation and thus the mechanical properties. A lower oxygen content results in a higher amount of alpha-Sialon and hence higher hardness as seen in the example of a Sialon composition made of Silzot HQ. In addition, the lower oxygen content also leads to a smaller amount of oxidic grain boundary phase being formed, resulting in a slightly lower toughness.

Results of a detailed microstructure analysis using XRD and FESEM (EDX- and EBSD-mapping) will also be presented. It is shown that alpha-Sialon is formed on existing alpha-$Si_3N_4$ grains of the starting powder and anisotropic grain growth of alpha-Sialon takes place, independent of the starting powder. Therefore, it is possible to prepare customized wear-resistant alpha-sialon materials even from cost-efficient, beta-rich powders.

## Acknowledgements:

The IGF Project 20076 BR of the German Ceramic Society (Deutsche Keramische Gesellschaft / DKG) is supported via AiF within the program for promoting the Industrial Collective Research (IGF) of the Federal Ministry of Economic Affairs and Energy (BMWi), based on a resolution of the German Bundestag.

# Modified silicon nitride for high temperature bearing applications

Willy Kunz[1], Mathias Herrmann[1], Tobias Rosenstingl[2], Eveline Zschippang[1]

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## Abstract:

Silicon nitride is a high-performance ceramic. Basically, it is characterized by high toughness and thus very good strength at room and elevated temperatures. Due to its chemical resistance to many media, it is often considered as a bearing material. However, the exact properties of silicon nitride are strongly determined by the precise chemical composition and microstructure. This talk describes the preparation and tribological properties of composites based on a standard material with yttrium oxide and aluminum oxide as sintering aids. By adding molybdenum silicide and titanium nitride, it was possible to minimize the coefficient of friction and wear significantly depending on load and temperature due to special wear mechanisms. The temperature dependence of the properties is presented and potential applications are discussed.

# Symposium E: Functional Ceramics (Dielectrics, Antiferroelectrics, Ion Conductors, Electronics, Piezoelectrics, Ferroelectrics, Multiferroics, Magnetics, Electrocalorics, Thermistors, Thermoelectrics)

## Invited presentation:

# Functional materials based on the oxide magnetic nanosystems

Anatolii Belous, Yuliia Shlapa, Serhii Solopan, Olexandr Fedorchuk

*V. I. Vernadsky Institute of General & Inorganic Chemistry of the NAS of Ukraine, Kyiv, Ukraine*

### Abstract:

At the beginning of 2000s, magnetic materials got some new scientific interest. It was caused by the several reasons, particularly, by the active development of the communication systems and radiolocations, which working frequency range shifts to the high-frequency area. The last requires development of novel microwave magnetic materials and searching for new ways to control their magnetic properties. Moreover, ferromagnetic nanoparticles can find the application in medicine (MRI, hyperthermia, drug delivery etc.). To solve the practical issues, it is often necessary to obtain the weakly agglomerated, superparamagnetic nanoparticles as well as the film-materials, which synthesis is the complicated scientific and technological task. On the example of magnetic materials with the spinel, perovskite structures and barium hexaferrite, it was clarified the conditions for obtaining weakly agglomerated nanoparticles and polycrystalline films with the anisotropic shape of the particles. The effect of the crystalline structure on conditions of synthesis of weakly agglomerated particles was demonstrated. Magnetic properties of synthesized nanosystems in the wide temperature range were studied. Composite resonance microwave elements "high-Q dielectric/magnetic film", which frequency can be controlled by an external magnetic field, were developed based on the synthesized magnetic films. It was shown the possibility to obtain left-handed materials. Magnetic fluids were prepared based on the synthesized nanoparticles and their ability to be used as the inducers of the hyperthermia of malignant tumors was demonstrated in vitro and in vivo.

### Acknowledgements:

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## Invited presentation:

# Transmission electron microscopy study of the local structure in Na1/2Bi1/2TiO3-BaTiO3 ceramics

Ann-Katrin Fetzer, Andreas Wohninsland, Lalitha Kodumudi Venkataraman, Hans-Joachim Kleebe

*Department of Materials and Earth Sciences, Technical University of Darmstadt, Darmstadt, Germany*

### Abstract:

The relaxor ferroelectric solid solution (1-x)$Na_{1/2}Bi_{1/2}TiO_3$-x$BaTiO_3$ (NBT-BT) has gained considerable attention as a lead-free alternative, which exhibits enhanced piezoelectric properties at its morphotropic phase boundary (MPB) near x = 0.06. The presence of short-range ordered polar nanoregions (PNRs) and their dynamic response allows for a high permittivity and electrostriction. Quenching NBT-BT ceramics in air from the sintering temperature has been established as a viable strategy to increase the depolarization temperature.

The local structural characteristics of NBT-BT with 6, 9 and 12 mol.% $BaTiO_3$ (BT) were studied by transmission electron microscopy (TEM). Different regions within one grain can be assigned to the rhombohedral R3c and the tetragonal P4bm phase in the MPB-composition by deploying dark-field (DF) imaging of superlattice reflections. In the relaxor state, the P4bm structure consist of elongated PNRs in the size range of 5–20 nm. With increasing BT fraction, the tetragonal phase exhibits a larger fraction of long-range ordered domains. Within domain bands, the PNR contrast in the DF images declines, which is associated with the disappearance of octahedral tilting in the P4bm phase and a transition to an overall P4mm symmetry with higher BT content. Remnants of PNRs are observed within the ferroelectric domains indicating a complex hierarchical structure. Quenching the MPB composition results, on the one hand, in an increased domain contrast of the R3c phase, but also in the appearance of lamellar domains in the tetragonal phase. Quenching therefore affects the tetragonal phase in a similar manner akin to the increase in BT content, resulting in the coexistence of ferroelectric domains (P4mm) and PNRs (P4bm), thus stabilizing the ferroelectric state.

### Acknowledgements:

The financial support of the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under grant no. 414311761 is gratefully acknowledged.

Invited presentation:

# Dislocation-tuned properties of functional ceramics

Till Frömling[1], Lukas Porz[2], Marion Höfling[3], Qaisar Khushi Muhammad[1], Michael Scherer[1], Fangping Zhuo[1], Jurij Koruza[4], Xufei Fang[1], Jürgen Rödel[1]

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## Abstract:

The functional properties of ceramics are usually tailored by designing point defects and interfaces. Dislocations as one-dimensional line defects have so far been underappreciated as a means to tune functionality but are finding increasing attention today. For example, the opportunity to tune ceramics beyond what can be achieved by chemical doping is of significant interest. Based on ceramic electronic and ionic conductors and ferroelectrics, we illustrate that mechanically introduced dislocations possess the ability to modify the functional properties significantly. A giant increase in dielectric and ferroelectric constants was determined for deformed barium titanate (high field permittivity =5300 and large-signal $d_{33}$ = 1890 pm/V) [1]. The conductivity of electronic and ionic oxide ceramic conductors could be enhanced by multiple orders of magnitude. This will be rationalized based on investigations on $TiO_2$ [2] and yttria-stabilized zirconia. The impact of dislocations on the ceramics depends on a convolution of dislocation character, core properties, possibly existing space charges, and mesoscopic structure. This is difficult to control as ceramics are usually not plastically deformable. We combine the understanding of mesoscopic dislocation structure and its behavior at elevated temperatures. The interaction of dislocations and bulk properties is thus both complex and exciting as it allows for multiple modification possibilities in functional ceramics.

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## Acknowledgements:

DAAD for the fellowship with award number 91669061. DFG for funding (398795637, 41417937). Athene Young Investigator program of TUDarmstadt.

Invited presentation:

# Structure properties relationships in functional ceramics for energy conversion

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## Abstract:

Functional ceramics for energy conversion will play a crucial role in the future in order to tackle the challenges of our society for the transition to an era of renewable energies. Functional ceramics are already in use for electromechanical or thermal energy conversion or as energy storage materials. For the design and tailoring of new materials and the increase of the related conversion efficiency a detailed knowledge of the material mechanisms is necessary.

In this contribution we will elucidate the structure-properties relationships in functional ceramics for energy conversion. The focus will be on the correlation of the crystal structure and microstructure with the macroscopic properties of these materials. In recent studies, we were able to describe material mechanisms in electromechanical energy conversion materials and calculate the macroscopic response based on an atomic scale model[1]. Our techniques are capable of elucidating formerly unknown structural mechanisms in classical materials such as barium titanate[2]. With simulations we are able to model the influences of microstructural effects on the material behaviour[3]. Additive manufacturing with capillary suspensions allows mesostructuring on a wide range of length scales from µm to mm[4]. This way, we can bridge a wide range of length scales from nm to mm and correlate the structure with the macroscopic properties.

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## Invited presentation:

# Properties of bulk graded (Ba,Sr)TiO3 ceramics with various architectures obtained by spark plasma sintering

Adelina Ianculescu[1], Catalina Stanciu[1], Bogdan Vasile[1], Adrian Surdu[1], Roxana Trusca[1], Patru Roxana[2], Lucian Pintilie[2], Ioana Pintilie[2], Mihaela Botea[2], Mircea Udrea[3]

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### Abstract:

This research is dedicated to the investigation of structural, compositional, dielectric and pyroelectric properties of some graded bulk ceramics, with symmetric and asymmetric architectures based on $(Ba_{1-x}Sr_x)TiO_3$ (BST) solid solutions, with focus on the thermal stability of the dielectric constant and pyroelectric coefficient. Graded structures with different architectures were obtained by spark plasma sintering from BST ( $x = 0.10$; 0.20; 0.30) powders. The presence of the composition gradient was confirmed by structural and compositional investigations using X-ray diffraction and electron microscopy combined with energy dispersive X-ray spectroscopy. The concentration gradient was either asymmetric (3 layers, starting with $x = 0.10$ and ending with $x = 0.30$) or symmetric (5 or 6 layers, starting and ending with $x = 0.10$, and with a single or double $x = 0.30$ layer in the middle, respectively). Electrical measurements reveal a decrease of the dielectric constant with increasing the number of the layers. It was found that the symmetric graded structure with 6 layers has the best thermal stability of both, the dielectric constant (variation of only 8% between zero and 100 C) and the pyroelectric coefficient (6% variation between zero and 80 C). In addition, an enhancement of the pyroelectric signal for frequencies above 100 Hz is obtained in symmetric structures, an effect that is attributed to the additive contributions of the signals originated from the layers with different Sr content.

Invited presentation:

# Ferroelectric hardening by microstructural elements

Jurij Koruza[1], Mihail Slabki[2]

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[2] Technical University of Darmstadt, Darmstadt, Germany

## Abstract:

Piezoceramics are widely used in sensors, actuators, and transducers, enabling a range of modern technologies in industrial automation, consumer electronics, smart vehicles, microrobotics, and medicine [1]. The highest piezoelectric properties are achieved in ferroelectric materials, where the electromechanical conversion originates predominantly from the crystal lattice and ferroelectric domains [2]. Ferroelectric hardening by point defects is a well-established concept and enables the use of piezoceramics at resonance conditions, affording large oscillating strain amplitudes and high vibration velocities. However, this mechanism is prone to degradation at elevated temperatures and field amplitudes, which is mostly related to the mobility of oxygen vacancies forming the defect complexes.

Several new ferroelectric hardening mechanisms, developed over the recent years, will be reported: composite hardening [3], precipitation hardening [4], and dislocation imprint [5]. A detailed study of various $(Na_{1/2}Bi_{1/2})TiO_3$-based systems will be presented, which exhibit increased depolarization temperatures and excellent stability at high vibration velocities. The microscopic origin of this behavior was identified using synchrotron radiation, revealing that the strain is dominated by lattice contributions, induced by the emerging dynamic mechanical stress. The importance of mechanical properties will be discussed and outlook for possible future material developments will be provided.

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Invited presentation:

# Charged Ferroelectric Domain Walls for Deterministic AC Signal Control at the Nanoscale

Jan Schultheiß[1], Erik Lysne[2], Lukas Puntigam[3], Zewu Yan[4], Edith Bourret[5], Stephan Krohns[3], Dennis Meier[1]

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## Abstract:

Ferroelectric domain walls are natural interfaces separating volumes with different orientation of the spontaneous polarization vector. Depending on the local charge state, the domain walls exhibit unusual direct current (d.c.) conduction ranging from insulating to metallic-like behavior. Because of their unique electronic properties, they are highly attractive as nanoelectronic components, serving, e.g., as switches and synaptic devices. In contrast to the functional d.c. behavior at charged walls, their response to alternating currents (a.c.) falls into an uncharted territory.

Here, we explore the a.c. characteristics of charged ferroelectric walls in $ErMnO_3$ in the adiabatic regime (kHz-MHz), using a combination of atomic force microscopy and macroscopic dielectric spectroscopy. We demonstrate a pronounced non-linear response at the electrode–domain wall junction, which correlates with the charge state of the wall. The dependence on the a.c. drive voltage and frequency enables us to reversible switch between uni- and bipolar output signal, providing conceptually new opportunities for the application of charged domain walls as functional nano-elements in a.c. circuitry.

Invited presentation:

# Transverse Multilayer Thermoelectric Generators with Thermoelectric Oxides

Romy Löhnert, Arne Bochmann, Ahmed Ibrahim, Jörg Töpfer

*Ernst-Abbe-Hochschule Jena, Jena, Germany*

## Abstract:

Thermoelectric generators (TEG) convert waste heat into electrical energy and can be used to drive low-power applications, e.g. autonomous sensors and transmitters in sensor networks. Oxides represent a versatile class of thermoelectric materials with promising properties, e.g. low-cost, non-toxicity, and stability at increased temperature. The standard dual-leg design of thermoelectric generators requires manufacturing, arranging and contacting many individual sintered p- and n-type ceramic blocks. Alternatively, application of the ceramic multilayer technology represents a promising option enabling miniaturization and simple fabrication of multilayer TEGs.

We present the concept of transverse multilayer thermoelectric generators (TMLTEG) with charge transport perpendicular to the heat flow. Such generators consist of layers of tape-cast p- or n-type thermoelectric oxides in combination with metal stripes printed at an angle with respect to the heat flow direction to create anisotropic thermoelectric behavior.

We report on the fabrication and characterization of TMLTEGs, as well on the synthesis, sintering behavior and thermoelectric properties of the materials. Due to the specific properties of thermoelectric oxides and metal contacts, the geometry of the TMLTEG must be adapted for each material combination for optimized thermoelectric performance. Based on analytical calculations, we have developed Babin-plots describing the power output and thermoelectric energy conversion efficiency as function of the internal and external device geometry. We demonstrate this approach in combination with device simulations. TMLTEGs were fabricated using various thermoelectric oxide materials, e.g., $Ca_3Co_4O_9$, $La_2CuO_4$, and $CaMnO_3$ and the power output of the devices is discussed.

## Acknowledgements:

The authors acknowledge financial support from the Carl-Zeiss-Stiftung, Germany (grant P2018-03-001).

# Ferroelectric properties and phase transitions dynamics of Ag1-xLixNbO3 (x≤0.08) ceramics

Edita Palaimiene[1], Jan Macutkevic[1], Juras Banys[1], Ewa Talik[2], Antoni Kania[2], Artyom Plyushch[1]

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## Abstract:

The dielectric properties of $Ag_{1-x}Li_xNbO_3$ (ALNx) ceramics (x≤0.08) were investigated in a broad frequency range (20 Hz – 90 THz). The ferroelectric nature of ALN was confirmed by the polarization versus electric field measurements. The frequency dependence of dielectric permittivity is mainly caused by the relaxational soft mode close to the ferroelectric phase transition temperature and ferroelectric domains dynamics at lower temperatures. At room temperature and 10 GHz frequency the dielectric permittivity is quite high (270 for ALN0), while dielectric losses low (10 for ALN0) for all ALN ceramics, therefore these ceramics are attractive for various microwave applications. Moreover piezoelectric properties of ceramics were also investigated and the highest piezoelectric coefficient value was observed for ALN6 (200 pC/N at room temperature and 750 pC/N at 465 K). For ALNx ceramics when x ≥0.06 15 polar modes were distinguished in the IR spectra and 20 polar modes were distinguished in the IR spectra of ALN ceramics for x<0.06, however the number or modes is temperature independent in all investigated temperatures range (103 - 500 K).

# High temperature thermal conductivity of multicomponent oxide glasses

Anna Berezicka, J. Kuczek, M. Maruszak, M. Szumera

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## Abstract:

The central aspect of the considerations of this thesis was the analysis of the effect of iron and cobalt ions on the value of thermal conductivity of multi-component oxide glasses. The first part of the research project involved making glasses from systems $P_2O_5$-$SiO_2$-$K_2O$-MgO-CaO-$Fe_2O_3$ and $P_2O_5$-$SiO_2$-$K_2O$-MgO-CaO-$Co_2O_3$ based on four different sets of raw materials, where the main differentiating factor was mol%. Content of $Fe_2O3$ and $Co_2O_3$ oxides in the chemical composition. The analysis of the XRF chemical composition of the prepared samples confirmed that it was possible to obtain phosphate-silicate matrix glasses with the assumed addition of iron and cobalt ions, while the XRD examination allowed to check their amorphousness. In the next part, the thermal conductivity of glasses was determined using the LFA laser pulse method, based on measurements of heat diffusivity, specific heat using the DSC technique and dilatometric measurements carried out in parallel. The obtained results allowed for a comprehensive analysis of the effect of metal ions on the thermal properties of oxide glasses.

## Acknowledgements:

This work was performed within the framework of funding for statutory activities of AGH University of Science and Technology in Krakow, Faculty of Materials Science and Ceramics (16.16.160.557). Research project partly supported by program "Excellence initiative – research university" for the AGH University of Science and Technology.

# Structural studies of sulfur-bearing silicate-phosphate glasses

Anna Berezicka, Magdalena Szumera, Justyna Sułowska

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## Abstract:

Silicate-phosphate glasses of certain composition are capable of supplying plants with essential nutrients and address their deficiencies in soil substrate. Therefore, given progressive sulfur deficiency in soils and its significance for plant development, an attempt has been made to incorporate this element into the structure of glasses from the $SiO_2$-$P_2O_5$-$K_2O$-MgO system. Materials loaded with 0-5 mol.% of $SO_3$ were obtained by conventional melt-quenching technique, preliminarily studied by XRD (verification of the amorphous state) and XRF (determination of the actual composition, especially sulfur content) methods and then thoroughly investigated by numerous spectroscopic techniques (Raman, FTIR, NMR, XAS). It was established that sulfur, present in glassy matrix as isolated [$SO_4^{2-}$] tetrahedra surrounded by modifier cations ($K^+$), induces polymerizing effect on glass network. Although such sulfate groupings maintain their individuality without direct bonding to silico-oxygen or phospho-oxygen subnetwork, they affect the former framework to a greater extent than the latter. Performed studies also showed that along with $SO_3$ addition, the more polymerized units increase in abundance at the expense of less polymerized groups. Furthermore, implementation of XAS technique allowed to determine the local environment and speciation of S, P, Si and Mg atoms as well as their impact on the local structure of other glass components. Obtained results are believed to contribute to better understanding of structural aspects governing sulfur incorporation into the silicate-phosphate glasses and optimize the chemical composition of ecological glassy fertilizers, suitable for sulfur deficient soils.

## Acknowledgements:

This project was financed by the National Science Centre, Poland, project number 2018/31/D/ST8/03148.

# Novel Entropy-stabilized NiO-free Rock Salt Ceramic

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## Abstract:

Entropy-stabilized rock salt ceramics with composition (Mg, Co, Ni, Cu, Zn)O are of great scientific and technological interest due to their excellent Li storage capacity and conductivity. Nevertheless, they contain elements that are extremely dangerous for the health and environment like Ni.

In the present work, we developed a novel Ni-free high entropy rock salt phase by replacing NiO with MnO. The ceramic powder was produced by co-precipitation starting from an equimolar cations solution and using NaOH as precipitating agent. Mineralogical, compositional and microstructural evolution upon annealing in air was studied by combining XRD, SEM, EDXS, TGA/DTA and dilatometry. It is shown that both annealing temperature and $Li_2O$ addition to (Mg, Co, Mn, Cu, Zn)O play a key role in the high entropy phase stabilization, controlling the content of a secondary spinel-like phase. In detail, the charge compensation between and in the rock salt structure is proposed to enhance the stability of the high entropy phase. Interesting preliminary electrochemical properties evaluated by EIS are also observed.

## Acknowledgements:

Caritro Fundation (Cassa di Risparmio di Trento e Rovereto), Innovative processing routes to green high entropy ceramics with enhanced functional properties (HiEnCer)

# Tailoring of electrical and electromechanical properties in Mg-doped 0.94Na1/2Bi1/2TiO3-0.06BaTiO3

Daniel Bremecker, Mihail Slabki, Jurij Koruza, Jürgen Rödel

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## Abstract:

Lead-free $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ (NBT-BT) piezoceramics are potential candidates to replace $Pb(Zr,Ti)O_3$ (PZT) in high-power applications. Hard ferroelectrics with low losses and a broad temperature range of stable ferroelectric properties are required. Both can be improved by doping the NBT-BT-system with acceptors. In this work, the $0.94Na_{1/2}Bi_{1/2}TiO_3$-$0.06BaTiO_3$ (NBT-6BT) was modified with different amounts of Mg (0.1, 0.3, 0.5, 1 mol.%) by B-site substitution.

Temperature stability (ferroelectric to relaxor transition temperature, $T_{F-R}$), electromechanical properties (piezoelectric activity, vibration velocity dependent mechanical quality factor, $Q_m(v)$), electrical properties (conductivity, $\delta$), and crystal structure (X-ray diffraction) were quantified.

An increase in $T_{F-R}$ by up to 44°C was found for the NBT-6BT compositions doped with 0.3 & 0.5 mol.% Mg, which was related to a higher tetragonality and a higher tetragonal phase fraction in the doped compositions, as compared to the pure NBT-6BT. A similar correlation of tetragonality and $T_{F-R}$ was found before for Zn- or $BaAl_{2.5}$-modified NBT-BT. A very high $Q^p_m$ (planar mode) of up to 800 was observed for NBT-6BT-0.5 Mg, which was retained to a very high vibration velocity of 2 m/s. In comparison, pure NBT-6BT had a $Q^p_m$ of 119. The electrical conductivity, $\delta$, experienced an increase for NBT-6BT doped with 0.3 and 0.5 mol% Mg.

The increase in $Q_m$ and $\delta$ could both be connected to the local mobility of charged defects. The $Q^p_m$ of >800 is the highest value reported for polycrystalline NBT-BT so far and demonstrates its suitability for high power applications. The results were contrasted to the same compositions with Zn doping and benchmark PZT.

## Acknowledgements:

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# Thermoelectric multilayer generators: development from oxide powder to demonstrator

Sophie Bresch[1], Patrick Stargardt[1], Jörg Töpfer[2], Ralf Moos[3], Björn Mieller[1]

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## Abstract:

Thermoelectric generators can be used for energy harvesting by directly transforming a temperature gradient into a voltage. Multilayer generators based on ceramic multilayer technology are an interesting alternative to conventional π-type generators. They exhibit several advantages like high filling factor, possibility of texturing, co-firing of all materials in one single-step, and reduction of production costs due to the high possible degree of automation. But, co-firing of promising oxide thermoelectric materials, $Ca_3Co_4O_9$ (p-type) and $CaMnO_3$ (n-type), is very challenging due to the large difference in sintering temperature (300 K).

In this work we show the material development of $Ca_3Co_4O_9$, $CaMnO_3$, and insulation for multilayer generators co-fired under uniaxial pressure at 900 °C. The materials are tailored regarding their sintering behavior, electrical performance and coefficients of thermal expansion. Tape-casting and pressure assisted sintering are applied to fabricate textured $Ca_3Co_4O_9$. Compared to conventional sintering, pressure assisted sintering increases the strength by the factor 10 and the power factor by the factor of 20. The combination of sintering additives and uniaxial pressure is used to decrease the sintering temperature of $CaMnO_3$ to 900 °C while maintaining acceptable thermoelectric properties.

Different generator designs (unileg and pn-type) were fabricated and analyzed regarding microstructure and thermoelectric performance. A lower level of complexity is beneficial for co-firing and performance. The unileg demonstrators reach 80% of the simulated output power and the power output is highly reproducible between the different demonstrators (99%).

# Effect of Zr content on the wetting of BaTi1-xZrxO3 perovskites by Ag-based liquids

Giovanna Canu, Vincenzo Buscaglia, Fabrizio Valenza

*CNR - ICMATE, Genova, Italy*

## Abstract:

$BaTiO_3$-based ceramic materials are broadly used as electronic components as, for instance, multilayer ceramics capacitors (MLCCs), electrical ceramic filters, and transducers. In the development of new devices based on these materials, the contact characteristics between these ceramics and the liquid metals used to create internal and termination electrodes are of great importance.

Zirconium is a common substituent for titanium in $BaTiO_3$, and $BaTi_{1-x}Zr_xO_3$ an excellent model system to study the effect of composition on several properties. Here, we report on the effect of the zirconium substituent on the contact angles and the work of adhesion of liquid Ag and Ag-3 at.% Cu alloy in contact to $BaTi_{1-x}Zr_xO_3$ (x = 0, 0.1, 0.2, 0.4) ferroelectric perovskites. The contact angles and the work of adhesion were determined by the sessile drop method at 1000 °C in air atmosphere and the obtained metal/ceramic interfaces were characterized by SEM and EDS. Working in air, rather than under a protective atmosphere, presents several advantages such as the process simplicity, improved wetting due to the presence of oxygen, and prevents the reduction of $BaTiO_3$-based ceramics.

Compared to pure Ag, the liquid Ag-3 at.% Cu alloy exhibited improved wetting due to the formation of interfacial CuO; no further interfacial phenomena nor mutual interdiffusion which could deteriorate the ceramic properties were detected. An increasing trend in the contact angles was observed as a function of Zr content in the perovskite. With x increasing from 0 to 0.4, the contact angles increased from 83° to 104° and from 46° to 72° for pure Ag and Ag-3 at.% Cu respectively. This result is in agreement with the band-gap energy which rises as Ti is substituted by Zr.

# Photoluminescence studies of Eu- and Tb-doped (1-x)Na0.5Bi0.5TiO3 – xBaTiO3 ceramics

Giovanna Canu[1], Gregorio Bottaro[2], Maria Teresa Buscaglia[3], Pamela Isola[4], Enrico Casamassa[3], Lidia Armelao[5], Vincenzo Buscaglia[3]

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## Abstract:

The phenomenon of luminescence is exploited for large scale applications such as light emitting diodes (LEDs), optical fibres and lasers. Luminescence is traditionally tuned via chemical methods, e.g. by changing the type and concentration of lanthanide ions, co-doping, or changing the host matrix. However, photoluminescence emission can also be modulated by the application of physical stimuli, with a significant application potential for light sources with variable colour and intensity, optical memories, switches and sensors.

The goal of our work is the fabrication of ferroelectric materials whose photoluminescence emission, induced by the incorporation of small amounts of rare earth ions in the crystal lattice, can be modulated in intensity or colour, by the application of external physical stimuli, such as a temperature variation, and to elucidate the fundamental mechanisms behind the process. This has been recently proved by our group in europium-doped (1-x)$BaTiO_3$ – x$BaZrO_3$ (BZT, x = 0-1) [1], exploiting the different polar order encountered by changing both temperature and composition.

Here, we present our results on several compositions in the (1-x)$Na_{0.5}Bi_{0.5}TiO_3$ – x$BaTiO_3$ (BNBT, x = 0-0.06) system. The polar order of BNBT can be modified by changing the composition x, and ceramics doped with two different rare-earth ions, i.e. $Eu^{3+}$ and $Tb^{3+}$, were prepared. With the aim to correlate composition, dielectric and photoluminescence properties, the powder synthesis and ceramics preparation, together with the microstructural and dielectric characterisation and preliminary studies of the photoluminescence properties of the ceramics as a function of temperature are reported.

## References:

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## Acknowledgements:

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# Characterization of BaZrO3 doped-KNLNS ceramic

Brenda Carreño-Jiménez[1], Mónica Acuautla[2], Armando Reyes-Montero[3], Rigoberto López-Juárez[4]

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## Abstract:

Dielectric, elastic and piezoelectric characterization depends on the different resonance modes: radial, thickness and shear. For each one, the samples are designed as rectangular plates or disks and polarized in the different directions. In addition, the crystallographic structure and fabrication process are two important characteristics to improve in the search of efficient electroceramic materials. In this work, we analyze a KNN-based ceramic doped with $BaZrO_3$ which has similar properties as commercial PZT-based material. The main interest in these compositions is to exploit their thermal stability with the improvement of their piezoelectric properties by adding some cations ($Li^{+1}$, $Sb^{5+}$, $Ba^{2+}$, $Zr^{4+}$). The $0.96(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}Nb_{0.93}Sb_{0.07}O_3$-$0.04BaZrO_3$ composition was prepared by conventional solid-state method. The crystallographic and structural characterizations were carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. We obtained a pure perovskite structure with a rhombohedral-tetragonal phase coexistence and a cubic-shape morphology. The ferroelectric properties were measured using a Radian Precision Workstation showing a good saturation of the ferroelectric dipoles and a high value of the remnant polarization (12.0 $\mu C/cm^2$), as well as coercive field (8.40 kV/cm). The piezoelectric and dielectric properties were measured by means of complex impedance spectroscopy. Some determined parameters are $-d_{31} = 141$ pC/N, $d_{33} = 408$ pC/N and $d_{15} = 305$ pC/N, which are comparable with commercial PZT values, such as PZT-5 ($-d_{31} = 190$ pC/N and $d_{33} = 350$ pC/N). Piezoelectric ceramics with this similar parameters values are using as generators or sensors.

## Acknowledgements:

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# Origins of low lattice thermal conductivity in novel quaternary Cu2MHf3S8 (M – Mn, Fe, Co, Ni) thiospinels

Oleksandr Cherniushok[1], Oleksandr Smitiukh[2], Janusz Tobola[3], Rafal Knura[4], Oleg Marchuk[2], Taras Parashchuk[1], Krzysztof Wojciechowski[1]

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## Abstract:

Searching for novel crystalline solids with intrinsically low thermal conductivity and uncovering its origin is among the main streams in modern thermoelectricity. Due to earth-abundant nature and environmentally friendly content, Cu-based thiospinels are attractive functional semiconductors, including thermoelectric materials. Herein, we report the crystal structure, electronic and thermoelectric properties of four new $Cu_2MHf_3S_8$ (M – Mn, Fe, Co, and Ni) thiospinels. The performed DFT calculations predicted the decrease of the bandgap and transition from p- to n-type of conductivity in the Mn–Fe–Co–Ni series, which was confirmed experimentally. The best thermoelectric performance in this work was observed for the $Cu_2NiHf_3S_8$ thiospinel due to the highest power factor and low thermal conductivity. Moreover, all discovered compounds possess very low lattice thermal conductivity $\kappa_{lat}$ over the investigated temperature range. The $\kappa_{lat}$ for $Cu_2CoHf_3S_8$ have been found to be as low as 0.8 W $m^{-1}K^{-1}$ at 298 K and 0.5 W $m^{-1}K^{-1}$ at 673 K, which are significantly lower values compared to the other Cu-based thiospinels reported up to date. The strongly disturbed phonon transport of the investigated alloys is mainly coming from the peculiar crystal structure where the large cubic unit cells contain many vacant octahedral voids. As it was evaluated from the Callaway approach and confirmed by the speed of sound measurements, such crystal structure promotes the increase of the lattice anharmonicity, which is the main reason for the low $\kappa_{lat}$. This work provides a guideline for the engineering of thermal transport in thiospinels and offers the discovered $Cu_2MHf_3S_8$ (M – Mn, Fe, Co, and Ni) compounds, as new promising functional materials with low lattice thermal conductivity.

## Acknowledgements:

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# Role and activity of Fe3+ and In3+ impurities on coarsening and functional properties in MgO nanoparticle derived ceramics

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## Abstract:

Nanoscale grain boundary design is an emerging field in materials science. It addresses the knowledge based transformation of well-defined nanocrystalline starting materials into consolidated networks of nanograins, with designed particle interfaces and grain boundaries. Moreover, controlled impurity segregation into solid-solid interfaces during sintering can be a strategy to induce functional properties that originate from interparticular, impurity-rich crystalline phases.[1,2]

In this study the flexibility of flame spray pyrolysis was used to synthesize MgO based mixed metal oxide nanopowders from the gas phase, with high control over composition up to 20 at% of $Fe^{3+}$ and $In^{3+}$ admixtures. Functional oxide ceramics were obtained by dry uniaxial pressing of as-synthesized nanoparticle powders followed by a pressureless sintering step up to 1373 K and/ or 1673 K, respectively.

Comprehensive structural characterization of the porous ceramics (X-ray diffraction and electron microscopy) revealed both phase separation and impurity segregation. Moreover, we tracked that impurity concentration sensitively influences the intergranular wetting behaviour, thus either favouring the formation of thin intergranular films or the formation of triple- and/or multiple grain junctions. Whereas, sintering at 1373 K of Fe-Mg-O was found to be sufficient to form the magnetic magnesioferrite phase (VSM PPMS) in case of In-Mg-O sintering at 1673 K triggered the formation of an intergranular $MgIn_2O_4$ percolation path, decreasing the ceramics' grain boundary resistivity by orders of magnitude (4 Point Probe Resistivity).

[1] M. Niedermaier, T. Schwab et al., ChemNanoMat 2019, 5, 634.

[2] M. Niedermaier, T. Schwab et al., J. Phys. Chem. C 2019, 42, 25991

## Acknowledgements:

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# Effect of CuO added BNST-BF lead-free piezoelectric ceramics

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## Abstract:

Large strain response of bismuth-based lead-free ceramics represents them as the most promising candidates for actuator applications. Despite the large strains in bismuth-based piezoelectric ceramics, there still remain challenges regarding their utilization in practical applications. For instance, a relatively high operating field is required to obtain the large strain properties. In this work, effect of CuO as a sintering aid for lead-free $Bi_{1/2}Na_{1/2}TiO_3$-$SrTiO_3$-$BiFeO_3$ (BNT-ST-BF) ternary piezoelectric ceramics were studied and proposed as materials that could enhance the electromechanical strain performance under low driving field. We found that the highest normalized strain d33 * value of 800 pm/V was achieved at a relatively low electric field of 3 kV/mm from 1 mol.% CuO-modified BNT-ST-BF ceramics. We suggest that the naturally induced nonergodicities in the ergodic relaxor generate internal stress. This induced internal stress is responsible for the excellent strain properties of this material. We believe that the materials synthesized in this study are promising candidates for actuator applications.

# Ductility - A new functionality to ceramics?

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## Abstract:

Oxide glasses are an integral part of the modern world, but their usefulness can be limited by their characteristic brittleness at room temperature. We show show that amorphous aluminum oxide can permanently deform without fracture at room temperature and high strain rate by a viscous creep mechanism. These thin-films can reach flow stress at room temperature and can flow plastically up to a total elongation of 100%, provided that the material is dense and free of geometrical flaws. Our study demonstrates a much higher ductility for an amorphous oxide at low temperature than previous observations. This discovery may facilitate the realization of damage-tolerant glass materials that contribute in new ways, with the potential to improve the mechanical resistance and reliability of applications such as electronic devices and batteries (E.J. Frankberg et al. Science 2019). Follow up studies confirm that the available plasticity mechanisms can be scalable to thermodynamic bulk scale by using microcompression and large scale atomistic simulations.

# A novel indentation method for dielectric breakdown strength investigation

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## Abstract:

Dielectric breakdown strength (DBS) is defined as the maximum voltage divided by the sample thickness that an investigated insulator can withstand. It is a critical and limiting factor for many electronic devices, such as high-power capacitors or piezoelectric transducers. The fundamentals have been already defined in the last century; nevertheless, the mechanisms of dielectric breakdown are still not completely understood. From empirical studies, it is known that the measurement setup along with sample geometry can influence the DBS, such as voltage ramp or electrode shape and area. In addition, DBS is known to reduce due to the concentration of the electric field and mechanical stresses at the edge of the electrode.

With the intention of avoiding such stress concentrations, a novel sample preparation method is proposed for the investigation of DBS. In our proposition, the upper electrode is of a concave shape. Furthermore, our numerical modeling confirmed that with such geometry, the concentration of the high electric fields at the electrode edges is diminished, while the position of the breakdown spot can be anticipated. The concave indentations were generated in the green sample state, in order to benefit from the viscoplastic regime of a tape-casted sample. Thus, the indented surface is free of microcracks after sintering. The reliability of the method was verified on $BaTiO_3$, a prototype material used for ceramic capacitors. The results of the DBS investigation revealed that the breakdown occurred mostly in the center of the indentation. Moreover, the variations of the thickness and voltage ramp have a significant influence on the DBS, as proposed in the literature. DBS differed by up to 60 % and 30 %, with the change of thickness and voltage ramp, respectively.

## Acknowledgements:

This work was supported by the Hessian State Ministry for Higher Education, Research and the Arts under the LOEWE collaborative project FLAME (Fermi level engineering of antiferroelectric materials for energy storage and insulation systems).

# Microstructure and growth mechanism of LiNbO3 hardening precipitate in Li-doped NaNbO3

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## Abstract:

Precipitation hardening in Li-doped $NaNbO_3$ was realized by homogenous formation of plate-like intragranular $LiNbO_3$ (LNN). Crystallographic orientation relationship between LNN and matrix is concluded as $[241]_{LNN}$ // $[100]_{matrix}$; $(0\text{-}14)_{LNN}$ // $(020)_{matrix}$ (or $(0\text{-}14)_{LNN}$ // $(002)_{matrix}$), $(\text{-}210)_{LNN}$ // $(002)_{matrix}$ (or $(\text{-}210)_{LNN}$ // $(020)_{matrix}$), revealing coherent interfaces with lattice misfit of 0.36% (or 1.45%) and 7.46% (or 6.38%). Interfacial incompatibility strains govern the shape of LNN as orthogonal needle-like morphology, as such they are embedded in domains to pin domain walls with a 45° angle. Another equivalent crystallographic orientation relationship was identified as $[100]_{LNN}$ // $[001]_{matrix}$; $(02\text{-}2)_{LNN}$ // $(220)_{matrix}$. Heavy planar defects were found parallel to the $(02\text{-}2)_{LNN}$ plane. TEM study suggests that the growth mechanism of LNN precipitate is closely related to formation and extension of {02-2} planar defects.

# Towards a light-driven actuator based on ferroelectric ceramics

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## Abstract:

Photostrictive effect, understood as any manifestation of the light-induced nonthermal dimension change of materials, is atractting notable interest because it provides a facile principle for the non-contact remote control of a new generation of opto-mechanical systems. In this context, the optical control of macroscopic strain in ferroelectrics has recently attracted remarkable attention as an effective alternative to the conventional electric control of strain. In this work, we show that a macroscopic strain can be reversibly driven by light power control in ferroelectric ceramics. $BaTiO_3$ ceramics with tailored microstructure is used as model system for reveling that charged domain walls appear to be the functional interfaces for the light-driven domain rearrangement in ferroelectrics. Results indicate that an adequate domain engineering strategy plays a fundamental role in the photo-functional response of polycrystalline ferroelectrics. The attained photo-strain proves to be comparable to the conventional electro-strain values, allowing the development of low-cost photo-controlled actuators.

## Acknowledgements:

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# Multistep polarization switching on orthorhombic domain walls: a molecular dynamics study

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## Abstract:

Ferroelectric switching is the key property for a wide range of devices, ranging from actuators to memory devices. In spite of its fundamental relevance the ferroelectric switching process and its coupling to the microstructure is still not fully understood [1,2,3].

In this contribution, we use ab initio based molecular dynamics simulations [4] to study the field-induced switching of the orthorhombic phase of $BaTiO_3$.

In addition to the analysis of the field-induced dynamics of existing domain walls, we monitor the microscopic processes on the travelling wall. Surprisingly, we observe local non-180° switching in connection with the formation of transient local Bloch type walls and dipole vortices.

[1] R. J. Xu et al, Nat. Mater. 14, 79 (2015).

[2] Y. A. Genenko et al, Phys. Rev. B 104, 184106 (2021).

[3] A. Grünebohm et al., J. Phys.: Condens. Matt. 34, 073002 (2021).

[4] T. Nishimatsu et al, Phys. Rev. B 82, 134106 (2010).</li>

## Acknowledgements:

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# UHTC composites in the system 40% vol. ZrB2- 40% vol. HfB2- 20% vol. MX (MX= SiC, B4C, WC, MoSi2 and CrSi2)

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## Abstract:

UHTC (Ultra High Temperature Ceramics) based on metal borides such as $ZrB_2$ and $HfB_2$ belong to the group of materials which are difficult to sinter. In this case, the selection of additives for improving the sinterability requires a special approach. These additives, apart from improving sinterability, should not deteriorate the properties of $ZrB_2$-$HfB_2$ composites, i.e. high melting point (3200-3400 °C), high thermal conductivity (up to 100 W/(m·K)) and good mechanical parameters, as well as should not decrease oxidation resistance (1200-1400 °C). Some of the additives (SiC and $MoSi_2$), as reported in the literature data [1,2], contribute to the chemical resistance of composites.

In this work, sinterability research on composites 40% vol. $ZrB_2$- 40% vol. $HfB_2$- 20% vol. MX was conducted. Two sintering techniques were used: hot pressing HP as well as pressure and electric field assisted sintering SPS. Carbides (SiC, $B_4C$, WC) and silicides ($MoSi_2$ and $CrSi_2$) were used as MX sintering additives. Sintering was carried out at a temperature adjusted to the starting composition, which ranged from 1400 to 2000 °C. On the basis of density measurements and microstructure observations (SEM, TEM) the effectiveness of the additives was determined and both sintering techniques were compared. It was found that a promising additive is chromium silicide, which was used for the first time in this type of study.

## Literature:

W.G. Fahrenholtz, G. E. Hilmas, I.G. Talmy, J.A. Zaykoski. J. Am. Ceram. Soc., 90 (2007) 1347–1364. DOI: 10.1111/j.1551-2916.2007.01583.x

W.G. Fahrenholtz. J. Am. Ceram. Soc. 90 (2007) 43-148, 2007

## Acknowledgements:

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# Investigating the Effect of Silicon on Microstructural Evolution during Crystallization in Long Persistence Strontium Aluminate Compounds

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## Abstract:

Strontium aluminate ceramics when co-doped with Eu and Dy, are well-known for persistent luminescence when a boron-based flux agent is used during synthesis. Clustering of ionic point defects was suggested to be the origin of persistent luminescence in such compounds, through computational studies. While $B_2O_3$ extends afterglow duration from minutes to > 14 hours, the role of boron in inducing clustering of the optically active ionic point defects has become elucidated only recently. Because the contribution of borate polyanions may be also offered by silicate polyanions, we report here a study on persistence luminescence when $B_2O_3$ is replaced with TEOS.

We synthesized $4SrO·7Al_2O_3$ ($S_4A_7$) co-doped with 1 at% Eu and 1 at% Dy by the Pechini method, using 30 mol% TEOS, and analyzed the thermal behavior and microstructural evolution from an amorphous pre-ceramic via TG-DTA and XRD analysis. To elucidate the effect of Si on the activation energies of phase evolution, we applied different models of non-isothermal crystallization kinetics. When the TEOS content exceeded 30 mol%, formation of the metastable phases of $SrAl_2O_4$ (SA) and $SrAl_4O_7$ ($SA_2$) was suppressed at the first crystallization event. Further, the maximum phase fraction of the long afterglow $S_4A_7$ phase was obtained when the concentration of TEOS did not exceed 30 mol%. When the concentration of TEOS was increased from 0 to 30 mol%, the activation energy of crystallization of the first exothermic reaction increased by ca. 250 kJ/mol, as opposed to a decrease of ca. 340 kJ/mol in the case of $B_2O_3$, an indication of increased 3D-connectivity and increased viscosity during crystallization, when the sintering flux agent was a form of silica.

# Multiscale 2D/3D microshaping of property-contrast polymer-derived SiCN

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## Abstract:

Polymer-derived ceramics are a unique class of materials known for their outstanding properties and versatile applicability. The liquid nature of the precursors allows easy addition of fillers in order to alter the resulting ceramics' properties. We use a polysilazane with a thermal initiator and 0 – 60wt.% divinyl benzene to vary the final free carbon content and tune the electrical conductivity. Casting of mm-sized parts is performed in PTFE molds whereas high-resolution microparts are made in KOH-etched silicon molds. Furthermore, due to silicon's high melting temperature, pyrolysis of the preceramic material can be conducted at 1000°C directly in the mold. This brings the additional advantage that the part is conveniently released due to its shrinkage and the typical flat and smooth surfaces of KOH-etched monocrystalline silicon. By means of direct laser writing, we have added sacrificial polymeric 3D microstructures at the mold bottom which decompose during pyrolysis and replicate into the cast PDC part at sub-micrometer resolution. Parts are manufactured with flexural strength up to 1.7 GPa and an electrical conductivity ranging from $\sim 10^{-11}$ to 1 S/cm. Additionally, monolithic parts with a seamless composition and conductivity contrast have been obtained by subsequent casting and crosslinking of precursor formulations with dissimilar DVB concentrations. Different levels of carbon concentration profiles across the interface are achieved by varied degrees of first phase pre-crosslinking. The interfaces are visualized and their transition lengths quantified by means of synchrotron-microtomography. Our new approach of heterogeneous PDCs opens novel opportunities towards all-ceramic functionality integration for harsh environment applications.

## Acknowledgements:

This work was supported by the ETH domain, through the Strategic Focus Area (SFA) – Advanced Manufacturing program under the project named Ceramic X.0 – High-precision micro-manufacturing of ceramics.

# Effect of sintering additives and sintering conditions on electrical and thermal properties of SiC-GNPs and SiC-GO composites

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## Abstract:

Almost fully dense silicon carbide - graphene composites with either $Y_2O_3$–$Sc_2O_3$ or $Y_2O_3$–$Al_2O_3$ sintering additives and with different amount of graphene nanoplatelets (GNPs) from 1 to 5 wt. % or 1 wt. % of graphene oxide (GO) were sintered in rapid hot press (RHP).

Electrical conductivity and thermal conductivity as a function of amount of graphene, its orientation in SiC matrix and also effect of sintering additives, sintering conditions and effect of annealing were investigated.

In case of composites with $Y_2O_3$–$Al_2O_3$ as a sintering additives electrical conductivity increased in both direction, with more prominent improvement in parallel direction to graphene layers, reaching the highest value of 8 $S \times cm^{-1}$ for SiC with 1 wt.% of GO. The highest thermal conductivity was obtained also for the same composite materials in parallel direction ($l = 119$ $W \times m^{-1}K^{-1}$).

In case of composites with $Y_2O_3$–$Sc_2O_3$ as a sintering additives electrical conductivity increased with increasing GO or GNP content, reaching the highest value of 62 $S \times cm^{-1}$ for SiC with 5 wt.% GNPs in parallel direction to graphene layers. Remarkable improvement of electrical conductivity was achieved by annealing the samples in $N_2$ atmosphere and the highest value of 92 $S \times cm^{-1}$ was obtained for the sample with 5 wt.% GNPs. The highest thermal conductivities were obtained at room temperature in parallel direction to GNPs for annealed SiC samples with 1% GO ($l = 238$ $W \times m^{-1}K^{-1}$) and 5% GNPs ($l = 233$ $W \times m^{-1}K^{-1}$).

The obtained results show that homogeneous distribution of GNPs in SiC matrix, appropriate choice of sintering additives, preferential orientation of graphene, rapid hot-pressing and annealing of samples at 1800 °C for 6h in $N_2$ atmosphere allows to obtain SiC ceramics with very high electrical and thermal conductivity.

## Acknowledgements:

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# Broadband dielectric investigations of 0.7BiFeO3-0.3BaTiO3 ceramics

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## Abstract:

Bismuth ferrite (BF) is a well-known and widely investigated multiferroic material having a high Curie temperature (~825° C) and weak ferromagnetic properties below 370° C. A large polarization and moderately high piezoelectric activity were reported above room temperature thus leading to possible practical applications. However, the high leakage conductivity of BF and quite low dielectric permittivity makes most of the applications impractical. A solid solution of BF with another ferroelectric material such as barium titanate (BT) can improve both ferroelectricity and piezoelectricity and with the addition of minor dopants (e.g. Mn or Nb) significantly suppress leakage currents. The goal of this work was to compare the dielectric dispersion of three BF-BT solid solutions: 0.7BF-0.3BT annealed in air, 0.7BF-0.3BT annealed in an argon atmosphere, and 0.7BF-0.3BT with 0.5 mol% Nb substitution.

The dielectric properties of all ceramics were investigated in a temperature region between 500 K and 200 K employing several spectroscopic techniques: capacitance bridge HP 4284A at frequencies below 1 MHz, vector network analyzer Agilent 8714ET in 1 MHz-1 GHz, and custom-made scalar waveguide system in 25 GHz-38 GHz frequency regions. All specimens show considerable dispersion in all measured temperature ranges. Annealing in an argon atmosphere induces only a small decrease of both parts of complex dielectric permittivity while more significant changes (suppression of dielectric losses) can be visible for Nb-doped samples. Calculated activation energies from electrical modulus fits are similar for both undoped samples while for Nb-doped one it increases, supporting the decrease of its conductivity.

# In situ studies of crystallization and texturing in SrxBa1-xNb2O6 thin films prepared by aqueous chemical solution deposition

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## Abstract:

Tetragonal tungsten bronze $Sr_xBa_{1-x}Nb_2O_6$ (SBN) is a ferroelectric material offering flexible chemistry which opens up for tunability of the properties. Aqueous chemical solution deposition (CSD) is an environmentally friendly and highly flexible route to tailored oxide thin films. Here we present a new and robust aqueous CSD route to SBN thin films on $SrTiO_3$ (STO) single crystals. In situ X-ray diffraction revealed that the nucleation and growth occur via a classical Volmer–Weber (VW) growth mode and that the SBN grains preferably grow along the c-axis. The average thickness of the films was 29-45 nm and the grain size varied between 130 and 175 nm. The degree of texture was governed by the heating rate and two main orientations of SBN, (001) and (310), were observed on STO(100) while only the (311) orientation was observed on STO(110). It was further concluded that the (001) orientation is the thermodynamically stable orientation on STO(100) while the (310) orientation is kinetically favored. To preferably grow the (001) orientation, an ultra-slow heating rate of 0.04 °C/s should be used, while the (310) orientation is favored at higher Sr content and moderate heating rates. These studies demonstrate that control of nucleation and growth is a prerequisite to deposit films with different orientations and textures, which is detrimental for the properties.

## Acknowledgements:

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# Novel physical properties in high-entropy oxides

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## Abstract:

High-entropy oxides belong to the domain of high-entropy materials with multiple cations ( ≥5 elements) and have calculated configurational entropy larger than 1.5R (with R, the gas constant). The cations in these compounds distribute randomly and homogeneously within a well-defined crystalline structure, resulting in increased intrinsic disorder and configurational entropy. This high-entropy configuration leads to: i) cocktail effects of multiple elements, ii) sluggish diffusion effects, iii) severe lattice distortions, and iv) change in solubility limits and lattice stability, which can be explored to improve and fine-tune material properties.

Some of the high-entropy oxides character anisotropic space groups, in which the metal-oxide octahedra are distorted, being either elongated or compressed. Owing to their different outer shell d-electrons, transition-metal ions are particularly sensitive to such distortions, undergoing rearrangement of d-orbitals. This may result in the degeneration of d-orbitals from an isotropic to anisotropic state and lead to technologically relevant electronic and magnetic behaviors, which are temperature sensitive. Indeed, this rearrangement usually occurs as the temperature exceeds a critical threshold. The high tenability of high entropy oxides may furthermore reveal other physical properties such as superconductivity, colossal magnetoresistivity, or magnetic orders.

We will present physical properties, e.g. electron transport and spin-glass behavior, of selected high-entropy oxide samples. It will be furthermore elucidated how these properties can be adjusted by altering the chemical composition of the material. The work highlights the benefits of high-entropy ceramics in technological applications, e.g. sensors for various conditions.

# Mechanical dislocation imprint as tool to control the polarization in ferroelectric BaTiO3 single crystals

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## Abstract:

Defect engineering is one of the most promising tools to modify the functionality of electroceramics. While most defect types are widely used, dislocations are often considered a culprit in thin films or irrelevant in bulk materials due to the brittle nature of most electroceramics. In the last decade, dislocations have attracted considerable attention due to their ability to affect electronic, ionic, and thermal conductivity. Their long-range stress field and charged dislocation core offer the potential to interact with other defect types, making them attractive for ferroelectric domain wall engineering. In this study, we applied the dislocation approach to ferroelectric $BaTiO_3$ single crystals and reveal that dislocations alter not only the domain structure but also affect the macroscopic electromechanical properties. High-temperature compression experiments introduce a mechanical dislocation imprint, which is investigated by complementary characterization techniques. The results indicate a preferential domain arrangement after deformation, which can be directly related to the nucleation and pinning of the domain walls at the dislocations. Dielectric, piezoelectric and ferroelectric measurements at room temperature highlight the resulting changes in the macroscopic electromechanical properties. Due to the interplay between the pinning force and the macroscopic restoring force, a huge increase in the piezoelectric coefficient ($d_{33}$*=1890 pm/V) and electric field dependent permittivity ($d_{33}$=5800) is observed at intermediate electric fields. In summary, mechanical dislocation imprint is a powerful tool to control the polarization and thus extends the available methods to tailor electromechanical properties in bulk ferroelectrics.

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# Revealing defects and domains in bulk ferroelectrics with dark-field X-ray microscopy

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## Abstract:

In recent years, the demand for reliable piezoelectric and ferroelectric materials has increased dramatically, triggered by the trend toward miniaturization and the wide variety of applications. Therefore, a detailed understanding of the defect-engineered domain structure (defect ordering, domain wall arrangement, domain wall defect interaction) is essential to modify the electromechanical properties. Significant innovations in X-ray based techniques in the last decades now allow the imaging of structural properties inside the bulk. One of these techniques is dark-field X-ray microscopy (DFXRM). We can not only observe ferroelectric domain structures and defects in single and polycrystalline ceramic samples, but also perform in-situ measurements as a function of temperature and electric field with this non-destructive microscopy technique.

In addition to a general overview of the technique and its capabilities, we will focus on the visualization and interpretation of multidimensional defects, including domains in the ferroelectric model materials $KNbO_3$ and $BaTiO_3$. This ability paves the way for unique insights into the interactions between domain walls and defects on the local bulk scale and the overall electromechanical behavior of the samples in the future. A special focus will be on the domain distribution in single crystalline $KNbO_3$ and the determination of the respective domain orientations

# Electrospun Ferroelectric Fibers and Their Applications

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## Abstract:

The advancements in the field of nanotechnology have unravelled possibilities to harness unique material properties which otherwise would have been inaccessible in the case of bulk material. Among different material fabrication techniques, one such technique which offers an abundance of scope for exploiting the material properties is electrospinning. It is a highly versatile, low energy consumption, simple, and scalable process that has already found applications in various industries, like pharmaceutical, textile, etc. Electrospinning is a potent tool for the fabrication of micro to nanoscale fibers from a plethora of materials like polymers, ceramics, and composites. Ferroelectric materials in form of nanofibers present inherent benefits like high surface-to-volume ratio and high mechanical flexibility. In this work, we present an overview of the preparation and characterisation, and application of electrospun ferroelectric nanofibers. In the second part, we will demonstrate the synthesis of $BaTiO_3$ hollow nanofibers (BT NTs). XRD and Raman analysis was used to investigate the crystallite sizes and tetragonality for different sintering temperatures. Crystallization of BT NTs occurs in tetragonal structures already at a temperature range between 550 and 630 °C. Finally, we will present the fabrication and characterisation of $(K,Na)NbO_3$ (KNN) nanofibers and their composite, based on a PVDF polymer matrix. The KNN nanofibers were modified with incorporation of Li and Ta ions at A- and B-site in the perovskite lattice, respectively. The nanogenerator based on Li and Ta modified KNN nanofibers were successfully tested as an energy nanogenerator, and we could achieve an output voltage of 5.6V and a power of 6 μW.

## Acknowledgements:

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# Development of LTCC and SiCer Compatible Ag-based Metallization Pastes for High-Performance Sensors

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## Abstract:

The state-of-the-art SiCer technology is now being implemented to develop LTCC (Low-Temperature Cofired Ceramics) compatible highly integrated sensors for various applications. SiCer combines Silicon with Ceramics by forming a monolithic compound. By joining Silicon with LTCC technology microsystems with significantly higher complexity can be produced. BCT-based (Bondable Ceramic Tape) multilayer ceramics developed at Fraunhofer IKTS for sensor applications must be supplemented with tailored metallizations. Currently, SiCer compatible commercial pastes are mostly gold-based. To be more competent, silver-based metallization pastes for conductor paths, vias, and solder pads are being developed. The requirements for such pastes are to have adapted shrinkage and compatibility to BCT along with commercial pastes for the further electrical connection e.g., wire bonding. To meet these requirements and to achieve appropriate print resolution; paste composition, metal powder morphology, and rheology have been optimized. The pastes have been characterized by analyzing the microstructure and interface with SEM analysis. Elemental analysis (EDX) was used to investigate the diffusion and distribution of paste elements into the LTCC substrates. Also, thermomechanical analysis, shrinkage, roughness measurements were conducted. Besides, stability against solute melting in a solder bath was investigated together with solder wetting tests, wire peel tests. Based on the comprehensive analysis from all these investigations each paste composition and subsequent process parameters are being carefully optimized to meet the performance criteria. The focus of the developments for all application areas is the compatibility of the metallization pastes with the LTCC in cofiring SiCer process.

# Subsequent displacive and spin-induced ferroelectric phase transitions in multiferroic BiMn3Cr4O12 ceramics

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## Abstract:

$BiMn_3Cr_4O_{12}$ is not a typical multiferroic as type-I and type-II multiferroic phases emerge subsequently at 125 and 48 K, leading to the coexistence of a considerable ferroelectric polarization and strong magnetoelectric coupling. We report low-frequency dielectric properties together with infrared, terahertz, and Raman spectra of $BiMn_3Cr_4O_{12}$ ceramics. Infrared reflectivity and time-domain terahertz transmission spectra of $BiMn_3Cr_4O_{12}$ ceramics reveal a polar soft phonon near 26 $cm^{-1}$ at 300 K whose softening down to 13 $cm^{-1}$ is fully responsible for the ferroelectric phase transition around 135 K. No additional central mode was observed. In this way, we confirmed the theoretical prediction (Dai and Zhang, J. Amer. Ceram. Soc. 102, 6048 (2019)) that the ferroelectric phase transition should be of the displacive type. Raman spectroscopy reveals a deviation of the temperature dependence of some phonon frequencies from the classical anharmonic behavior due to spin-phonon coupling below 130 K and it is explained by the Dzyaloshinskii-Moriya interaction. The observed phonon activities are compared with the predictions from factor-group analysis and first-principles calculations. Type-II multiferroic order emerges at 48 K, where the antiferromagnetic order induces a new ferroelectric phase, which enhances the polarization by 0.19 $microC/cm^2$.

## Acknowledgements:

This work has been supported by the Czech Science Foundation (Project No. 21-06802S) and the MŠMT Project SOLID 21- CZ.02.1.01/0.0/0.0/16_019/0000760.

# Boosting zT of CaMnO3-based ceramics by controlled micro-structuring

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## Abstract:

The thermoelectric properties of $CaMnO_3/CaMn_2O_4$ composites are tuned via microstructuring and compositional adjustment. Single phase rock salt-structured materials with Mn:Ca ratios larger than unity were produced in reducing atmosphere and subsequently fully densified by spark plasma sintering in vacuum. Annealing in air at 1340 °C between 1 and 8 hours activated redox exsolution and resulted in a variation in microstructure and composites with 10 and 15 vol.% $CaMn_2O_4$, respectively. The nature of the $CaMnO_{3-\delta}/CaMn_2O_4$ interface was analyzed by scanning electron microscopy and transmission electron microscopy, and further complemented by density functional theory calculations. The thermoelectric properties (s, k and S) were characterized at temperatures between 300 and 900 °C in air and will be reported.

## Acknowledgements:

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# Linking Microstructure and Transport Properties in Sm/Yb-doped AlN Ceramics

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## Abstract:

Aluminium nitride (AlN) ceramics have received increased attention not only in the field of ceramics research but also in semiconductor technology due to their very high thermal conductivity and excellent electrical insulation properties. However, densification of the starting powder is challenging due to the strong covalent bonding between Al and N, which challenges manufacturing with high densities. One way to improve densification is implementing sintering aids, such as rare-earth and/or alkaline earth oxides that could contribute to the transport behaviour[1]. Moreover, it is known that the electrical transport along the grain boundaries, designed interfaces and particular crystallographic directions can be tuned, even by several orders of magnitudes. Several examples such as $La_2CuO_4$-based interfaces[2,3], TiCN/SiAlON composites[4], mesoscopic $SrTiO_3$[5] and polycrystalline $PdCoO_2$[6] have been extensively studied. Relatedly, microstructural design, particularly the utilization of the grain boundaries and interfaces, can be critical for tailoring the transport properties. From this point of view, we have investigated the microstructural effects on the electrical and thermal transport properties of the AlN ceramics in terms of cation size and nature of sintering aids (i.e. $Sm_2O_3$ and $Yb_2O_3$)[7].

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## Acknowledgements:

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# Analysis of lattice dynamics in Pb1-xSnxTe solid solutions by XAFS spectroscopy

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## Abstract:

The lattice thermal conductivity ($\kappa_L$) of materials is an important property with a great impact on many processes. In the case of functional materials such as thermoelectrics, it has a direct impact on the heat-to-electricity conversion efficiency of the material. A relation between the lattice thermal conductivity and the Grüneisen parameter is widely present in the literature, however, due to difficulties in calculation of the latter, these methods are rarely utilised for in-depth quantitative analysis. In this work, the X-ray Absorption Fine Structure (XAFS) spectroscopy have been utilised to examine the lattice dynamics in $Pb_{1-x}Sn_xTe$ solid solutions and calculate the bond specific values of the Grüneisen parameter. The obtained results indicated that increasing the configurational entropy in the solid solution through substitution increases the Grüneisen parameter of the material, which directly leads to lowering of its lattice thermal conductivity ($\delta_L$). The predicted dependency of the lattice thermal conductivity vs. material composition is in agreement with experimental data. This study aims to explain the lattice thermal conductivity from the point of view of a more basic property which is bond anharmonicity rather than scattering of phonons on mass and volume fluctuations, thus offering guidelines for optimization of thermal transport in functional materials.

## Acknowledgements:

The research was funded by the Foundation for Polish Science (TEAM-TECH/2016-2/14 Grant "New approach for the development of efficient materials for direct conversion of heat into electricity"), co-financed by the European Union under the European Regional Development Fund.

# Microstructure properties and thermal conductivity of PbTe nanopowder prepared by Pulsed Plasma in Liquid technique

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## Abstract:

Thermoelectric nanomaterials are gaining interest due to their unique properties related to phonon scattering and energy filtering phenomena, however, their preparation is usually done by costly and non-scalable processes e.g. high-energy ball milling. Pulsed Plasma in Liquid (PPL) is a novel, low-cost, and easily scalable, top-down method for the preparation of nanopowders of conductive materials. In this work, the PPL method was applied to prepare the PbTe nanopowder and its thermal properties have been measured. SEM and EDX analyses confirmed the desired elemental composition of PbTe with slight random deviations from stoichiometry. Powder XRD analysis revealed single phased materials with patterns matching that of PbTe (s.g. Fm-3m). TEM observation of the finest grains revealed amorphic clusters of Pb and Te atoms. Grain sizes varied from below 20 nm in the finest amorphic fraction, up to a few tens of nanometers in the highly crystalline fraction. The measured thermal conductivity was reduced by over 40% with respect to the conventionally prepared PbTe with microsized grains. The result is in agreement with predictions on lattice thermal conductivity reduction based on the Callaway model discussed in this work and molecular dynamics simulations reported in the literature.

## Acknowledgements:

The research was funded by the Foundation for Polish Science (TEAM-TECH/2016-2/14 Grant "New approach for the development of efficient materials for direct conversion of heat into electricity"), co-financed by the European Union under the European Regional Development Fund.

# The influence of contact resistance on electrical conductivity in PbTe/CoSb3 thermoelectric composite

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## Abstract:

In this study, we discuss the role of the electrical contact resistance ($R_{cont}$) and its origin in the PbTe/$CoSb_3$ thermoelectric composite. A series of (1-x)PbTe/(x)$CoSb_3$ polycrystalline composite was prepared for x=0.00, 0.25, 0.50, 0.75 and 1.00. The phase and chemical stability of prepared composites were investigated using XRD and SEM techniques. The Seebeck coefficient (S) and electrical conductivity ($\sigma$) measured across a temperature range of 25-400°C show a degenerate semiconductor nature for all obtained composites. The $\sigma$ decreases from 3300 to 1000 S/cm with x and is attributed to a strong decrease in carrier mobility from 330 to 25 $cm^2/(s \cdot V)$.

To explain the reduced $\sigma$ in the composite, $R_{cont}$ between the phases is measured on PbTe/$CoSb_3$ layered sample using the scanning thermoelectric microprobe (STeM) technique ($R_{cont}=14.1$ $Ohm \cdot cm^2$). Effective media theory that considers $R_{cont}$ shows agreement with experimental values of $\sigma$ vs. x. The origin of $R_{cont}$ was investigated by preparing the band diagram for both phases using the Kelvin probe force microscopy (KPFM). Results indicated the presence of a potential barrier at the junction. The current-voltage (I-V) characteristic of the heterojunction shows that the flow of the charge carrier follows the ohmic nature in one direction and non-ohmic in the opposite. Hence, it indicates a possible scattering of carriers at the PbTe/$CoSb_3$ interface in the composite that reduces $\mu$. This study shows that proper selection of the composite components with aligned band structures can be a promising approach to designing efficient TE composite materials.

## Acknowledgements:

This research was financed by the 'New approach for the development of efficient materials for direct conversion of heat into electricity' project (grant number: TEAM-TECH/2016-2/14), which is carried out within the TEAM-TECH program of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund.

# Obtaining and Study Nanocomposites in the B4C-SiC-Si-Al-Al2O3 –Carbon fiber System

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## Abstract:

Abstract: Goal- to obtain nanocomposites by reactive sintering and hot pressing method in SiC-$B_4$C-Si-Al-$Al_2O_3$ -Carbon fiber system. Using this method of synthesis, it became possible to obtain composites with different percentages of SIALON. Our task was also to study the phase composition in the SiC-$B_4$C-Si-Al-$Al_2O_3$-Carbon fiber system. Method. The obtained mass was grounded in an attritor and the consolidated composite was obtained by hot pressing at $1800^0$C. , 40 minutes, delaying at final temperature for 8 min. under 30 MPa pressure. To study the phase composition of the composites, we conducted an X-ray structural analysis on the DRON-3 device, and to study the microstructure, we conducted research on an optical microscope and a raster electron microscope "Nanolab 7" of the company "OPTON". The values of the electrical parameters of the study composites were calculated on the basis of the obtained "lg p-t" dependence. Result. In SiC-$B_4$C-Si-Al-$Al_2O_3$ –Carbon fiber system we obtained composites with a matrix composed of: β-SIALON, silicon carbide, corundum and nanoparticles of boron nitride. Conclusion.The phase composition of the obtained composite provides high physical-technical and performance properties of these composites. Compression strength-2187 MPA, Bending strength-285 MPa, Thermal expansion coefficient $a_{20-700}$-3.8 $10^{-6}$ $^0$C.

## Acknowledgements:

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# Optical properties of RE-doped potassium sodium niobate ceramics obtained using the sol-gel method

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## Abstract:

Ferroelectric perovskite materials have recently started to be considered as hosts for lanthanide-doped photoluminescent materials. Such multifunctional materials that incorporate desirable electrical and optical properties could be used in new applications and would allow the cost and size of electronic and electrooptical components to be reduced. In the present study, lead-free potassium sodium niobate (KNN) ceramics doped with Eu and Dy were synthesized by means of the sol-gel method and their optical properties were evaluated. The applied water-based synthesis made it possible to obtain powders and sinters with improved compositional homogeneity. XRD measurements and Raman spectroscopy were used to determine the structural differences between samples. The optical properties of materials were examined by recording optical absorption, excitation and emission spectra. Measurements of luminescence demonstrated that the Eu-doped KNN fluorescent powders and sinters produced yellow and red emission bands, which are attributed to $Eu^{3+}$ transitions. The luminescence spectra were obtained using an optical parametric oscillator laser after excitation with a wavelength ranging from 210 to 300 nm at room temperature. The influence of the RE dopant and the ferroelectric host on optical properties was also investigated.

## Acknowledgements:

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# Field-induced ferroelectric phase transformation in barium titanate

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## Abstract:

Piezoelectric materials are part of our daily routine: whether as microelectronics, sensors or actuators. Barium titanate (BT) is the classic model for ferroelectric systems and it is indispensable for dielectric applications. In addition, its properties are highly temperature and grain size dependent. BT has excellent properties with grain sizes of approximately 1 µm, but undergoes marked weakening as the grain size decreases. However, the fundamental mechanisms behind the electromechanical behaviour are still not fully understood.

A wide range of unimodal grain size distributions between 0.4 and 15 µm was successfully sintered via spark plasma sintering, quenched sintering and two-step sintering, avoiding abnormal grain growth.[1] Samples with intermediate grain size, showed excellent electromechanical and dielectric properties. They possess a balance between microstructural strain, existence and mobility of domain walls, which in turn allows the field induced crystal phase transformation.

In order to elucidate the structural response to an applied electric field, the samples were measured with in situ high energy X-rays. The structural data obtained were processed by means of STRAP[2] and the field induced phase transformations were quantified. This induced phase transformation is stronger in samples whose grain size distribution curve is located around 1 µm. These results contribute to the understanding of fundamental questions about the ferroelectric effect in barium titanate and consequently other similar systems.

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# Optimization of (Ba,Ca)(Zr,Ti)O3 lead-free piezoelectric ceramics properties by variation of the composition

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## Abstract:

$PbZr_{(1-x)}Ti_xO_3$ (PZT) materials show piezoelectric properties ($d_{33}$ up to 700pC/N) and a Curie temperature (up to 360°C) much higher than other piezoelectric ceramics. Yet, PZT are associated to many health and environmental problems linked to the lead they contain. It is thus crucial to turn to so called "lead-free" ceramics. Among the alternatives, one is the family of barium and calcium zirconate-titanates $(Ba_{1-x}Ca_x)(Ti_{1-y}Zr_y)O_3$ (BCTZ). These compounds have very promising piezoelectric properties, but a low Curie temperature. They have fewer applications than PZT but they can still be used at low temperatures as sensors or for energy harvesting, for example.

In this work, focus was first put on the composition $(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ as reference, and the Zr/Ti ratio (y/(1-y)) on one hand and the Ca/Ba ratio (x/(1-x)) on the other hand were then varied. The aim was to finely modulate the piezoelectric properties. Each composition was characterized by X-ray diffraction and scanning electron microscopy. The piezoelectric, ferroelectric and dielectric properties were also studied.

This work made it possible to highlight a $d_{33}$ piezoelectric coefficient varying from ~290 pC/N to 400 pC/N for small modifications of the Zr content (from 0.07 to 0.09 at.%), as well as a Curie temperature reaching 90°C for some compositions (y = 0.07 – 0.08). Interesting $K_p$ values as high as 54% were measured when slightly decreasing Zr (y = 0.09) or increasing Ca content (x = 0.16), compared to the reference composition. The variation of Zr content also leads to improved ferroelectric properties when y decreases (Pr = 9.7 and Ps = 18.8 µC/cm² for y = 0.08). Modification of the Ca/Ba ratio has lower effect on ferroelectric properties and almost no effect on the Curie temperature.

## Acknowledgements:

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# Investigation of electrical properties of potassium sodium niobate ceramics obtained via the sol-gel method

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## Abstract:

Lead-based ceramics are currently the most commonly used piezoelectric materials. However, due to their toxicity it has become necessary to develop lead-free alternatives. Promising candidates include sodium-potassium niobate with the composition $K_{0.5}Na_{0.5}NbO_3$ (KNN). Unfortunately, the volatilization of alkali elements during thermal treatment leads to lower density and higher leakage current of this material. The application of nanopowders prepared by means of the sol-gel method makes it possible to reduce the thermal treatment temperature and obtain higher density. The present study investigated the electrical properties of water-based KNN ceramics obtained using this method. Dielectric permittivity and dielectric loss were measured in the temperature range from 293 K to 873 K and over a wide range of frequency. At room temperature the sinters were determined to exhibit a dielectric permittivity of ~400 and a dielectric loss of ~0.05. The samples' DC and AC conductivity was determined and their activation energy of electrical conduction was estimated. Impedance spectroscopic measurements were performed and complex modulus spectra were analyzed. The sinters were characterized by typical ferroelectric hysteresis loops, with a coercive field of about 20 $kV \times cm^{-1}$. The obtained results indicated a correlation between the electrical properties of samples and their phase composition and microstructure.

# Elaboration of lead-free piezoelectric thick films by Aerosol Deposition Method

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## Abstract:

Some piezoelectric devices (sensors, energy-harvesting devices…) need the deposition of ceramic material on suitable substrate, with thickness of 10-100 µm. Now, only screen-printing appears as the possible method for their elaboration. Unfortunately, this process needs sintering of the active material after shaping (thermal treatment). Thus, CTTC and IRCER have developed an innovative printing method of thick films ceramic coatings, based on the Aerosol Deposition method (AD).

The principle of AD is to spray a gaseous aerosol of dry powder particles onto a substrate through a supersonic nozzle. The kinetic energy of particles allows obtaining directly dense thick ceramic coatings. Although the consolidation mechanisms are not fully understood yet, ADM is an efficient way for the manufacturing of dense films at room temperature, allowing ceramic coatings onto multiple kinds (metals, flexible materials like polymers...).

This talk focuses on the coating by AD of lead-free piezoelectric materials for energy harvesting applications. The selected material is 0.94 $Na_{0.5}Bi_{0.5}TiO_3$ – 0.06 $BaTiO_3$ (NBT-BT). Firstly, we developed our own solid-state synthesis route and obtained ceramics powders suitable for AD. Then we studied the deposition parameters onto different substrate (glass, metallic substrates…) in order to obtain films with thickness close to 100µm. Then, we investigated the structure, microstructure and electrical properties of the obtained thick films. The ability to obtain thick and dense films at room temperature, without post coating sintering or thermal annealing, is the most benefit of this method. Finally, we realized a simple prototype device for investigating the energy harvesting.

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# Nanogenerators based on BaTiO3/PDMS composites for high-frequency applications

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## Abstract:

The development of miniaturized power sources is crucial for portable electronics. The most attractive source of energy is mechanical movements (acoustic waves, fluid flow, and body deflection, compression, vibration, etc.) due to their availability. Thus, over the past few years, energy-harvesting devices, called nanogenerators, have been developed to convert efficiently mechanical energy into electricity. Piezoelectric (PENGs) [1] and triboelectric (TENGs) [2] nanogenerators, as well as hybrids of TENG with other energy-harvesting techniques (solar cells, electromagnetic induction generators) [3] have been repeatedly reported. The generation of electricity from ambient vibrations in PENGs is clearly based on the electromechanical effect in piezoelectric materials. Due to this, nanoscale piezoelectrics or composites have great potential in terms of developing high-performance mechanical energy harvesting devices.

However, despite the quite significant activity of scientists in recent years in this direction, most investigations are devoted to the quasi-static frequency range. While for many existing devices, nanogenerators could be beneficial in converting high-frequency vibrations into useful electrical energy. Therefore, in this study, composites containing nanoparticles of ferroelectric barium titanate ($BaTiO_3$) in a polydimethylsiloxane (PDMS) polymer matrix are considered in terms of their suitability as nanogenerators for high-frequency (10 MHz) applications.

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# Integration and Characterization of a Ferroelectric Polymer PVDF-TrFE into the Grain Boundary Structure of ZnO via Cold Sintering

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## Abstract:

In this study, the Cold Sintering Process (CSP) is used to design ceramic-polymer composites with Polyvinylidene fluoride Trifluoroethylene (PVDF-TrFE), a ferroelectric co-polymer, as an active intergranular grain boundary phase in a semiconducting Zinc Oxide (ZnO) electroceramic matrix. The conductivity is modelled with Schottky thermionic emission and Fowler-Nordheim tunneling as a function of both temperature and voltage. In addition, through details of the dielectric characterization, the interfaces are also considered with the effective permittivity resulting with a space charge relaxation of the PVDF-TrFE. Analysis of the dielectric data using the Maxwell-Wagner-Sillars (MWS) model exhibit that the electrical properties are controlled by an intergranular PVDF-TrFE phase with approximatively at thickness of ~3 nm across the composites. Transmission electron microscopy (TEM) investigation of the grain boundary phase confirms the polymer thicknesses to the dimensions predicted from the various electric measurements and subsequent modeling.

## Acknowledgements:

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# Tuning Functional Properties in Porous Electroceramics through 3D Printing of Capillary Suspensions

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## Abstract:

Dedicated hierarchical structuring of functional ceramics can be used to shift the limits of functionality. This work presents the manufacturing of highly open porous, hierarchically structured barium titanate ceramics with 3-3 connectivity via direct ink writing of capillary suspension type inks. The pore size of the printed struts (~ 1 µm) is combined with a printed mesostructure (~ 100 µm). The self-organized particle network, driven by strong capillary forces in the ternary solid-fluid-fluid-ink, results in a high strut porosity and the distinct flow properties of the ink allow for printing high strut size to pore size ratios, resulting in total porosities > 60%. These unique and highly porous additive manufactured log-pile structures with closed bottom and top layers enable tailored dielectric and electromechanical coupling, resulting in an energy harvesting figure of merit $FOM_{33}$ more than four times higher than any documented data for barium titanate. This demonstrates, that combining additive manufacturing of capillary suspensions in combination with appropriate sintering allows for creation of complex architected 3D-structures with unprecedented properties. This opens up new opportunities in a broad variety of applications, including electromechanical energy harvesting, electrode materials for batteries or fuel cells, thermoelectrics, or bone tissue engineering with piezoelectrically stimulated cell growth.

## Acknowledgements:

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# How the addition of chemically synthesized powder affects the final properties of KNN ceramics

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## Abstract:

Potassium Sodium Niobate is an attractive lead-free piezoceramic thoroughly studied in the last two decades. However, one of the most critical issues that still hinders its widespread utilization is the reproducibility of the whole ceramic process, from the powder synthesis to its consolidation and final sintering. In this work, a new strategy to produce $K_{0.5}Na_{0.5}NbO_3$ (KNN) piezoceramics with reliable and improved piezoelectric performance is presented for the first time. Highly reactive chemically synthesized powder ($KNN_{chem}$) was added to KNN powders obtained via solid state reaction in different weight ratios (0, 3, 5, 10 and 20 wt%). The influence of the addition of $KNN_{chem}$ powders on crystal phase, microstructure, and piezoelectric properties of the resulting sintered pellets was deeply investigated. It was found that the gradual increase of $KNN_{chem}$ content promotes the conversion of the undesired phase present in $KNN_{SSR}$ into the stoichiometric one. Moreover, the addition of $KNN_{chem}$ between 5-10 wt% improves piezoelectric properties leading to $d_{33}$ values of 113-115 pC/N. The innovative strategy described in this work could be potentially applied for the production of a wide range of KNN based piezoelectric systems.

# Robocasting of Alkaline Niobate-based Piezoelectric Ceramics

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## Abstract:

With the merit of enhanced design flexibility and microstructure controllability, 3D Printing (3DP) aka. Additive Manufacturing (AM) is changing the processing method of piezoelectric ceramics for the fabrication of piezoelectric sensors, actuators, ultrasonic transducers and energy harvesting devices. Here, we investigate the use of robocasting aka. Direct Ink Writing (DIW) for the processing of potassium sodium niobate [(K, Na) NbO3, KNN] which is being considered as one of the promising candidates for the lead-free piezoelectric ceramics. Robocasting of ceramics involves 1) designing of ceramic inks with proper rheological behavior, 2) deposition of the inks via a controlled micronozzle to make green bodies in a layer-wise manner, and 3) heat treatment of green bodies to obtain dense ceramics. Ceramic ink characteristics, robocasting process parameters and heat treatment conditions govern the ultimate quality of the piezoelectric ceramics. Hence, it is an imperative need to scrutinize and fine-tune the processing parameters for achieving the piezoelectric ceramics with desired microstructure and with maximum electrical performance. Herein, we will elaborate the influence of the ink characteristics (e.g., solid loading, polymeric additives, etc.), as well as sintering conditions (e.g., time, temperature, atmosphere, etc.) on the microstructure and physical properties, e.g., porosity, density, shrinkage, and piezoelectric performance of KNN-based piezoelectric ceramics.

# Perovskite thin films for high energy density capacitor devices from chemical solution deposition

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## Abstract:

Oxides with the perovskite structure can exhibit a wide range of functional properties, where the compositions showing ferroelectric response are of special interest for energy storage. Ferroelectric thin films are key to the successful miniaturization of multilayer ceramic capacitors as thinner layers can improve the microstructure and therefore the performance of the device. Optimal properties for energy storage are found in relaxor ferroelectrics and antiferroelectrics. However, in order to realize high quality perovskite thin films for energy storage devices, a reliable fabrication procedure giving control over chemistry and properties is required. Chemical solution deposition (CSD) is an inexpensive and flexible method for producing oxide thin films, where the properties depend on the heating procedure and precursor solution chemistry.

In our group, we are developing CSD routes for relaxor and antiferroelectric perovskite thin films for energy storage applications. Moreover, conductive oxide buffer layers are implemented as bottom electrodes to promote texture in the perovskite layer. Relaxor films based on the $BaTiO_3$- and $Bi_{0.5}Na_{0.5}TiO_3$-systems with homo- and heterovalent substitution and antiferroelectric films based on the $NaNbO_3$-system have been prepared. Conductive oxide films of $RuO_2$ and $LaNiO_3$ have also been fabricated, all with CSD. By tailoring the processing parameters and stoichiometry, the microstructure and ferroelectric response were optimized for energy storage applications. The microstructure and phase composition of the films were characterized by scanning electron microscopy, Raman spectroscopy and X-ray diffraction, while the ferroelectric response was investigated on an electric measurement setup by depositing Au or oxide top electrodes.

# Investigaton of phase formation, structure and functional properties of bismuth sodium titanate based piezoceramics

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## Abstract:

The investigation of lead-free piezoelectric materials has been intensified over the past two decades, due to need to replace widely used lead-based materials. The development of these materials is tightly connected with the development of piezoelectric energy harvesting technologies. One of the most promising lead-free materials is (1-x)$Bi_{0.5}Na_{0.5}TiO_3$–x$BaTiO_3$ (BNT-BT) solid solution due to existence of morphotropic phase boundary near x=0.06-0.08, when the functional properties are significantly improved compared to the pure BNT. Most of the research has been focused on obtaining BNT-BT materials by conventional solid-state route which has many disadvantages such as repeated grinding and calcination and high sintering temperatures. Thus, development of innovative synthesis routes is needed. Wet chemical methods (such as sol-gel and hydrothermal synthesis) offer possibility to prepare nanosized high purity powders with different morphologies at relative low synthesis temperatures and without a lot of investment.

(1-x)BNT–xBT where x= 0, 0.02, 0.04, 0.06, 0.08, 0.1 powders were hydrothermally synthetized in alkaline environment. Bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$), barium nitrate ($Ba(NO_3)_2$), titanium butoxide ($C_{16}H_{36}O_4Ti$) and sodium hydroxide were used as starting materials. The first part of this work investigates the influence of the synthesis temperature and time as well as type of precursors on the phase composition and morphology of the BNT-BT powders. In the second part of the work the obtained powders were pressed into pellets and sintered at the various temperatures up to 1100 °C to obtain dense ceramics. The influence of $Ba^{2+}$ addition and different processing parameters on the phase composition, sinterabilty, dielectric and piezoelectric properties were investigated.

## Acknowledgements:

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Project program 451-03-9/2021-14/200134.

# Effect of B2O3 and/or Sb2O3 addition on microwave dielectric properties of Ba(Mg1/3Ta2/3)O3

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## Abstract:

With the development of telecommunication systems, microwave filters suitable for high frequencies are required. The compound $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) is one of the high-performance dielectric materials, which is used as Band-pass filters with low loss and sharp cut-off frequencies in the microwave range. However, BMT is sintering resistant because residual sintering products reduce the Qf value and inhibit densification.

In this study, microwave dielectric ceramics $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) were fabricated using starting materials with conventional purity, together with $B_2O_3$ and/or $Sb_2O_3$ as a sintering additive, to improve the densification and Qf value and reduce the sintering time.

The BMT samples were fabricated using $BaCO_3$, MgO, and $Ta_2O_5$, powders as starting materials, and $B_2O_3$ (0-1.4mol%) and/or $Sb_2O_3$ (0-1.4 mol%) powder as the sintering additive. The 12 different samples (in triplicate for a total of 36 samples) were sintered simultaneously in a sintering container at 1580 to 1650°C for 5 or 25 h in an electric furnace and then allowed to cool to room temperature.

BMT ceramics that had a high Qf value of $3.5\times10^5$ GHz, with a 93% density was achieved by adding 0.4 mol% $Sb_2O_3$. When $B_2O_3$ was added, a maximum relative density of 94% was obtained. This is due to the existence of $CO_2$ released from $BaCO_3$, which combined with $B_2O_3$ accelerated the sintering process. However, the Qf value was not high. Since Sb2O3 increases Qf value, and B2O3 increases density. Therefore, it is suggested that by co-doping Sb and B into BMT, high Qf value and high density can be achieved.

# Synthesis and characterization of 0.15SrTiO3-0.85BaTi0.95Zr0.05O3 composites

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## Abstract:

Dense ceramic composites with limited interdiffusion between the component phases were fabricated using spark plasma sintering method starting from a $0.15SrTiO_3$-$0.85BaTi_{0.95}Zr_{0.05}O_3$ (0.15ST-0.85BZT) composite powder synthesized in-situ by a two-step process. First, $SrTiO_3$ particles with cubic morphology and two different sizes (average diameter of 250 nm and 400 nm) were prepared by a precipitation-like method. Then, these particles were added to a gel suspension obtained by hydrolysis of $BaCl_2$-$ZrOCl_2$-$TiOCl_2$ aqueous solution with NaOH and heated at $98^0$C for 3h. The resulting powder was washed with distilled water and dried at $98^0$C for 2h.

The phase composition and crystal structure of the ceramic composites were investigated by X-ray diffraction measurements. The results indicate only the presence of diffraction maxima characteristic for the component phases ($SrTiO_3$ and $BaTi_{0.95}Zr_{0.05}O_3$) with perovskite structure, no secondary phases detectable by X-ray diffraction were formed during the sintering process. In both types of ceramics, BZT phase is orthorhombic, while ST is cubic for finer structure and tetragonal for the coarser ST.

The SEM analysis indicated the formation of ceramic composites formed by large BZT grains (average grain size of ~2mm) and well dispersed fine ST grains with submicron diameters, with a relatively good density and homogeneity.

The dielectric properties for ceramic composites with two different grain sizes were compared and the relaxation mechanisms were discussed. The ceramics present a very large and flattened maximum in permittivity approximatively at the same temperature near 340 K, with a visible thermal hysteresis between data measured during heating and cooling and a permittivity variation of about 30% between the two types of samples.

## Acknowledgements:

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# Nanostructured TiO2 photocatalysts modified with Cu for imidacloprid degradation

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## Abstract:

<div>In this work we investigated Cu modified immobilized photocatalysts based on $TiO_2$ nanotubes, used for the degradation of imidacloprid. Specifically, we paid attention to the role of Cu(II) ions, namely their local structure and chemical state in the photocatalyst. The photocatalysts were prepared by electrochemical anodization and modified using Cu solutions with various Cu concentrations (0.2–1.0 M). Morphology and structure of the derived photocatalysts were characterized by X-ray diffraction, Scanning Electron Microscopy and Energy Dispersive X-ray, UV-VIS-NIR, Raman and Photoluminescence spectroscopies. Particularity detailed was the X-ray absorption spectroscopy analysis: extended X-ray absorption fine structure and X-ray absorption near edge structure. The EXAFS results indicated the formation of Ti–O–Cu connections, suggesting that the Cu(II) cations are attached to $TiO_2$ surface which contributes to the improvement of the photocatalytic activity.

## Acknowledgements:

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# Synergistic effect of resonance scattering and lattice softening on thermoelectric performance of p-type PbTe

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## Abstract:

Lead telluride is one of the best materials for the fabrication of medium-temperature thermoelectric modules. In this work, we show the simultaneous enhancement of electrical transport and reduction of phonon propagation in p-type PbTe co-doped with Tl and Na. The effective use of advanced electronic structure engineering improves the thermoelectric power factor $S^2s$ over the temperature range from 300 to 825 K. A rise in the Seebeck coefficient S was obtained due to the enhanced effective mass $m^*$, coming from the Tl resonance state in lead telluride. Due to the presence of additional carriers brought by Na co-doping, electrical conductivity became significantly improved. Furthermore, Tl and Na impurities induced crystal lattice softening, remarkably reducing lattice thermal conductivity, which was confirmed by the measured low speed of sound $v_m$ and high internal strain $Ce_{XRD}$. Eventually, the combination of both the attuned electronic structure and the lattice softening effects led to a very high ZT value of up to ~2.1 for the $Pb_{1-x-y}Tl_xNa_yTe$ samples. The estimated energy conversion efficiency shows the extraordinary value of 15.4% ($T_c$ = 300 K, $T_h$ = 825 K), due to the significantly improved average thermoelectric figure of merit $ZT_{ave}$ = 1.05. This work demonstrates that the combination of resonance scattering and crystal lattice softening can be a breakthrough combination for advancing thermoelectric.

## Acknowledgements:

The research was funded by the Foundation for Polish Science (TEAM-TECH/2016-2/14 Grant "New approach for the development of efficient materials for direct conversion of heat into electricity"), co-financed by the European Union under the European Regional Development Fund.

# Low and high field electrical properties of dense fine-grained ferroelectric ceramics prepared via sol-gel method

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## Abstract:

When nanostructured, the ferroelectrics' multifunctionality is strongly influenced by the dimensional effects due to their impressive intrinsic/extrinsic contributions. To study such phenomena, dense ceramics with grain sizes of a few tenths of nanometers are needed.

$Ba_{0.8}Sr_{0.2}TiO_3$ and $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) ferroelectric ceramics in a tetragonal state at room temperature ($P_s \neq 0$) and cubic state at room temperature ($P_s = 0$) were produced by combining innovative synthesis methods and sintering strategies to obtain a grain size reduction below 100 nm. The stoichiometric precursor powders with controlled particle size and morphology were chemically synthesized via the sol-gel method. The ultra-fine powders were sintered by spark plasma in different conditions of time and temperature at 1000 °C for 4 minutes, 1050 °C for 2 minutes, and 1050 °C for 4 minutes and thermally treated for re-oxidation.

The structural and microstructural characterizations were performed to investigate the phase purity and the impact of processing parameters on the grains' sizes and morphology. The transition from ferroelectric to relaxor state is induced by reducing the grain size towards a few tenths of nanometers in a ferroelectric ceramic, being enhanced some of the functional properties and affecting others. At the same time, there is a significant increase in the non-ferroelectric boundary regions of the grains, which are of a nanometer size with a much lower permittivity. To follow this aspect, the dielectric properties determined in a wide range of temperature (50-465 K) and frequency (100Hz-1MHz) and the high field ferroelectric properties were discussed in terms of composition (Strontium content), processing (sintering parameters), and microstructural features (grains' size, shape, morphology).

## Acknowledgements:

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# Polycrystalline and epitaxial thin films based on LaMnO3/(La,Sr)MnO3 and BaTiO3/(Ba,Sr)TiO3 prepared by chemical solution deposition techniques

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## Abstract:

Magnetoelectric coupling in multiferroics makes these materials very interesting in different fields of applications. Multiferroic materials in a form of thin films are attractive due to their different functionality which is based on changing physical parameters by strain at the interface and their nano-scale size which follows miniaturization trends in microelectronics. By controlling the strain at the interface, it is possible to directly couple ferroelectric and ferromagnetic orders and produce strong magnetoelectric coupling. In addition, some multiferroic systems are very sensitive to external stimuli such as magnetic and electric field or light. Special interest is caused by possibility of manipulation of magnetic order by ultrashort laser pulses. This phenomenon is very desirable for application in spintronics and data storage devices.

In the first part of this research, focus was on preparation of ferromagnetic $LaMnO_3/La_{0,67}Sr_{0,33}MnO_3$ and ferroelectric $BaTiO_3/Ba_{0,5}Sr_{0,5}TiO_3$ layers on Si and $SrTiO_3$ (001) substrates and their structural analysis. $LaMnO_3$ and $(La,Sr)MnO_3$ were synthesized by polymer-assisted deposition (PAD) technique using aqueous solution of corresponding cations stabilized with PEI and EDTA. $BaTiO_3$ and $(Ba,Sr)TiO_3$ were prepared by classical solution deposition method using $BaCO_3$, $Sr(C_2H_4O_2)_2$ and Ti-alcoxide. Monolayers based on lanthanum manganite and barium titanate, as well as bilayers, were deposited on Si and $SrTiO_3$ (001) substrates by spin-coating method and annealed up to 850 °C. Structural characterization of thin films was done by X-ray diffraction and HRTEM, while thickness and surface properties were determined by AFM. Electrical and magnetic measurements were also performed. </div>

## Acknowledgements:

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# BaTiO3 – CoFe2O4 unsintered magnetoelectric composites.

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## Abstract:

Composite magnetoelectrics is the class of materials that can be polarized by an external magnetic field and magnetized by an electric field. The interaction between ferro- or ferrimagnetic and ferroelectric phases occurs through mechanical strain at the interfaces. Upon the sintering, unexpected reactions and interdiffusions occur between different phases. That limits the possible combinations of the components. Additionally, upon conventional sintering, the grains grow. Bigger grains means lower surface area. Several complex approaches like spark plasma sintering, core-shell are aimed to avoid or reduce the mentioned factors.

The report delivers a novel approach to the synthesis of composite magnetoelectrics. Phosphate binding of powders was utilized instead of the classical sintering. Such a method allows avoiding the unexpected reactions at interfaces, interdiffusion of chemical elements of the constituents, etc. At the same time, the absence of the sintering step means that the grains of both phases remain of the same size. That allows to develop of composites with extremely high interface area.

Bulk (1-x)BaTiO3 – xCoFe2O4 (x=0.1 – 0.6) composite materials were successfully synthesized and studied. That combination was selected since it is a well-studied and direct comparison with the previously reported results allows concluding the effectiveness of the method. XRD pattern proves the absence of unexpected phases. Dielectric permittivity analysis demonstrates the para-ferroelectric phase transition of BaTiO3 and the contributions of several Maxwell-Wagner relaxations. Measured direct magnetoelectric coupling coefficient depends on the composition and successfully competes with the values reported for sintered ceramics.

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# Paper-templated, porous piezoceramics as functional platforms

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## Abstract:

Porous piezoceramics show many advantages as compared to their dense counterparts, e.g., decoupling of the directionality of electromechanical parameters or tunability of the hydrostatic figure of merit and electrical permittivity by changing the type and orientation of pores [1]. In addition, they enable the preparation of metal- or polymer-ceramic composites [2].

Paper-templating, a sacrificial processing method for ceramics, in which paper is used as negative-form for the green body, turned out as a simple, very flexible, and inexpensive way of shaping such porous ceramics. Combining this processing method with lead-free materials with excellent piezoelectric properties like $Ba(Zr_{0.2}Ti_{0.8})O_3$-$(Ba_{0.7}Ca_{0.3})TiO_3$ (short: BCZT), enables an auspicious, environmentally friendly way of processing of energy-harvesters, hydrophones, biomedical scaffolds, transducers for medical applications or piezo-catalysts.

In this work, influences of several parameters on paper-templating of BCZT have been investigated, like slurry composition, template texture, and thermal treatment. Porosities from 33 % to 70 % were manufactured via paper-templating. Light and scanning electron microscopy were utilized to characterize the produced structures. Moreover, the correlation of the electromechanical performance and the microstructure type will be presented. The results demonstrate the suitability of the porous structures as lead-free piezo-active functional platforms.

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# Flash Sintering of Barium Strontium Titanate (BST) ceramics

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## Abstract:

The development of high-performance lead-free materials has become a high priority in a digitized society dominated by the Internet of Things (IoT). Further development of high-speed and large-capacity wireless communication technologies is in intensive progress. A widely used lead-free material for tunable microwave devices (phase shifters, antennas...) is barium strontium titanate (BST) since it has unique dielectric properties. To prepare BST ceramics, typical sintering temperatures are in the range of 1250-1400 °C which avoid BST integration with other materials as polymers and metals for specific applications, e.g. metal-insulator-metal (MIM)-structures. Therefore, in this work, FLASH sintering, a Field Assisted Sintering Technique, was investigated as a promising alternative sintering technology for BST production at lower temperatures. FLASH allows the abrupt densification of ceramics at a significantly lower temperature and time (less than 60 seconds) when a threshold combination of furnace temperature and DC electric field directly applied to the specimen is reached. The role of particle size and particle size distribution (PSD) in FLASH sintering was evaluated; for that, BST powders were processed using ball milling and attrition milling. For each powder, the optimized FLASH parameters of the electrical field and current limit were experimentally established. Conventionally sintered specimens were set as standards for the structural, microstructural, and electrical evaluation of the FLASH sintered ceramics.

## Acknowledgements:

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# High-temperature giant piezoresistivity of SiOC film for strain gauge application

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## Abstract:

High-temperature strain measurement is a formative element in the development of air-breathing engines, turbines, motors, or generators. The selection of material that can withstand extreme environments is distinctively one of the most challenging tasks in the strain gauge process chain. In addition to temperature stability, it is desired to use materials that show a high gauge factor and a low-temperature coefficient of resistance (TCR) to minimize any temperature-induced impact on the sensor output characteristics. In this study, thin-film strain gauge element arrays were prepared on large-area silicon oxycarbide thin films followed by lithographic deposition of structured electrodes. The individual strain gauge elements were systematically investigated concerning their piezoresistive behavior and shown to possess giant piezoresistivity with gauge factors in the range of 3–5 x $10^3$ at room temperature and above 200 at 100 - 700°C. This has been correlated with the large charge carrier mobility in the SiOC thin films (i.e., 186 $cm^2 V^{-1} s^{-1}$) as well as with a unique phase composition and morphology thereof, consisting of high-conductivity carbon-rich segregations homogeneously dispersed within a SiOC-based matrix. The studied strain gauge elements were evaluated in both cyclic tensile and compression loads and showed excellent reversibility as well as short response times. The processing capability of the elements has been statistically assessed and revealed good robustness and replicability which may be further improved. The present work provides a robust and highly reproducible manufacturing process for an ultrasensitive strain gauge prototype and thus points towards a great potential concerning the use of silicon oxycarbides in MEMS-related applications.

## Acknowledgements:

The authors gratefully acknowledge funding from the German Science Foundation (DFG Germany) – grants no. 411658150 (Microstructured C/SiCX (X = O,N)-based high temperature strain gauge). Additionally, EI acknowledges funding from DFG within the Heisenberg program (IO 64/14-1).

# Scanning Thermoelectric Microscope - characterization of electronic properties of functional materials

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[2] *AGH University of Science and Technology/ Faculty of Materials Science and Ceramics, Department of Inorganic Chemistry, Thermoelectric Research Laboratory, Kraków, Poland*

## Abstract:

Scanning Thermoelectric Microscope (STeM) is a unique device for characterization of the distribution of thermoelectric parameters (i.e. Seebeck coefficient $\alpha$ and electrical conductivity $\sigma$) on the surface of a given sample. The prototype of the device was developed and constructed at the Thermoelectric Research Laboratory at the AGH-UST in Krakow. A probe scans the investigated area creating a surface distribution map of the physical parameter with the maximum spatial resolution of 1 μm.

STeM allows measurements of electrical properties ($\alpha$ and $\sigma$) of a wide range of materials: from conductive ceramics, semiconductors and polymers to metals and alloys. It can be used in particular to assess uniformity of electronic properties of functional materials (e.g. thermoelectric, photovoltaic, solid electrolytes, etc). However, the range of application of the method, with the conjunction of other methods such as XRD or SEM, can be vastly extended for local analysis of other parameters indirectly influencing carrier concentration and electronic structure of the materials e.g.: residual strain, distribution of dopants, concentration of structural defects and many others.

In this study, we present two new possible applications: the analysis of hydrogen distribution in steel and analysis of residual thermal stress in polycrystalline PbTe/$CoSb_3$ composites. The STeM method could be an answer to a growing demand for quick and non-destructive testing of hydrogen content and its distribution in load-bearing materials which can suffer from hydrogen embrittlement. Additionally, we will show that the variation of a values near the grain boundaries can be correlated with the residual thermal stress in composites subjected to heat treatment.

## Acknowledgements:

Research project partly supported by program „Excellence initiative – research university" for the AGH University of Science and Technology. Moreover, the authors would like to thank Collins Aerospace in Tajecina for financing the research necessary to conduct this research.

# Quantitative mapping of nanotwin variants in the bulk of ferroelectric/ferroelastic materials

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## Abstract:

Most state-of-the-art high-resolution imaging techniques are limited to probing the sample surface. This is a major drawback for the characterization of bulk functional ceramics as the strain state changes from biaxial at the surface to triaxial in the bulk, dramatically influencing the performance. Here, we demonstrate mapping of nanotwin variants highly localized in the bulk utilizing the full reciprocal space intensity distributions obtained from Dark-Field X-Ray microscopy. We demonstrate our method for a high-performance polycrystalline ferroelectric/ferroelastic $(Ba,Ca)(Zr,Ti)O_3$ model system whose excellent piezoelectric properties originate from domain sizes of 10-100 nm. The density of twin variants inside the grain is 30% smaller compared to the density in the vicinity of the grain boundary, following the trend of the elastic energy. The obtained elasto-morphological correlations are crucial for many twinned functional ceramics, including oxides for dielectric or piezoelectric applications.

# Dielectric Properties of Upside-Down SrTiO3/Li2MoO4 Composites Fabricated at Room Temperature

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## Abstract:

Synthesis procedures of ceramic upside-down lithium molybdate-strontium titanate (LMO-ST) composites prepared at room temperature are described. Room temperature fabrication (RTF) is a promising alternative to the time- and energy-consuming high-temperature sintering of electroceramics, which involves mixing the initial phases, molding with a steel dye, pressing, and drying, while in the last two phases the action of densification takes place. The LMO-ST composites are based on a high ratio of filler ST, coupled with the corresponding LMO binder. Part of the binder is admixed to the ceramic particles and an additional part is added as a saturated aqueous solution, which crystallizes during pressing and drying, leading to its deposition on the surface of the filler particles. As a result, sufficient binding with 76–84% relative density was achieved. The deeper insight into the method was provided by various processing aspects and corresponding microstructural investigations. The particle size distribution, pressure, pressing time, ultrasonic treatment, drying time, and processing conditions were optimized to obtain improved functional properties of the LMO-ST composites. The results of this study with relative permittivity in the range of 65–78 and dielectric loss tangent values of 0.002–0.05 can attract considerable attention for the use of LMO-ST composites in the industry of electroceramics.

# Synthesis and characterization of 50% vol. GdIG-50% vol. YIG ceramic material fabricated by a new reactive sintering method

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## Abstract:

Gadolinium-iron garnet ($Gd_3Fe_5O_{12}$, GdIG) based materials attract growing interest, especially in the advanced electronic industry as waveguide optical insulators or memory devices, and microwave insulators, due to their outstanding magneto-optic properties. There are several recent literature reports regarding enhanced properties of the garnets in one of three forms: polycrystalline, monocrystalline and thin films.

Current research efforts arefocused on doping of GdIG with other ions in order to enhance its properties, e.g., the introduction of yttrium ($Y_{(3-x)}Gd_xFe_5O_{12}$, YIG) or dysprosium ($Dy_{(3-x)}Gd_xFe_5O_{12}$, DyIG), which improve magnetic properties of gadolinium-iron garnets,. The typical garnet synthesis route involves a solid-state reaction between rare-earth (III) oxide and iron (III) oxide ($Fe_2O_3$). Thus, although being effortless, such an approach has several disadvantages like extended and energy-consuming grinding or need for elongated sintering time (12h) at elevated temperatures (1400°C). From the industrial-scale production point of view, developing novel, cheaper, and more efficient synthesis routes seems to be of peculiar interest. Additionally, such methods can possibly be further transferred to different types of garnet materials.

A major contribution to these attractive properties, Fe ions, are localized in two different crystallographic sites; $Fe^{2+}$ ions occupy the octahedral sites, where$Fe^{3+}$ the tetrahedral sites formed by the nearest oxygen ions. The magnetic moment of Fe is coupled by two spin-antiparallel a-site and d-site Fe through super-exchange interaction. The magnetic moment of a rare-earth element introduced at the c-site is antiparallel to the iron atoms. GdIG/YIG composite possesses three different magnetic temperatures: compensated ($T_{comp}$), the magnetocaloric effect ($T_o$) and the Neel ($T_N$). These temperatures are between the values of the pure GdIG and YIG bulk. The composite GdIG/ YIG change from the insulator to semiconductor behavior with energy gap at 1eV, between $T_{comp}$ to $T_o$.

The aim of this work was to obtain dense polycrystalline gadolinium-dysprosium-iron-garnet material (50% vol. GdIG, 50% vol. YIG) by a reactive sintering method based on a solid-state reaction between yttrium-iron perovskite ($YFeO_3$), gadolinium-iron perovskite ($GdFeO_3$) and iron oxide ($\alpha$-$Fe_2O_3$) and characterization of magnetic and transport properties the composite was performed.

# Dielectric properties of plasma sprayed coatings for insulation application

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## Abstract:

Thermal spraying provides a rapid method for additive deposition of various ceramics as electrical insulation in applications where polymers are not suitable. New applications in complex shaped additive manufactured metal parts are emerging for example in large scale electrical devices. Microstructural and dielectric evaluation of coatings is crucial to the employment of such free-form processes. The properties and microstructure of the plasma sprayed alumina coatings are compared with dense reference samples of the same powder produced by spark plasma sintering (SPS). To obtain dense bulk samples from the coarse alumina powder for spray coating, SPS is used.

Samples are fabricated by atmospheric plasma spraying (APS) of commercially available alumina powder ($d_{50}$ = 33 μm) on copper substrates and by SPS of the same powder. Microstructure and porosity were analyzed by optical microscopy and scanning electron microscopy (SEM). Phase compositions were determined by X-ray diffraction (XRD). Dielectric properties such as DC resistance, dielectric strength, dielectric loss, and relative permittivity were determined according to the standards. The microstructure and dielectric properties of the coating and bulk material are compared to assess whether the coating is suitable for use in electrical insulation application.

## Acknowledgements:

This work was funded by the Werner-von-Siemens Centre for Industry and Science (WvSC).

# BaTiO3-based thermistor hollow fibers prepared using a phase inversion spinning process for energy efficient gas sorption

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## Abstract:

Current temperature swing adsorption technologies are inefficient, due to waste heat generation and long adsorbent regeneration times. Functional electroceramic hollow fibers with self-regulated heating for adsorbent regeneration may offer an energy efficient alternative to prevailing current technologies.

In this work, La-doped $BaTiO_3$ hollow fibers with a positive temperature coefficient of resistivity (PTCR) have been developed. They offer self-regulating and self-limiting thermistor heating characteristics, with low thermal mass for the rapid regeneration of an inner adsorbent layer through directed Joule heating. Such a hollow fiber design furthermore limits the pressure drop and prevents adsorbent bed settling and channeling.

As an alternative to other predominant extrusion based shaping techniques, an economic phase inversion process was developed to shape the fibers directly from a powder suspension. Though phase inversion may introduce certain flaw typologies in the green body, which depend on the phase inversion conditions, some could be removed during sintering depending on the type and size. It illustrates that the process may be suitable for applications where low mechanical strength is required, notwithstanding further optimisation of the phase inversion process or post-processings steps. Hydrothermal synthesis was then implemented to deposit an adsorbent porous zeolite X layer within the hollow fiber lumen, which was confirmed by electron dispersive X-ray spectroscopy and $CO_2$ adsorption at 0°C. The interrelationships between hollow fiber synthesis route, microstructure, adsorption characteristics, electrical properties and self-regulating heating performance were then studied.

## Acknowledgements:

The authors gratefully acknowledge financial support from Horizon 2020 Marie Sklodowska-Curie Actions for funding of the Individual Fellowship SmartSorp project (Smart Ceramic Hollow Fibers for Energy Efficient Gas and Vapour Sorption), grant agreement no. 843988.

# The Piezotronic Effect of Single Grain Boundaries in Zinc Oxide Varistors

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## Abstract:

ZnO varistors are electroceramic components used as overvoltage protection in electronic devices. Negative charges at the nanoscaled grain boundaries of polycrystalline ZnO varistor materials generate so-called Double-Schottky Barriers (DSBs). The DSBs cause the highly non-linear current-voltage (I-V) characteristics of such materials. Due to the piezoelectric nature of ZnO they can be piezotronically modified by mechanical stress induced surface charges.

In principle, depending on the direction of the polar axis in adjacent grains, the grain boundary barriers can be decreased, enhanced or remain almost constant. Hitherto, effectively only the piezotronic barrier decrease has been verified experimentally in macroscopic varistor components. Therefore compressive tests on selected low-voltage multilayer ZnO varistors, which are dominated by one single current path, have been performed in order to reveal all three theoretically predicted effects.

To investigate directly the impact of the mechanical stress state on selected DSBs polished micro-sections were attached on a piezo-ceramic stage. By applying different biaxial compressive stress states the modification of the IV-characteristics of single grain boundaries could be observed directly by a micro 4-point probe technique. In most cases a strong dependence on the current direction, but also on the applied stress has been found.

# Identification of Sr vacancies and Ti on Sr sites as the origin of ultra-low conductivity in doped SrTiO3 thin films

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## Abstract:

$SrTiO_3$ has been intensively investigated over many years. As a result, its bulk defect chemistry is very well understood, allowing the tailoring of electrochemical properties to application needs. However, recent developments in many fields, e.g., resistive switching in memristive devices or solar cells for the Internet of Things (IoT), are accompanied by a strong reduction in size. Thus, material engineering is faced with new challenges. Although, a change of electrochemical properties in $SrTiO_3$ due to size reduction has already been reported, the understanding of the relation between structure/composition and electrical properties is still limited for nanosized material such as thin films.

In this study, undoped as well as acceptor-doped $SrTiO_3$ thin films were prepared by pulsed laser deposition (PLD). Surprisingly, ultralow conductivity was found in such films irrespective of dopant (Fe, Al, Ni) and doping concentration (up to 10%). Actually, in all films the Fermi-level was pinned mid-gap. For a better understanding, the thin films were further characterized by reciprocal space mapping (RSM) and ICP-OES measurements, revealing a severe Sr deficiency. Further investigations indicate that Sr deficiency starts a cascade of defect chemical adjustments: Site changes ( and/or ), and Sr vacancy mid-gap states cause a Fermi level pinning for a broad doping range. Defect chemical modeling reveals a self-balancing of Ti site changes and this can explain the very robust pseudo-intrinsic conductivity found in all those samples.

# Study of the effect of heterovalent doping on the piezoelectrical properties of BiFeO3

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## Abstract:

$BiFeO_3$ has certain advantages over other piezoelectric materials. BFO is a lead-free ferroelectric with multiferroic properties. But BFO still have a problem with a high electrical leakage current and the associated difficulties in poling. Mostly, problems with leakage currents are associated with oxygen vacancies and defects associated with them. Through doping it is possible to control the density of free moving charges and oxygen vacancies in the sample, which ultimately helps to impart certain characteristics to the doped sample. The introduction of ions with greater positive valence, like $Ti^{4+}$, $Mn^{4+}$, will lead to a reduction of the net positive charge. This will lead to the conversion of $Fe^{3+}$ to $Fe^{2+}$ and the reduction of oxygen vacancies (lower leakage currents). $Co^{2+,3+}$ doping may also reduce the electrical conductivity and improve the ferroelectric properties.

We used the method of solid-phase reaction synthesis with subsequent sintering for sample preparation. To reduce the conductivity, doping with transition metals Ti (1-5 at%) and Co (0.125-3 at%) at the B-site has been investigated and is thought to reduce electrical conductivity by reducing the concentration of oxygen vacancies.

Cobalt doping reduces the required field for poling, but also increases the leakage currents. Titanium doping reduces the leakage currents but destroys the piezoelectric properties as the coercive field strength cannot be reached. However, when both elements are used simultaneously at their appropriate levels a piezo ceramic material is obtained requiring a low field field for full poling (9 kV/mm) compare to pure BFO(11-12 kV/mm) and excellent room temperature performance such as a $d_{33} = 40$ pC/N.

# Magnetic performance of SrFe12O19 magnets consolidated by Sintering by Intense thermal radiation (SITR)

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## Abstract:

Permanent magnets are key elements in modern devices and enabling technologies as they allow storing, delivering and converting energy. Ferrite-based permanent magnets are, in terms of volume, one of the most used permanent magnetic materials in the world [1]. The goal of our study was to produce a strontium hexaferrite magnet by sintering by the intense thermal radiation (SITR) route. To our knowledge, this is the first time that SITR is being used for the consolidation of ferrite magnets.

In our study, we performed tests on commercially available strontium hexaferrite (SrFe12O19, SFO) powder. First, we tested the consolidation rate of strontium hexaferrite at different temperatures with a dilatometer, and then we performed a set of experiments with different sintering conditions such as temperature, retention time, heating rate and magnetic pre-orientation. To begin with, we tested the magnetic properties of starting SFO powders and sintered pieces with a Vibrating Sample Magnetometer (VSM). We observed a noteworthy increase of coercivity, remanence and consequently increase in maximum energy product when changing sintering temperature and magnetic preorientation. On the other hand, other sintering parameters played only a minor role in enhancing the magnetic properties. Although we managed to produce samples with magnetic incentive properties, we are still struggling with achieving a good samples' density.

Based on the obtained results, we are confident that sintering by intense thermal radiation is a promising material consolidation path that will enable us a production of strontium hexaferrite magnets in a way that saves time and energy, which price has recently been rising sharply.

## Acknowledgements:

This work is supported by Slovenian Research Agency that is funding the research program Ceramics and complementary materials for advanced engineering and biomedical applications (P2-0087), CEMM, JSI for the use of EM.

# Synthesis and Photoluminescent Properties of Pr3+-Doped (Ba,Ca) TixZr(1-x)O3 Perovskite Diphasic Ceramics Obtained by the Modified Pechini Method

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## Abstract:

Rapid and intense development in the field of electromechanical devices directed the interest of the researchers toward multifunctional materials. Remarkable electrical and optical properties might be obtained in the $Pr^{3+}$-doped Ba-Ca-Ti-Zr-O system.

The solid solutions of $(Ba,Ca)Ti_xZr_{(1-x)}O_3:Pr^{3+}$, $0.7 \leq x \leq 1$ with 0.05 step and Ba:Ca ratio set as 1:1, were successfully synthesized using the Pechini method combined with the sintering at relatively low temperature (1450 °C). The obtained materials were characterized by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). The analysis revealed that all samples are diphasic and consist of orthorhombic Ca-rich phase and tetragonal (for $x=1$)/pseudocubic (for $x<1$) Ba-rich phase. The $Pr^{3+}$ doped-$(Ba,Ca)Ti_xZr_{(1-x)}O_3$ diphasic material generates intense, red photoluminescence (PL) emission at room temperature. The optical properties were significantly improved with the $Ti^{4+}$ substitution by $Zr^{4+}$ ions, achieving the highest intensity of the emission for $x=0.7$. The emission spectra patterns are identical to the characteristic emission lines of $Pr^{3+}$ ions and the narrow emission bands for all samples were centered at 612 nm, which corresponds to $^1D_2$-$^3H_4$ recombination. The dielectric properties of the obtained samples were systematically studied revealing stable dielectric properties with low $\tan\delta$ values.

As a result, the $Pr^{3+}$-doped $(Ba,Ca)(Ti,Zr)O_3$ ceramics is a promising candidate for environmentally friendly, versatile material by combining good dielectric and enhanced photoluminescence with a prognosis for the manifestation of multifunctional effects.

## Funding:

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# Effect of sintering temperature on microstructure and thermoelectric properties of pure and Al-doped n-type ZnO

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## Abstract:

Zinc oxide is an intrinsic n-type semiconductor and a promising thermoelectric material. The influence of thermal treatment on pure and doped ZnO yields different microstructures. Additives, such as $Al_2O_3$, not only modify electronic properties but also form inclusions of secondary phases that hinder the grain growth of the main phase and modify the obtained microstructure. Here we establish the relation between the microstructure of pressureless sintered ZnO-based materials and their thermal and electrical properties. Samples of pure and $Al_2O_3$-doped ZnO were sintered to over 90% theoretical density in the temperature range of 1000 to 1450°C. The samples with varying microstructures and grain sizes were investigated on their mean grain size and grain distribution, electrical conductivity, Seebeck coefficient, thermal conductivity, power factor and dimensionless figure of merit ZT.

## Acknowledgements:

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# Quenching-induced changes in crystallographic structure and polarized volume of Na1/2Bi1/2TiO3-BaTiO3 piezoceramics

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[2] *North Carolina State University, Raleigh, United States*

## Abstract:

($Na_{1/2}Bi_{1/2}$)$TiO_3$-based solid solutions are promising candidates for high power applications. Quenching has been established as a viable method to increase the depolarization temperature, $T_d$ (at which the piezoelectricity vanishes), without severely deteriorating the electromechanical properties.

To investigate the effect of quenching on the crystallographic structure and changes in the polarized volume, here the volume fraction of polar nanoregions in situ electric-field dependent synchrotron diffraction experiments and resonance frequency damping analysis (RFDA) on ($Na_{1/2}Bi_{1/2}$)$TiO_3$-$BaTiO_3$ with 6 and 9 mol.% BT were undertaken. RFDA was used to measure the temperature dependent Young's modulus from 25°C to 800°C. The sensitivity of mechanical properties to structural changes even on a nanoscale allows correlation of Young's modulus to the fraction of temperature-sensitive polarized volume by a composite model. For the quenched samples, the fraction of polarized volume is increased by up to ~ 12 % at elevated temperatures compared to the furnace cooled ones, reinforcing the assumption of a stabilized ferroelectric state. Additionally, changes in unit cell parameters and phase fraction were established and utilized to calculate volumetric strain as a function of electric field. Quenching enhances the lattice distortion and causes an absence of field-induced phase transformation, resulting in negligible volumetric strain and corroborating a stabilization of the ferroelectric order.

# Characterization of the thermal and mechanical properties of C12A7-Mo composites as electron emitting ceramic

Katja Wätzig[1], Jochen Schilm[1], Christian Drobny[2], Martin Tajmar[2], Mihails Kusnezoff[1]

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## Abstract:

Ceramic materials with electron-emitting properties are suitable for different applications, e. g. space propulsion of satellites, thermionic converter for power generation, and X-ray detection. To achieve high current densities by electron emission, the material has to provide a low electron work function combined with good thermal stability. The composition $[Ca_{12}Al_{14}O_{31}]^{4+}4e^{-}$ (C12A7) has a work function of < 2.4 eV, which results in considerable current measured below a temperature of 1000 °C in vacuum [1]. However, ceramic is brittle and has low thermal conductivity. These poor thermal and mechanical properties lead to failure due to thermal stress during application [2].

In this study, we are presenting the advantages by mixing C12A7 and Mo metal to prepare a C12A7-Mo composite cermet. The microstructure, thermal expansion coefficient, thermal conductivity, hardness, and 4-point bending strength of composites with varying Mo content are characterized. The improved properties of composites resulted in the enhanced performance of a heaterless hollow cathode (plasma electron source) showing endurance operation close to 1000 h [3].

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# Fabrication and Evaluation of Composites of Sendust-$Al_2O_3$

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## Abstract:

Sendusts are iron, silicon, and aluminum alloys, whose initial relative permeability varies dramatically depending on their composition, with some showing a maximum value of about 120,000. The complex relative permeability is highly dependent on the frequency, and the real part of the complex relative permeability becomes extremely small in the high frequency domain, and the magnetic effect cannot be utilized.

It is difficult to process sendust's sintered body due to its extremely high hardness.

In addition, since sendust is an alloy and has a large electric conductivity as metals, it is difficult to be applied as wave absorber.

It is considered that the decrease of complex relative permeability at high frequencies can be suppressed by mixing sendust with the insulator powders that do not react.

The aim of this study is to fabricate composites of sendust and $\alpha$-type aluminum oxide (alumina) with different mixing rate, to hinder the conductivity and enhance the magnetic characteristics in the microwave frequency region.

The composite was sintered above 1000°C at high vacuum carbon electric furnace, and the magnetic properties such as the complex relative permeability were evaluated.

The relative permeability of the sintered composite was larger than that of sendust in high frequencies, which suppressed the decrease of the permeability.

Furthermore, it was found that the boundary line of Snoek changed by changing the mixing rate. It is suggested that this sintered composite of sendust and alumina can be used as wave absorbers.

# Thermoelectric Properties and Phase Analysis of Cu-Rich Tetrahedrite Prepared by Solvothermal Synthesis

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## Abstract:

In the last decades, more and more sulfide-based thermoelectric materials have been reported as excellent candidates for the construction of TEG converters. Many transitional metal sulfides show good TE performance caused by their ultralow lattice thermal conductivity and promising electronic properties. They also possess excellent features for widespread commercial use, such as non-toxicity and low price caused by high abundance. Within the promising sulfide-based thermoelectrics, there are also materials that crystallize in the tetrahedrite-type structure. The early investigation of the naturally-occurring $Cu_{12}Sb_4S_{13}$ mineral has opened a large playground for this promising family of compounds.

DFT calculations reveal that the additional copper atoms in Cu-rich $Cu_{14}Sb_4S_{13}$ tetrahedrite can effectively engineer the chemical potential towards high thermoelectric performance. In this work the Cu-rich tetrahedrite phase was prepared using a novel approach, which is based on the solvothermal method and 1-(2-aminoethyl) piperazine (AEP) serving both as solvent and reagent. As only pure elements were used for the synthesis, the offered method allows us to avoid the typically observed inorganic salt contaminations in products. Prepared in such a way, $Cu_{14}Sb_4S_{13}$ tetrahedrite materials possess a very high Seebeck coefficient (above 400 $\mu VK^{-1}$) and low thermal conductivity (below 0.3 $Wm^{-1}K^{-1}$), yielding to an excellent dimensionless thermoelectric figure of merit $ZT \approx 0.65$ at 723 K. The further enhancement of the thermoelectric performance is expected after attuning the carrier con-centration to the optimal value for achieving the highest possible power factor in this system.

## Acknowledgements:

The research was funded by the Foundation for Polish Science (TEAM-TECH/2016-2/14 Grant “New approach for the development of efficient materials for direct conversion of heat into electricity”), co-financed by the European Union under the European Regional Development Fund.

# Effects of boron oxide addition on electrical properties of yttrium-doped bismuth-based zinc oxide varistors

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## Abstract:

Ultra-high voltage (UHV) transmission refers to transmission lines that operate at voltages higher than 800kV to 1100kV, and is expected to be an extremely efficient method of power transfer. To protect UHV systems from lightning strikes, the arresters must be large enough to maintain the voltage. This requires increasing working voltage while maintaining device size. The key component in arresters is the ZnO varistor, an electronic component with "diode-like" nonlinear voltage—current characteristics, due to the formation of double Schottky barriers at grain boundaries. Yttrium oxide can be used to increase varistor voltage by inhibiting ZnO grain sizes; in our previous research, the varistor voltage could be easily raised to over 1000V/mm by adjusting yttrium oxide content. However, the device shows a large leakage current under working bias, leading to an increase in power loss. In order to reduce leakage current while maintaining the other electrical properties of Y-doped varistors, boron oxide was added in different concentrations. The optimal amount of $B_2O_3$ (0.75mol%) drastically improved the electrical properties of Y-doped varistors, reducing the leakage current to 0.8μA/cm$^2$ while maintaining exceptional long-term stability to DC electrical degradation and a voltage around 900 V/mm. A Bi-B-O glass phase was observed at grain boundaries, correlated with increasing B amount. This thin layer led to a decrease of Co concentration in ZnO which affected the donor density and the electrical properties. A new analytical method using the differential resistance for the nonlinear voltage–current relation was proposed, separating three differential resistance values, and was used to analyze the corresponding conduction process in different regions of the energy band.

# Effect of temperature on permittivity and piezoelectric response in mechanically deformed BaTiO3 single crystals

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## Abstract:

Defect engineering is the most popular concept to tune electro-mechanical properties in ferroic materials. For example, point defect doping has been widely utilized to tune functionalities in ferroelectrics, but they have severe shortcomings with respect to temperature stability.[1] Recently, we demonstrated a new approach using mechanical dislocation imprint to control ferroelectric properties in bulk single-crystal $BaTiO_3$.[2] Mechanical dislocation imprint yielded a 19-fold increase of the piezoelectric response as compared to the reference sample without dislocations, and maintained a thermally-stable piezoelectric coefficient up to 75 °C.[2]

This talk is focused on temperature stability of dislocation-tuned dielectric and piezoelectric responses. For this purpose, we introduced dislocation networks in a controlled manner in bulk $BaTiO_3$ single crystals using high temperature plastic deformation. The compression experiments were carried out by loading along the [110] direction to activate the high temperature slip system {100}<010>. Our results revealed that large-signal permittivity and electromechanical properties remained stable and high [permittivity > 20000 and $d_{33}^* > 1800$ pm/V] up to the Curie temperature at 135 °C. Our findings demonstrate the potential of plastic deformation and opens new avenues to engineer defects in ferroelectrics beyond chemical doping.

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## Acknowledgements:

This work is supported by project no. 414179371 of the German Research Foundation (DFG). Fangping Zhuo acknowledges support from the Alexander von Humboldt Foundation for the fellowship with award number 1203828.

# Symposium F: Electronic Ceramics

Invited presentation:

# Peculiar and enhanced properties in BaTiO3 ceramics with structural instability induced by composition, density or grain size

Liliana Mitoseriu, Leontin Padurariu, Cristina Ciomaga, Lavinia Curecheriu, Nadejda Horchidan, Vlad Alexandru Lukacs

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## Abstract:

Peculiar and enhanced properties in $BaTiO_3$ ceramics with structural instability induced by composition, density or grain size

The presence of polymorph superposition in ferroelectric oxides promotes enhanced properties. For $BaTiO_3$ ceramics, the orthorhombic-tetragonal (O-T) phase transformation at around (-10, -5)°C can be raised up to room temperature by small amounts of homovalent ions on Ti positions [1], by changing porosity [2] or grain size [3]. Landau-based calculations for ceramics with randomly oriented grains indicated that at any grain size, the polymorph transformations take place within temperature ranges of phase coexistence, with impact on the functional properties. Permittivity vs. field dependences indicate field-induced structural transformation at specific fields, which were confirmed by XRD analysis on poled ceramics. The stability of amounts of O/T phases in 5%Sn-$BaTiO_3$ ceramics explains the field-induced predominant O state and the maximized observed properties around room temperature comparative with ones of $BaTiO_3$. Due to the twelve allowed spontaneous polarization directions, O state promotes enhanced polarization, tunability and piezoelectric properties with respect to the T state (six possible polarization orientations). Low/high porosity of $BaTiO_3$ ceramics with porosity below 26% favors the O/T symmetry around room temperature. The role of strained dislocations in the powders and ceramics is discussed as contributing to the mechanisms promoting the stabilization of O phase and of other low-symmetry polymorphs in $BaTiO_3$ ceramics.

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## Acknowledgements:

This work is supported by PN-III-P4-ID-PCCF-2016-0175 (HighKDevice) Romanian grant.

# Electrophoretic deposition of the protective layers on the SOC stack components using powders with multimodal grain size distribution.

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## Abstract:

SOC (Solid Oxide Cells) technologies offer the possibility of generating electricity with negligible emission of environmentally harmful compounds and offer storage of the energy in the form of P2G (power-to-gas) conversion. These features make SOCs attractive as for commercialization on a global scale, however there are issues, related to costs and long term operability, which should be solved on research level. One of such issues, related to stable and long-lasting operation of the SOC stack, is fabrication of the ceramic protective layers on interconnects made from ferritic chromium steel. These layers are designed to prevent the evaporation of volatile chromia compounds that lead to degradation of the air electrode and to reduce the formation of the low-conducting scale on steel surface. Ordinarily, protective layers are fabricated from spinel-type powders, which provide adequate thermal expansion and electrical conductivity under the operating conditions of the SOC stack.

As part of research carried out, commercially available manganese cobalt oxide $(Mn_{1.5}Co_{1.5})O_4$ (from Kceracell Korea) was used. The studies were focused on investigation of the process of forming the protective layer via electrophoretic deposition (EPD) taking into special consideration the influence of the grain size of the spinel powder on the final layer properties. Three fractions of MCO powder were prepared with different grain sizes (0.15-0.6 μm). The powders were mixed in different proportions to form multimodal compositions. The prepared layers were subjected to microstructural observations and area specific resistance (ASR) measurements. This approach allowed to deposit protective layers with better properties than those observed for the layer fabricated from unmodified powder.

## Acknowledgements:

National Science Centre Poland project Harmonia: Quest for novel materials for solid oxide cell interconnect coatings (CPE/010/Harmonia1/21).

# Effect of doping on the electrical and electrochemical characteristics of Potassium sodium niobate ceramics

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## Abstract:

The knowledge of point defect thermodynamics on lead-free KNN ceramics is not studied extensively compared to its lead-based counterparts. However, doping strategies could modify properties by altering the ferroelectric response. In this work, acceptor and donor dopants have been incorporated in Potassium sodium niobate-based ceramics to generate electronic defects in ferroelectric KNN. A-site and B-site substituted $(K_{0.4675}Na_{0.4675}Li_{0.065})(Nb_{0.92}Ta_{0.08})O_3$ perovskite were prepared via conventional solid oxide synthesis route. Materials properties of crystal structure, microstructures, electrical resistivity, and dielectric permittivity, in wide temperature range, are reported for the series of $(K_{0.4675}Na_{0.4675}Li_{0.065})_{(1-2x)}(Nb_{0.92}Ta_{0.08})O_3$-xCa and $(K_{0.4675}Na_{0.4675}Li_{0.065})(Nb_{0.92}Ta_{0.08})_{(1-y)}O_3$-yFe with concentration from x= 0 to x=0.04. The results indicate that doping decreases the Curie temperature; however, the induced extrinsic defects are responsible for increased electronic conductivity than the un-doped KNN (x=0). Nevertheless, further electromechanical investigations (large-signal polarization and strain measured in given applied electric fields) reveal that incorporating dopants leads to a significantly modified polarization (P-E) response.

## Acknowledgements:

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# Broadband dielectric spectroscopy of BaTi1-xSnxO3 solid solutions

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## Abstract:

The relaxor behavior of $BaTiO_3$ (BTO)-based solid solutions has been extensively studied due to their potential applications in energy harvesting, electrocalorics and multi-layered capacitors. The main focus is on the homovalent substituted barium titanate. The most common substitution for the B-site titanium ion are carried out with zirconium, cerium and tin which have larger ionic radius than titanium itself. These ions are ferroelectrically-inactive. The increase of concentration of substitutional species suppresses the ferroelectric phase by merging three phase transitions of barium titanate and developing of a broad relaxor-like dielectric dispersion.

It has been argued that BTO-based relaxors have features that are more common to the dipolar/spin glasses [1,2]. The broadband dielectric spectroscopy of $BaTi_{1-x}Zr_xO_3$ revealed that the mean relaxation time obeys Arrhenius law [3].

In this contribution we present the dielectric results of $BaTi_{1-x}Sn_xO_3$ ($x = 0.15; 0.2; 0.25; 0.3$) in 1 mHz – 1 THz frequency range. The system will be compared to the canonical Pb-based relaxors and other homovalent-substituted BTO relaxors. The presence of Vogel-Fulcher freezing phenomena will be discussed.

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## Acknowledgements:

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# Room Temperature H2 Sensing of a Pt-BaTiO3-Pt System Prepared by Spark Plasma Sintering

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## Abstract:

There is an increasing demand for metal oxide-based gas sensors, such as $TiO_2$, ZnO, $SnO_2$ and $BaTiO_3$, for flammable and toxic gas detection ($H_2$ and CO), due to their simplicity and low production costs. During processing of n-type metal oxides in oxygen containing atmospheres, adsorption of oxygen occurs at the grain boundaries, which can become charged, due to fast electron transfer from the conduction band to the adsorbed oxygen, forming ionosorbed oxygen species ($O_2^-$, $O^-$, $O^{2-}$). The $H_2$ sensing mechanism in metal oxides is thought to occur due to the interaction of $H_2$ with ionosorbed oxygen species, which causes lowering of the grain boundary Schottky barriers, resulting in an increase in electronic conductivity. However, this mechanism is still debated. Additionally, the incorporation of a thin surface layer of platinum can facilitate the dissociative chemisorption of $H_2$ at room temperature and increase the sensor sensitivity towards $H_2$.

In our recent work, we have used in-situ electrochemical impedance spectroscopy (EIS) to monitor the oxidation of n-type $BaTiO_3$. Upon cooling to room temperature, a significant $H_2$ sensing effect is observed for spark plasma sintered $BaTiO_3$ when platinum electrode contacts are used. Using the ambient pressure photoelectron spectroscopy (AP-XPS) facility at the Swiss Light Source, we have identified the ionosorbed species responsible for the room temperature $H_2$ sensing mechanism and studied their interaction with $H_2$ at various temperatures and $H_2$ pressures. The results are discussed in terms of EIS measurements performed on Pt-$BaTiO_3$-pt, as a function of $pH_2$ and temperature, as well as characterization of $H_2$ interactions with surface oxygen groups using AP-XPS.

## Acknowledgements:

The authors gratefully acknowledge financial support from the EU Commission, Horizon 2020, for funding of the Marie Sklodowska Curie Individual Fellowship SmartSorp project (Smart Ceramic Hollow Fibers for Energy Efficient Gas and Vapour Sorption), ERC grant agreement no. 843988.

# Ultra-thin zirconia diaphragm for electromechanical sensors

# Ultra-thin zirconia diaphragm for electromechanical sensors

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## Abstract:

In the last decades, MEMS (micro electromechanical systems) were established as standard for many sensor applications, due to high reliability, small dimensions, high integration level and low costs. Most devices as e.g. inertial or pressure sensors are based on thin membranes with the mechanical conditions of stress or deflection as a measure of the sensor device. However, this technology is limited to moderate temperatures of about 130°C mainly due to the semiconductor behaviour of silicon and materials used.

For higher temperatures, glass-ceramic LTCC (low temperature cofired ceramics) and HTCC materials are well-established alternatives and offer the possibility of 3-dimensional metallization due to the multilayer approach. However, high costs, the limitation to about 300°C in the case of LTCC are avoiding commercial success of ceramic MEMS sensors.

In the present work, we present a novel approach to use ultra-thin zirconia tapes down to 40 µm. These 3YSZ (yttrium doped zirconia) tapes exhibit excellent high temperature stability with perfect mechanical elastic behavior. The slurry composition for tape casting is optimized for subsequent lamination onto conventional zirconia sheets by different organic additives and ceramic powders (regarding for example BET and particle size). Consequently, lamination and sintering are adopted to the different tapes. Besides avoiding delamination, targeted goals are evenness and absence of cracks. This sensor design can be realized by one single metallization layer. This enables the compatibility with thin film technology and minimizes the production steps.

In the final presentation, we will show first pressure sensors with measurements at high temperatures and aging above 800°C.

## Acknowledgements:

The authors acknowledge the financial support by the Bavarian Research Foundation.

# In-situ scanning transmission electron microscopy study of ferroelectric domain walls

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## Abstract:

Ferroelectric domain walls (DWs), atomic-level interfaces between domains with different polarization orientation, are proposed as possible active components in nano and atomic level electronics [Nature Reviews. Physics 2, 634-648, 2020]. The key property of DWs is their dynamics: their structure can be changed, they can be moved or even erased when an electric field (EF) is applied. However, the generic understanding of ferroelectricity and polarization switching is currently based on macroscopic investigations. Extensive dynamic studies at the local level are required to make the DW "the device". Excitingly, the recent developments of transmission electron microscopy (TEM) allow sub-Angstrom spatial resolution and the capability to observe the material while simultaneously applying external stimuli.

Herein, we study the interaction between EF and DWs in lead-free ferroelectric single crystals (such as bismuth ferrite and sodium potassium niobate) by in-situ voltage bias atomic resolution scanning-TEM (STEM). The experiment takes place at values of the EF lower than the macroscopic coercive field; this approach brings the experiment within the temporal resolution of the STEM technique. Moreover, it has been shown that DW motion is only relevant at EF below the critical coercive fields, while above the coercive field, random nucleation is the dominant switching mechanism [Scientific Reports 7, 806, 2017]. We show several local events taking place at the DW level when EF is applied: DW movement, local alteration in the DW structure accompanied by a change in unit cell distortion and modification of the bound charge configuration. In addition, most of our experiments prove that the response is asymmetric to opposed biases.

# Exploring critical conditions (composition and grain size) as a new tool for enhancing electrocaloric properties of BaTiO3 -based ceramics

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## Abstract:

In the last years, there is a high interest in developing alternative cooling technologies because high current densities in integrated circuits impose higher demands on cooling systems that cannot met by the fan-based solutions. The main advantage of electrocaloric (EC) refrigeration is that by comparison with magnetocaloric solid-state refrigerators based on another solid-state cooling technology, the big-sized magnet is still a drawback. $BaTiO_3$ (BT) family as EC materials has been studied quite extensively in the past several years in various forms including thin films, bulk ceramics (also multilayer ceramic capacitors -MLCC) and single crystals and a large ΔT has been reported for BT-ceramics in the vicinity of ferroelectric-paraelectric (FE-PE) phase transition. Owing to the high transition temperature the using of pure BT as EC materials is limited, but this can be properly modified by incorporation of suitable dopants.

In the present work we proposed to study the effect of composition and grain size on the electrocaloric effect in $BaTiO_3$ based ceramics ($Ba_xCa_{1-x}TiO_3$, 1%Eu -$BaZr_xTi_{1-x}O_3$ and $BaZr_xTi_{1-x}O_3$ with $x<0.20$). Ceramics were obtained by sintering at 1400-1500 °C the solid-state powders. X-ray diffraction data showed the phase purity and SEM images demonstrated homogeneous microstructures and well-defined grain boundaries. Impedance spectroscopy in the temperature range of (25 to 150)°C shows good dielectric properties for all systems and a composition-induced ferroelectric-to-relaxor crossover for $BaZr_xTi_{1-x}O_3$ - based ceramics. ECE was indirect evaluated from P(E) loops with temperature and in case of Zr addition a maximum of 0.7 K was obtained for $x=0.04$ at 373K.

## Acknowledgements:

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# Ultralow thermal conductivity of molybdenum oxides

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## Abstract:

Materials exhibiting a low thermal conductivity (k) are the key components in several areas such as thermal barrier coatings (TBCs) or thermoelectric materials (figure of merit $ZT = S^2sT/k$, where S is the Seebeck coefficient, s the electrical conductivity and T the temperature). Winter & Clarke [1]. reported that $La_2Mo_2O_9$ exhibits a lower thermal conductivity than Yttrium-Stabilized Zirconia, the reference material for TBC applications. A 50% praseodymium substitution on the lanthanum site leads to the lowest thermal conductivity ever reported in this system (-11–18% compared to $La_2Mo_2O_9$, depending on temperature.) [2]. Recently, Liu et al. [3], predicted ultra-low thermal conductivity in scheelites ($ABO_4$). For instance, $BaMoO_4$ thermal conductivity is expected to reach value below 1 $Wm^{-1}K^{-1}$. In perovskites ($ABO_3$), it has been reported that A-site deficiency leads to significantly lowered lower thermal conductivity values [4]. Therefore, the thermal conductivity of A-deficient scheelite $La_2Mo_3O_{12}$ ceramics has been explored and one of the lowest thermal conductivity value reported for a dense crystalline oxide have been measured ($\approx 0.65$ $Wm^{-1}K^{-1}$ in the range of 400–1000 K) [5].

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# $BaZr0.8Y0.2O3$-δ as electrolyte material for Protonic Ceramic Fuel Cell: from its supercritical hydrothermal synthesis to its electrochemical properties.

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## Abstract:

One of the current global challenges is to find novel, clean and efficient techniques for energy production. The use of electrochemical cells and hydrogen is one of the solutions. Among the different fuel cells, the Protonic Ceramic Fuel Cells (PCFCs) have attracted much attention due to their high efficiency at intermediate temperature (400 – 600 °C). Despite intensive research around the world since 1990, several challenges remain in the PCFC area. One of the most important resides in the highly refractory nature of the conventional electrolyte materials such as $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (noted BZY) requiring very high synthesis temperatures by the ceramic route, typically 1500 °C and even higher temperatures during the sintering. To answer this problematic, the hydrothermal synthesis was used in this study.

BZY powder was produced by a novel continuous hydrothermal process at a temperature as low as 400 °C and under a pressure of 300 bar. The obtained BZY powder consists of spherical nanoparticles of about 50 nm in diameter. Secondary phases, $BaCO_3$ and (Y,Zr)O(OH), were also detected, however, a thermal treatment at 1000 °C for 2 hours allows to remove these secondary phases. A densification rate higher than 90 % was achieved after sintering at 1550 °C for 5 hours using 1wt% of ZnO as sintering aid. BZY synthesized by the continuous hydrothermal process presents a relatively high conductivity: $2.5*10^{-3}$ $S.cm^{-1}$ at 600 °C in wet $H_2$. In addition, an activation energy of about 0.5 eV was obtained in the 200 – 600 °C range. This value is typical of protonic conduction and suggests that the protons are the dominant charge carriers in BZY at a temperature lower than 600 °C.

## Acknowledgements:

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# Additive Manufacturing of Sodium Polyaluminate Solid-State Electrolytes

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## Abstract:

This presentation provides the results on the additive manufacture of sodium polyaluminate (Na-$\beta/\beta''$-$Al_2O_3$) electrolyte materials to be used in all solid-state battery structures. The materials of interest are formulated into a high solids content colloidal suspension with desirable viscoelastic properties, suitable for direct ink writing; an extrusion-based 3D printing process. The densification is attempted through a series of conventional and non-conventional processing techniques, to achieve near full density and high ionic conductivity. The physical and electrochemical properties of the electrolyte structures are comprehensively studied using a suite of analytical characterisation techniques, such as X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Electrochemical Impedance Spectroscopy (EIS).

## Acknowledgements:

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# Role of graphene on the electrical and thermal conductivies of doped aluminum nitride ceramics

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## Abstract:

In Power Electronics, the ceramic substrates capable of fulfilling the needed requirements of a power electronics module are $Al_2O_3$, AlN and $Si_3N_4$. Aluminum nitride (AlN) is the most promising material towards high temperature and voltage applications. AlN presents excellent thermal and electrical properties, a thermal expansion coefficient close to the one of silicon and high mechanical properties. The elaboration of dense aluminum nitride (AlN) ceramics can be obtained by Spark Plasma Sintering (SPS), known for its ability to accelerate the kinetics of sintering. Moreover, many papers have been reported on the development by SPS of composite ceramics (AlN + $Y_2O_3$) exhibiting a highly densified microstructure with compounds (YAG, YAP, YAM,..) concentrated at the grain boundaries. It has also been mentionned that the addition of calcium fluoride $CaF_2$ to a mixture of AlN and $Y_2O_3$ leads to the formation of secondary phases that clean the grain boundaries and improve thermal properties. However, little work has been reported on the electrical properties of these AlN based ceramics, especially the electrical conductivity. Indeed, it is only for a few years that the graphene multilayers (MCG) have been incorporated in the AlN microstructure in order to control its electrical conductivity.

In this work, dense AlN based ceramics, containing $Y_2O_3$, $CaF_2$ and MCG have been elaborated and characterized. We will focus on the evolution of the electrical conductivity and the thermal conductivity, as a function of MCG quality and quantity

# Composite cathode layers for solid-state lithium batteries: What should we pay attention to?

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## Abstract:

Rechargeable batteries are considered as the most efficient energy storage system for a large number of mobile and portable applications. Electrolytes, separators, electrodes architecture, and cell chemistry are key factors to extend the lifetime, enhance the safety, and lower the cost of such electrochemical systems. Ceramic materials are especially attractive as cathode active materials (CAM) and solid electrolytes, both for lithium and sodium chemistries.

In this presentation, strategies such as coating of CAMs will be described in order to increase their stability during electrochemical cycling and limit degradation in liquid organic electrolytes. Such coatings are also attractive to improve the compatibility between solid electrolyte and CAM. Combination of experimental and simulation approaches enable to better understand performance and stability issues. In a second step, advanced ceramic processing methods are required to manufacture composite cathodes for solid state batteries. Tape casting followed by controlled sintering step enables to get dense thick layers with high capacity. Field Assisted Sintering Technology can be applied to reduce time and temperature by applying mechanical pressure during the process and high heating/cooling rates. Finally, numerical simulations help design and optimize composite cathodes in order to reduce mechanical stresses related to volume changes during lithiation/delithiation while maintaining high performance and capacity.

# Scalable fabrication and microstructure optimization of garnet-based ceramic components

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## Abstract:

Ceramic solid state-electrolytes attract significant attention due to their intrinsic safety and, in case of the garnet type $Li_{6.45}Al_{0.05}La_3Zr_{1.6}Ta_{0.4}O_{12}$ (LLZO), the possibility to use Li-metal anodes to provide high energy densities on cell and battery level. However, the widespread application of all solid-state cells depends both on the development of scalable manufacturing processes and the increase of cell capacity.

The plausibility of such processes has been shown, yet the impact of the sensitivity of LLZO to air and protic solvents due to the $Li^+/H^+$-exchange on the reproducibility and the electrochemical properties of the component have only recently been described. This new mechanistic understanding allowed for the development of a new, tailored tape-casting process for LLZO components. Thin, free-standing LLZO separators with a total Li-ion conductivity of $3.90 \cdot 10^{-4}$ S cm$^{-1}$ and a critical current density of over 300 µA cm$^{-2}$ can now be fabricated.

Additionally, the fundamental understanding of the process allowed for the development of all-ceramic free-standing $LiCoO_2$/LLZO mixed cathodes. Further morphology engineering by introduction of a sequential layer casting enabled the production of mixed cathodes resulting with opposite concentration gradients for the active material and the electrolyte over the thickness of the cathode. With this optimized microstructure, the discharge capacity of the mixed cathodes was increased to 2.8 mAh cm$^{-2}$ utilizing 99% of the theoretical capacity. Additionally, the obtained free-standing cathodes have sufficient mechanical stability to allow the application of hybrid and ultra-thin separators to further increase the energy density on the full cell level to industrially relevant levels.

## Acknowledgements:

This work was funded by the German Federal Ministry of Education and Research (BMBF) within of the Festbatt project (FKZ: 13XP0173A) and the LISZUBA project (FKZ: 03XP0115B) and is gratefully acknowledged here. The authors thank Prof. Dina Fattakhova, Prof. Ollivier Guillon, Dr. Martin Finsterbusch, Dr Markus Mann and all the colleagues at IEK-1 for their support.

# Analytical modeling of the effective properties of lead-free piezoelectric ceramics

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## Abstract:

The growing interest in lead-free piezoelectric ceramics was triggered by the legislation regulating the use of lead due the environmental and health concerns. Although the widespread lead zirconate titanate (PZT) ceramics are still the gold standard for most applications, there are strong research initiatives towards alternative materials, and a major lead-free candidate for piezoelectric applications is potassium sodium niobate (KNN) ceramics. Apart from compositional changes, also microstructural changes can be used to obtain or tailor desired properties, e.g. dielectric, piezoelectric and elastic properties, as well as several figures of merit. This contribution presents analytical modeling approaches to predict the effective properties of piezoelectric ceramics, exemplified by KNN. In particular, the cubic cell model predictions for the longitudinal and transversal dielectric constants, piezoelectric charge coefficients, piezoelectric voltage coefficients, elastic constants (stiffness matrix components) and selected figures of merit are compared to the corresponding effective medium approximations based on the single-inclusion solution for oriented spheroids (generalized Eshelby matrix). Reasons for the deviation of real-world data from these model predictions are discussed.

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## Acknowledgements:

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# LSC-GDC and LSCF air electrodes with modified porosity designated for solid oxide cells

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## Abstract:

The development of solid oxide cells started in the Institute of Power Engineering 14 years ago. The standard cells are based on 8YSZ electrolyte, NiO/8YSZ fuel electrode and LSCF and LSC air electrodes, and are designed to operate at temperature of 700°C and lower. In order to produce fuel electrode supported solid oxide cells, low-cost and fast methods with high repeatability are under continuous development. For the preparation of thin layers screen printing is used. Porous fuel electrode support is produced using high pressure injection moulding (HPIM).

During recent years, R&D activities were focused on the improvement of electrical and electrochemical parameters of cells and their components using advanced materials for functional layers. In this study, modification of oxygen electrodes is presented. The aim of the studies was to reduce the thermomechanical stresses between the air electrode and the electrolyte and to modify the porosity in order to improve their gas permeability.

Presentation includes results, related to SOC with LSCF and LSC-GDC air electrodes with porosity modified by means of two pore formers PMMA and synthetic graphite with dimensions of cell up to 11 x 11 $cm^2$ and thickness of 1 mm. The properties of each air electrode layer were controlled by morphology of source powders, addition of poreformers and thermal treatment. Characterization of the cells includes both the microstructural analyses such as SEM with EDS and the methods of solid state electrochemistry. Performance of the fabricated cells was investigated in fuel cell (SOFC) and electrolysis (SOEC) modes with I-V scanning and impedance spectroscopy in temperature range of 650-700°C under current density in excess of 1000mA/$cm^2$ in SOFC, and up to -1900 mA/$cm^2$ in SOEC-mode.

## Acknowledgements:

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# Electrochemical behaviour of dry-processed and slurry-casted all-solid-state batteries with argyrodite electrolyte

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## Abstract:

All-solid-state-batteries (ASSB) represent the next generation of electrochemical energy storage devices to replace conventional Li-ion batteries. Particularly, ASSB offer a remarkable level of the capacity, without risks of explosion or self-ignition in case of leakage. Among solid-state electrolyte materials, sulfides with argyrodite structure, such as Li6PS5Cl, are attractive due to their low cost, ionic conductivity above 1 mS/cm and feasibility to scale up their processing, for example, by wet-casting methods. However, the large-scale fabrication requires understanding of the chemical compatibility of sulfides with binders and solvents applied for the wet-casting.

The present work focuses on the fabrication of full cells with Li6PS5Cl electrolyte, Li(Ni,Mn,Co)O2 cathode active material and Li anode. The electrolyte exhibits the ionic conductivity of 1.7 mS/cm and can withstand over 100 stripping-plating cycles (0.1 mA/cm2 current, 2 hours per step). The main factors that influence the cycling performance of the full cells are the loading of cathode active material, mechanical properties of the electrolyte, stacking pressure and interfacial phenomena. The cells prepared from dry-processed materials yield the specific capacity above 140 mAh/g at room temperature, with a coulombic efficiency of 95-100% and a high capacity retention over 50 cycles. Upscaling of the fabrication procedure following slurry-casting technique enables to obtain self-standing electrolyte membranes of 50-300 μm thickness. The slurry-casted cells display a slightly lower capacity owing to the lower conductivity of the electrolyte in the mixture with non-conductive binders, necessary to ensure the mechanical stability of the membrane.

## Acknowledgements:

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# Investigation of Structural Properties of Celsian Ceramics in the BaO-Al2O3-SiO2 System.

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## Abstract:

Barite based celsian ceramics with phase composition accordingly (mass%): of celsian 93; Barium Aluminate and Barium Silicate 4; Glass phase 3, has been synthesized with single stage technology. The material displays the best properties in conditions of synthesis at 1410-1460°C Its properties have been studied in complex. The material shows high resistanse to heat shock. A completely new mechanism of ceramic production is proposed. Structure of celsian ceramics in BaO-$Al_2O_3$-$SiO_2$ system is stadied with electron microscope, X-ray photographs, crystalline phase content, optical microscope. Water absorbtion W%-O. Bending strength of non glazed, $\delta$ N/mm$^2$ – 69. CLTE, $\alpha_{20\text{-}600}$ $10^6$C$^{-1}$ temperature areas-3.7. Tanget of a dielectric loss angle at 50 Hz and 20°C and tg $\delta$ $10^{-4}$. HV GPa-18.0. Volume resistivity, $\rho$ ohm/cm $20^0$C-$300^0$C-$10^{16}$. Elastic modulus, E N/mm$^2$$10^3$-78.5.

The process of pores filling, full consolidation of material and hardness growth at comparatively high temperatures of baking interval are studied.

# Elaboration of complete PCFCs and study of their performances.

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## Abstract:

One of the global challenges of our century in terms of energy production is to reduce the emission of greenhouse gases to slow down global warming. The use of hydrogen in fuel cells system is a promising alternative. Nowadays, Protonic Ceramic Fuel Cells (PCFC) are drawing more and more attention as they have a good efficiency in the temperature range of 400 – 600 °C. In this paper, the material used for the electrolyte is yttrium doped barium zirconate, with formula $BaZr_{0,8}Y_{0,2}O_{3-\delta}$ (BZY). It consists of a thin (2.5 µm) and dense layer. The anode is a NiO-BZY. Finally, the cathode is a porous layer made of $Ba_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ (BSCF).

In this study, PCFCs were elaborated by a innovating sequence gathering the tape-casting of the anode followed by a sintering treatment at 1350 °C. The electrolyte was deposited by reactive pulsed DC magnetron sputtering, and finally the cathode is deposited by spray-coating.

The advanced physical vapor deposition technic for the electrolyte was chosen in order to get an excellent control of the aspect in terms of thickness and density. The deposited electrolyte has a columnar microstructure which permits the protons to go through the electrolyte with no or few grain boundaries to cross, which lead to good performances in term of protonic conductivity. The performances of the cell were tested by electrochemical impedance spectroscopy, where an ohmic resistance of 7 $\Omega.cm^2$ and a global polarization resistance as low as 0.3 $\Omega.cm^2$ were obtained at 525°C.

## Acknowledgements:

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# Comparison of sintering behavior of barium-based solid oxide fuel cell cathode by conventional and microwave methods

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## Abstract:

In this research sintering behavior of synthesized intermediate temperature solid oxide fuel cell (IT-SOFC) cathode ($BaFe_{0.8}Cu_{0.1}Ni_{0.1}O_{3-x}$ powder) was investigated by heating in conventional electric furnace and microwave furnace. Then, the characteristics, structure and morphology of synthesized and sintered powders under different conditions were investigated using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

The results of sintered samples in conventional and microwave furnaces are also different in terms of morphology and sintering conditions. SEM/EDS images of the resulting pellets show needle like particles with different diameters but with the same composition as the rest of the sample. Also, there was no difference between the results of cathodic polarization resistance of two different samples.

# Utilisation of ceramic thin-films for sensing humidity at room temperature

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## Abstract:

For semiconducting oxides, recent advantages that allowed conducting synthesis to yield materials with the constituent domains in the nano-range, proved beneficial in terms both of greater surface and pore exposure. Among such nanomaterials, materials used for sensing attracted much attention. In this research we derived nanosized ceria powders by a simple hydrothermal method, prepared intermediate slurries and then tape casted them onto conducting glass substrates, to derive planar thin-films with range of thicknesses. The thin-films were thoroughly characterized: structurally (powder and grazing incidence X-ray diffraction), morphologically (scanning electron microscopy and atomic force microscopy) and electrically (solid state impedance spectroscopy) in a wide range of temperature, frequency and humidity. Depth profiling points to monophasic crystalline ceria in form of slightly agglomerated spherical particles and low-roughness thin-films. Interestingly, the electrical measurements were performed employing surface geometry and cross-section geometry. From the dielectric spectroscopy results we elucidated the influence of the composition and film thickness on the electrical properties and derivatively the humidity sensing performance of the samples. Overall the relative humidity increase lead to a shift to higher conductivity, with gradual relaxation of the films. Thus proving the sensitivity and reversibility of the ceria thin films as humidity sensors.

## Acknowledgements:

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# Advanced TNO-carbon ceramic material for fast-charging Li-ion batteries

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## Abstract:

Conventional carbon-based anode materials in lithium-ion batteries (LiBs) are widely available and dominant in the big market of energy storage systems. Performance limiting leakages of this setup like the formation of a passivating solid-electrolyte interphase (SEI) at a low working potential (~0.1 V vs. Li/$Li^+$) must be overcome by developing advanced ceramic anodes that exhibit good cycling stability, high energy, and power density.

$TiNb_2O_7$ (TNO), a promising alternative anode material for LiBs, has the cell advantages of a high operating potential of 1.55 V, a five-electron-redox process, and a good theoretical capacity of 388 mAh $g^{-1}$.

TNO nanocomposites were in-situ synthesized through a simple, controllable, and scalable sol-gel route. However, the electric and ionic conductivities in bulk TNO electrodes are too poor to support the requirements of power density for commercialization. Incorporating TNO into carbon nanocomposites by the usage of the electrospinning technique increases the electronic conductivity and enhances the $Li^+$ diffusion coefficient.

The synergetic positive effect of the carbon nanocomposites using a unique electrospinning technique and the crystalline phase exhibits benefits in high-rate $Li^+$ capability. An advanced and economical friendly anode material for LiBs using TNO and their embedding in carbon nanostructure paves the way for next-generation of energy storage.

## Acknowledgements:

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# Tuning the Electro-Catalytic Properties of Mixed Conducting Perovskite-Type Oxides

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## Abstract:

Perovskite-type oxides are promising materials for various applications reaching from electrochemistry to heterogeneous catalysis, since their properties can be widely tuned by doping. Achieving mixed conductivity, for example, is crucial for an electrode reaction, which involves ions and electrons. Depending on the composition of the perovskite-type oxide, the mobile ionic species can be oxide ions or protons. Determination of the mobile ionic species can be largely (but not exclusively) affected by the elements on the A-site of the perovskite-type crystal structure. For example, incorporating barium ensures an excellent protonic conductivity due to a resulting high basicity of the oxide.

If a reducible transition metal is incorporated on the B-site of the perovskite-type crystal structure, the electrode reaction can lead to an exsolution of this element under sufficiently reducing conditions. This results in finely dispersed metallic nano particles on the surface, which then can provide catalytic activity. If this is accomplished with an electrochemically polarizable perovskite electrode, these particles can be electrochemically switched between a catalytically low active oxide state and a highly active metallic species.

We demonstrate how controlled compositional changes of perovskite-type oxides can be used to achieve materials with strongly different electro-catalytic behaviour by modifying both their bulk defect chemistry and their surface chemical properties. Several perovskite-type oxide materials were synthesized and their electro-catalytic properties characterized by a combination of electrochemical and analytical techniques. Hence, we can show that depending on the composition of the perovskite, the preference of a certain surface reaction can be achieved.

# Application of stereolithography-based ceramic additive manufacturing in microsystems

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## Abstract:

Ceramic materials are highly valued in microelectronics. The Low Temperature Co-fired Ceramic (LTCC) technology is used for manufacturing of high-performance elements such as resistors and capacitors, heavy-duty components operating in high temperature or harsh chemical conditions, multi-layer circuits allowing for miniaturization, packages with dense interconnections as for microprocessors, microwave devices with high quality factor, microfluidic sensors with chemical and biological inertness and complex microsystems combing multiple features.

The LTCC manufacturing is based on semi-additive process, in which multiple sheets of green material are pressed together. Each layer can be shaped in a subtractive manner, usually through laser cutting, and contain screen-printed conductive, resistive, and functional patterns. The limiting factor is significant labour involvement, especially for complex structures, as well as high cost of developing non-planar spatial structures with high number of layers.

The presented solution is application of ceramic additive manufacturing. The stereolithography method was used to manufacture various microelectronic structures. Complex microfluidic channels were applied in miniature cryogenic cooler and very fine high aspect ratio needles were modified with carbon nanotubes to obtain miniature field emission source. To obtain the best performance for electronic application, an LTCC-based resin was developed. The properties of final parts have proven to be on par with the structures developed using traditional methods.

# Surface and defect chemistry of porous La0.6Sr0.4FeO3 electrodes on polarized 3-electrode cells

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## Abstract:

The performance of mixed conducting porous solid oxide cell (SOC) electrodes depends on the concentration and mobility of electronic and ionic defects in the bulk, as well as the surface structure and chemistry, which determines the reactivity for oxygen exchange reactions. However, these properties are not trivial to investigate in real SOFC electrodes, due to the complex interplay of reaction and conduction processes in anode and cathode.

To overcome these problems, we developed an optimized three electrode design, which enables measurement of virtually artefact free half-cell impedance spectra and overpotentials, which we experimentally prove on porous $La_{0.6}Sr_{0.4}FeO_3$ (LSF) electrodes. Moreover, the three-electrode cells are investigated in operandoby ambient pressure XPS (APXPS) measurements during polarization. From these measuremnts we get a direct correlation of surface chemistry and electrochemical properties.

Importantly, we get information on the bulk and surface defect chemistry and catalytic activity of LSF as a function of gas phase and overpotential. Therefore, we can track the oxygen vacancy concentration, transition metal oxidation states and Fermi level shifts during operation of the electrode. For example, during cathodic bias in reducing conditions, metallic Fe nanoparticles exsolve to the surface and lead to excellent $H_2O$ electrolysis kinetics. Apart from our successufl experiments on the LSF electrode, we are convinced that our experimental approach will deliver detailed information on many other relevant SOFC electrode types.

## Acknowledgements:

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# Investigation of the transport mechanism in 〖Ba〗_(0.5) 〖La〗_(0.5) 〖Co〗_(0.5-x) 〖Fe〗_(0.5) 〖Zn〗_x O_(3-δ)

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## Abstract:

The $Ba_{0.5}La_{0.5}Co_{0.5-x}Fe_{0.5}Zn_xO_{3-d}$ (BLCFZ) perovskite material is known to have good mixed ionic-electronic conductive properties which makes it a potential ceramic for cathodic applications in proton ceramic fuel cells. Cobalt has a high electron density [1]. Thus, its presence in $Ba_{0.5}La_{0.5}Co_{0.5-x}Fe_{0.5}Zn_xO_{3-d}$ enables improved electronic conductivity.

The introduction of iron into a $Ba_{0.5}La_{0.5}Co_{0.5-x}Fe_{0.5}Zn_xO_{3-d}$ perovskite increases the unit cell volume of the resultant material and an insignificant increase in the oxygen vacancy concentration. This material generally has a higher electron-hole defect concentration than vacancy concentration [2]. The presence of more iron content in the material promotes the hydrogenation reaction as the primary mode of proton defect formation over the hydration of vacancies [2]. Because zinc has a high electron affinity, it ought to serve the purpose of trapping electrons in the BLCFZ material.

In this work, we present the influence of zinc in $Ba_{0.5}La_{0.5}Co_{0.5-x}Fe_{0.5}Zn_xO_{3-d}$ perovskite on the structural and transport properties. Special attention was paid to how conductivity changes with varying concentrations of the dopant at the B site of the perovskite. The crystal structure of the material was studied with the X-ray diffraction (XRD) after annealing the oxides in nitrogen, air and oxygen to determine how the stated conditions influence the material and subsequently its conductivity. The change in conductivity against partial oxygen pressure and partial vapor pressure was of key interest for the different dopant concentrations.

## Acknowledgements:

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# Development of full ceramic electrodes for Li-ion batteries fabricated by 3d printing

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## Abstract:

The fabrication of energy storage devices and their components via 3D printing involves significant benefits and improvements compared to traditional manufacturing processes. Furthermore, 3D printing provides versatility for the development of electrodes with optimized surface area/active material ratio and allows the fabrication of devices with fanciful and non-conventional geometries required by specific product design requirements.

Among these technologies, fused filament fabrication (FFF) represents a promising and cost-effective method to develop lithium-ion batteries. Most of the current efforts to produce electrodes via FFF are based in the used of high amount of polymeric additives that constitute a continuous non-conductive matrix in the printed material. This translates into important capacity limitations and poor cycling performance under battery operating conditions. We have recently developed a procedure to fabricate full ceramic electrodes from highly loaded ceramic composite filament[1] and applied it to the printing of composite electrodes via FFF that after controlled sintering conditions (tailoring of microstructure, porosity, and phase stability) yields LTO- and LCO-based electrodes. Their electrical and electrochemical performance was assessed by EIC and charge/discharge experiments. Results show almost the same conductivity and capacity, i.e. 168 and 129 mAh $g^{-1}$, than that corresponding to the-state-of-the-art for lithium batteries anode and cathode, respectively. Therefore, 3D printing fabrication technique must be considered a valuable alternative tool to fabricate electrochemical devices, such batteries, and others. The impact of different electrode geometries will also be evaluated.

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# Characterization and stability of metal exsoluted perovskites as SOFCs electrodes

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## Abstract:

The "solid phase crystallization" procedure allows the development of new electrode materials for SOFC devices[1] as it provides a homogenous distribution of metal-catalyst nanoparticles onto the surface and within the electrode material by in situ exsolution under reducing conditions. The control of this process and the particles growing will enhance the catalytic, electrical and electrochemical properties of these materials.

Previous experience with related compounds[2] encourages us to study the exsolution process of $La_{0.5}Sr_{0.5-x}Ti_{1-y}M_yO_{3-d}$ ($x\leq 0.4$, $y\leq 0.3$, M = Ni/Fe) compounds. Metal segregation depends on the aliovalent substitution and charge compensation mechanisms and thus, their electrical and electrochemical properties will be largely affected. Characterization under oxidizing and reducing conditions by XRD, NPD, TEM and SEM provides evidence of metal exsolution at variable composition and temperature; for example, in $La_{0.5}Sr_{0.5}Ti_{0.75}Ni_{0.25}O_{3-d}$, Ni nanoparticle radius ranges from 8-10 to 90-110 nm at 900 and 1200ºC, respectively. NPD thermodiffraction experiments show the stability of the orthorhombic Imma phase and the Ni nanoparticles whilst EIC measurements show increasing conductivity with Sr content within the temperature range for both atmospheres. These results involve high temperature stability and reversibility in terms of structure, ion mobility and electrochemical behaviour which should be considered the initial stage to develop new electrode materials for SOFC devices.

[1] Nat Chem. 5, 2013, 916; Nat Comm 10, 2019, 1471; Adv. Energy Mater. 2020, 1903693

[2] J. Mat. Chem. 21, 2011, 13195; Chem. Mat. 25, 2013, 2484; J. Power Sources 227, 2013, 309; Int J. Hydrog En. 39, 2014, 5440

## Acknowledgements:

Thanks to JCCM project (SBPLY/19/180501/0 00240) and UCLM "Ayuda a Grupos Plan Propio" (FSE-FEDER 2020-GRIN-29130). JCPF acknowledges JCCM for a postdoctoral contract (SBPLY/16/180501/000409)

# The role of the electrolyte for the oxygen exchange mechanism close to the triple phase boundary of Pt|YSZ microelectrodes

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## Abstract:

The oxygen exchange reaction is one of the major factors limiting the performance of the air electrode in solid oxide fuel and electrolysis cells (SOFCs/SOECs). Hence, gaining deeper mechanistic understanding of this reaction on solid oxide ion conductors is of high importance. Even though Pt is not a typical electrode material for SOFCs/SOECs, Pt microelectrodes on an yttria-stabilised zirconia (YSZ) electrolyte represent an excellent model system for studying oxygen exchange kinetics in a predominantly triple phase boundary (TPB) active system. Despite a long history of inquiry, the exact oxygen exchange mechanism at the TPB of Pt|YSZ is still not completely understood.

The aim of this study was to obtain further understanding of the mechanic intricacies of the oxygen exchange reaction on the free YSZ surface close to the TPB. The main focus was laid on considering the possibility of an electron transfer via the electrolyte. Dense Pt microelectrodes with a well-defined TPB were prepared onto YSZ single crystals via magnetron sputter deposition followed by micro-structuring using photolithography and ion-beam etching. To alter the lateral electronic conductivity of the electrolyte, buried oxide layers with different electronic conductivities were applied. Electrochemical characterisation was done by impedance spectroscopy (EIS) and current voltage curve measurements.

Moreover, the effect of applying a strong cathodic bias to the defect chemistry of YSZ was studied by in-situ near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). Besides the appearance of a reduced Zr species in the electrolyte, a strong polarization-induced change of the wetting behaviour between Pt and YSZ was observed, which was confirmed also by electron microscopic investigations.

# Preparation and characterization of ytterbia stabilised zirconia for SOFC/EC

Teresa Rey Wojcik[1], Joanna Szymanska[1], Veronika Müller[1], Sarah Griesser[1], Andreas Börger[1], Mario Turner[1], Angelika Priese[2]

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## Abstract:

Ytterbium stabilised zirconia was produced by fusing the oxides in an electric arc furnace. The ingot was crushed and milled and the obtained material was milled to submicron particle size. XRF and ICP-OES analyses confirmed the high purity of the products and presence of 15.7wt% ytterbium oxide, corresponding to 5.6mol%. Powder X-ray diffraction proved that the cubic phase (F3m3m) was formed. Impedance spectroscopy carried out in the temperature range between 200 - 900°C showed high ionic conductivity - approximately 20% higher at 650°C than for 8mol% yttria stabilised zirconia. This could make ytterbium stabilised zirconia an interesting candidate as electrolyte material in SOFC/EC applications.

# Investigation of the electrical properties of hafnium doped barium – titanate ceramics

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## Abstract:

In the last years there has been a growing interest in the study of $BaTiO_3$-based ceramics as possible substitutes in microelectronics for Pb-based relaxor materials. Among the solid solutions of $BaTiO_3$, $BaHf_xTi_{1-x}O_3$ (BHT) is the least studied, due to the purity problems of $HfO_2$, but it is very attractive both for the fundamental study and for the applied research, being expected better results than in the case of doping with Zr (BZT).

In the present work, we proposed a detailed study of the electrical properties of $BaHf_xTi_{1-x}O_3$ ceramics with x = 0.04, 0.08, 0.10, 0.12, obtained by solid state reaction and densified at 1450 ° C / 2h and 1500 ° C/ 2h. All ceramics have the densityof over 94%. X-ray diffraction data showed the phase purity and SEM images demonstrated homogeneous microstructures with well-defined grain boundaries. Impedance spectroscopy in the temperature range of (25 to 150) °C shows a composition-induced ferroelectric-to-relaxor crossover with compositional dependent shifts of the structural transition temperatures by comparison with ones of the pure $BaTiO_3$. Polarization vs. E loops indicate regular variation with increasing Hf addition, a reducing of loop area, remanent and saturation polarization (in case of Hf addition from $P_{sat} = 15\mu C/cm^2$ to $P_{sat} = 13\ \mu C/cm^2$) and increasing of loop tilting. It is desired the analyze of the correlation between the electrical properties and the microstructure of ceramics (influence of grain size) and to calculate the electrocaloric effect, the $BaHf_xTi_{1-x}O_3$ ceramics having high potential for developing alternative cooling technologies.

## Acknowledgements:

This work was supported by grants of the Ministry of Research, Innovation and Digitization, CNCS/CCCDI – UEFISCDI, project number PN-III-P1-1.1-TE -2019-1689, within PNCDI III, CritEC and project number PN-III-P4-ID-PCCF-2016-017, HIGHkDEVICE.

# Composition-dependent characteristics of sol-gel BaTi1-xHfxO3 ceramics

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## Abstract:

Dense $BaTi_{1-x}Hf_xO_3$ (BTH) (x = 0.03; 0.05; 0.10; 0.20; 0.30) ceramics were obtained from powders prepared by the "acetate" variant of the sol-gel method and consolidated by alterative techniques, i.e. conventional sintering (CS) at 1400°C/4 hours and spark plasma sintering (SPS) at 1200°C/2 min, respectively. All the BTH ceramics are single-phased, regardless of the sintering procedure. For the BTH-CS samples the increase of Hf content from x=0.03 to x=0.30 induces the decrease of the average grain size, while for the BTH-SPS specimens the same trend was observed. For the BTH-CS ceramics with lower Hf content (x<0.10), very sharp permittivitty maxima, indicating a typical ferroelectric behaviour, were recorded. The presence of an increasingly higher proportion of Hf solute induces the shift of the lower-temperature phase transitions, i.e. tetragonal-orthorhombic and orthorhombic-rhombohedral towards higher temperature values, so that a single "pinched" ferroelectric-paraelectric phase transition was found for BHT-CS ceramics with x>0.20. In this case, the increase of the diffuseness of the permittivity maximum shows a second order phase transition, specific to a ferroelectric-relaxor crossover. Concerning the BTH-SPS ceramics, excepting the sample with the lowest Hf content, the other ceramics exhibit (at 1 kHz frequency) higher relative permittivity values over all the investigated temperature range, than those recorded for the conventionally sintered specimens of similar composition. For the specimens with lower Hf content ( x< 0.05 ),all the three phase transitions are still detectable, but they are much more flattened relative to the samples consolidated by conventional sintering.

## Acknowledgements:

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# Temperature dependent dielectric behavior of (Ba,Sr)TiO3 solid solutions sintered from sol-gel derived powders

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## Abstract:

Single-phase $Ba_{1-x}Sr_xTiO_3$ (BST) perovskite ceramics with $0.3 \leq x \leq 0.4$ were prepared from powders synthesized via sol-gel route. The compositions have the ferroelectric-paraelectric phase transition close to room temperature. At 20 °C the BST ceramics are ferroelectric for $0.3 \leq x \leq 0.35$ and paraelectric for $x = 0.375$ and $x = 0.40$. The study follows the relation between the structural changes produced when increasing the Sr content and the dielectric properties at low intensity electric fields. It is found that the grain size and tetragonality decreases as the Sr content increases. Analyses of complex permittivity and impedance spectroscopy reveal the temperature and frequency dependencies of the dielectric properties. The phase transitions seem to be of first order for all compositions, with a thermal hysteresis that decreases with increasing the Sr content, fact attributed to the corresponding increase of the grain boundaries weight allowing a more efficient stress relaxation in the structure during the change of the symmetry from cubic to tetragonal. The diffusiveness degree during the phase transition is increasing with Sr content, suggesting some relaxor-type contribution attributed to smaller grain size. The ac conductivity follows the universal Jonscher law, with an ac component having the power parameter s independent of Sr content, and a dc component that it is thermally activated with an activation energy of about 0.7-0.77 eV attributed to oxygen vacancies acting as donor-like defects. The fit of impedance spectra at different temperatures and frequencies is obtained by using an equivalent circuit accounting the grains, grain boundaries, electrode interfaces and the local contributions 2 produced by reorientation of defect dipoles or defect clusters.

# Tuning Oxygen Non-Stoichiometry in Spark Plasma Sintered LiNi0.5Mn1.5O4 High Voltage Cathode Materials

Michael Stuer

*Swiss Federal Institute for Materials Science and Technology, Duebendorf, Switzerland*

## Abstract:

Solid-state batteries (SSBs) that contain a co-sintered cathode and electrolyte offer higher safety, energy and power densities compared to liquid electrolyte analogues. However, these materials suffer from barriers at the grain boundaries, which hinder Li-ion transport, significantly reducing battery performance. Spark plasma sintering can control grain growth, densification and grain boundary formation and has been heralded as an alternative method for controlling the microstructure of the cathode-electrolyte interfaces in SSBs. Additionally, spinel $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is a potential candidate for the next generation high energy density cathode materials, due to its high voltage characteristics. However, consolidation of SSBs using SPS requires the use of either vacuum or argon atmospheres, which causes an increase in the oxygen non-stoichiometry and this has a dramatic impact on the electronic and ionic conduction properties of LNMO. Therefore, SSBs consolidated using SPS may require a post-oxidation treatment under controlled oxygen atmospheres in order to optimise the electrical characteristics of the battery. In this model study, the role of oxygen non-stoichiometry on the electronic and ionic conduction properties of LNMO was studied. Samples were subjected to a reoxidation procedure under controlled $pO_2$ atmospheres. Electrochemical impedance spectroscopy (EIS) was performed on the reoxidised samples and activation energies were calculated for bulk and grain boundary electroactive components. The EIS data were related to the valence band density of states in order to deepen the understanding of the interplay between LNMO oxygen non-stoichiometry, microstructure and electrical properties by precisely controlling $pO_2$ during reoxidation.

## Acknowledgements:

The authors acknowledge internal funding from EMPA.

# Laminated lithium-conducting oxide ceramics for use as solid state electrolytes

Leonhard Tannesia, Richard Todd

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**Abstract:**

The use of ceramic solid-state electrolytes in all-solid-state batteries is currently limited by the failure of the electrolyte due to metallic lithium filament (dendrite) penetration. This project seeks to suppress filament penetration by using residual stresses due to thermal expansion coefficient mismatch in a layered structure containing different oxide electrolytes. The layered ceramic pellets are prepared by SPS, and their electrical properties characterized by EIS. Thermal expansion coefficients of each constituent phase are measured by a dilatometer. Crack resistance and Young's modulus of each material and the final layered structure are measured by nano- and micro-indentation. Electrochemical charge-discharge cycling simulates the filament formation in a working battery. Potential interactions between the layers are investigated by EDS mapping. SEM micrographs are used to reveal the filament penetration and fracture path in the oxide ceramic electrolytes, showing the effect of compressive residual stresses on the failure process.

# Development of Co-Sintering Regimes for Phosphate Based Composite Cathodes in Solid-State Batteries

Jean Philippe Beaupain, Katja Wätzig, Henry Auer, Kristian Nikolowski, Mareike Partsch, Mihails Kusnezoff, Alexander Michaelis

*Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden, Germany*

## Abstract:

Solid-state batteries with ion-conducting solid electrolytes (SE) enable increased safety of energy storage devices. Phosphate SE, as $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP), are featured by high ionic conductivity and electrochemical stability to cathode active materials (CAM) [1].

In composite cathodes, a percolating system of the ion-conducting SE must be formed around the Li-storing CAM. High ionic conductivities of the SE are achieved through densification by sintering [2]. Layered oxide CAM show decomposition reactions during co-sintering with LATP, which irreversibly destroy the intrinsic material properties [3], whereas the combination of phosphate materials has higher chemical compatibilities.

In this study, the co-sintering of LATP and $LiFePO_4$ as pellets and tape-casted composite cathodes is investigated by optical dilatometry, X-ray diffraction, FESEM/EDX and thermogravimetry. The pellets densify during heat treatment and form ion-conducting paths. In contrast, the sintered tape-casted composite cathodes form a porous microstructure. In order to increase the ionic conductivity, the cathodes are infiltrate with an auxiliary electrolyte, which enables electrochemical cell tests.

The results indicate redox reactions and element diffusions of $Ti^{4+}$ and $Fe^{2+}$ during co-sintering. The decomposition products are correlated with the electrochemical potential profile of the infiltrated composite cathodes. Thereby, capacities of up to 125 mAh/g are achieved depending on the sintering temperature.

[1] Rettenwander, D. et al., J. Mater. Chem. A, 2016, 4, 1506. DOI: 10.1039/C5TA08545D

[2] Waetzig, K. et al., Crystals 2020, 10, 5, 408. DOI: 10.3390/cryst10050408

[3] Beaupain, J.P. et al., ACS Appl. Mater. Interfaces 2021, 13, 40, 47488. DOI: 10.1021/acsami.1c11750

## Acknowledgements:

The authors acknowledge the financial support of the German Federal Ministry of Education and Research (Germany) in the competence cluster for solid-state batteries “FestBatt” (03XP0173D and 03XP0434B).

# Developing Composition Stability of La0.6Sr0.4Co0.8Fe0.2O3-δ (LSCF) Under Reducing Conditions by Molybdenum Doping for Anode Applications in LT-SOFCs

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*University of Trento, Trento, Italy*

## Abstract:

Solid oxide fuel cells are a new generation in producing electricity and heat with almost no emissions, usually working at high temperatures. The most impressive benefits of lowering the operating temperature are decreased materials degradation, longer fuel cell life time, and lower manufacturing costs. $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) perovskite exhibits excellent catalytic activity towards oxidation and reduction reactions as well as high electroconductivity at low temperatures (≤600°C). By incorporating an element with higher redox stability into the B-site, like molybdenum, the limitations of using it as an anode material can be reduced. In this study, the influence of molybdenum dopant amount on structural stability was evaluated by doping different amounts of molybdenum into the LSCF structure. Powder was synthesized by auto-combustion and tape casting was used to fabricate electrodes. We exposed the sintered tapes to reducing and oxidizing conditions at 900°C, and measured their morphology, composition stability, and electrical conductivity. It was found that increasing molybdenum content led to improved structural stability even under reducing conditions, but only up to an optimal amount above which a secondary phase with electric insulating properties forms, resulting in degradation of the performance.

## Acknowledgements:

The author acknowledge the Italian Ministry of Research and Education for the financial support within the program PROGRAMMI DI RICERCA SCIENTIFICA DI RILEVANTE INTERESSENAZIONALE PRIN PROGRAMMA DI RICERCA

# Microstructural, thermo-mechanical and corrosion properties of electrophoretically co-deposited Cu and Fe doped Mn–Co spinel coatings for solid oxide cell interconnects

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## Abstract:

Chromia forming ferritic stainless steels are employed as interconnects in SOC stacks; the deposition of a manganese-cobalt spinel protective coating is widely accepted as a viable solution to mitigate both the oxidation and the chromium evaporation. Electrophoretic deposition (EPD) offers the possibility to deposit homogeneous coatings in few seconds and at room conditions and the need of a simple and adaptable apparatus, thus reducing processing time and cost. A successful deposition is ensured by the optimization of both the starting suspensions in terms of colloidal properties and the post-deposition sintering profile. Electrophoretic co-deposition is an innovative approach for the simultaneous deposition of spinel precursors and for designing in-situ modified manganese-cobalt spinel coatings.

A systematic microstructural, thermo-mechanical and electrical characterization of simultaneous Fe–Cu doped Mn–Co spinel coatings processed by electrophoretic co-deposition on Crofer 22 APU is here reported and discussed. We demonstrate the feasibility to co-deposit $Fe_2O_3$, CuO and Mn–Co spinel to produce dense, stable and effective doped spinel coatings. Improved functional properties of produced coatings are assessed in terms of microstructure development, oxidation kinetics and area specific resistance at SOC stack relevant conditions. Furthermore, an assessment of the dilatometric properties of the Fe–Cu doped spinels reveals the influence of different doping levels on the thermo-mechanical compatibility of the Fe–Cu doped Mn–Co spinel coatings with the interconnect.

This work proposes the electrophoretic co-deposition method as an innovative approach for the simultaneous deposition of spinel precursors and for designing in-situ modified coatings.

# Outstanding Unipolar Strain of Textured Pb(Mg1/3Nb2/3)O3–PbZrO3–PbTiO3 Piezoelectric Ceramics Manufactured by Particle Size Distribution Control of the Plate-like BaTiO3 Template

Temesgen Zate[1], Minsu Kim[2], Jae-ho Jeon[1]

[1] *KIMS - Korea Institute of Materials Science, UST - University of Science and Technology, Changwon, South Korea*

[2] *KIMS - Korea Institute of Materials Science, Changwon, South Korea*

## Abstract:

High-strain piezoelectric ceramics are required to miniaturize actuators for use in machinery and electronic systems. This paper reports an ultra-high strain of textured $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbZrO_3$–$PbTiO_3$ (PMN–PZ–PT) ceramics prepared using a plate-like $BaTiO_3$ (BT) template. Small BT particles (< 5 μm), which are difficult to orient as desired during tape casting, were removed from the as-synthesized BT (as-BT) template via a simple sedimentation method. Then, the residual BT (rs-BT) was used to prepare textured PMN–PZ–PT ceramics, which were compared with the textured ceramics prepared using the as-BT. Results show that the textured 0.4PMN–0.22PZ–0.38PT ceramics prepared with 5 vol% of rs-BT yield a significantly enhanced unipolar strain of 0.26 % at 2 kV $mm^{-1}$, when compared to the strain of 0.21 % obtained from the textured 0.4PMN–0.22PZ–0.38PT ceramics prepared with the same amount of as-BT.

## Acknowledgements:

We would like to acknowledge financial support from the R&D Convergence Program (CAP-16-09-KITECH) of NST (National Research Council of Science & Technology) and UST Young Scientist Research Program 2021 (2021YS28) through the University of Scientist and Technology of the Republic of Korea.

# The effect of synthesis method and Sr-dopant amount on the electrical conductivity of strontium-doped lanthanum manganites

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[1] *University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia*
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## Abstract:

Strontium-doped lanthanum manganites ($La_{1-x}Sr_xMnO_3$, LSMO) are perovskite ceramics that have potential use in devices for energy conversion and storage due to their chemical stability and high electrical conductivity. In this study, LSMO (x = 0, 0.1, 0.2, 0.3) were prepared using two different synthesis methods: citrate-nitrate autocombustion (CNA) and coprecipitation. Upon synthesis, all prepared powders were pressed into pellets (6 mm in diameter) and sintered at 1200 °C/2 h. The formation of the LSMO phase was confirmed by X-ray diffraction analysis and the lattice parameters were determined by Rietveld refinement analysis. The oxygen nonstoichiometry in samples was determined by permanganate titration with Mohr's salt. The electrical properties of calcined pellets were measured using impedance spectroscopy in a wide temperature (–80 – 240 °C) and frequency (0.01 Hz – 1 MHz) range. All samples have shown semiconductor behavior, their conductivity rising with temperature and Sr-amount. For all analyzed samples, the conductivity was frequency-independent over the entire frequency range. The non-existence of frequency-dependent conductivity indicates undisturbed electrical transport through the grain boundaries and the absence of any effect that could block fast electron transport. Furthermore, it was observed that LSMO samples prepared by the coprecipitation method possess higher conductivity than samples prepared with the CNA method due to the higher oxygen nonstoichiometry. Electrical conductivities of all LSMO samples were in $10^{-2}$ – 0.45 $\Omega^{-1}$ $cm^{-1}$ range, which is comparable to the conductivity of Si.

## Acknowledgements:

This work has been supported in part by Croatian Science Foundation under the project IP-2018-01-5246, and by the Virtulab project (KK.01.1.1.02.0022), co-funded by the European Regional Development Fund.

# Symposium G: Ceramics for Energy and Environmental Technology / Membranes

Invited presentation:

# Supplying safe drinking water to developing countries: Adsorption of viruses on porous ceramics structures and nanofibers

Thomas Graule[1], Sena Yüzbasi[1], Kamila Domagala[1], Michael Stuer[1], Dariusz Kata[2]

[1] *Empa, Duebendorf, Switzerland*
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## Abstract:

Water purification is necessary to prevent the spread of different diseases, which are caused by water-borne germs like bacteria, protozoa, and viruses. The germs can be separated from the water by a physical process, where the contaminated water is passing a porous medium like a filter.

The presentation will focus on the physical separation of germs from water applying nanostructured, ceramic based filters as well as modified fibers originating from CNT's and granular oxide materials. Virus particle separation (MS 2 bacteriophages and PhiX 174 bacteriophages ; size 25 nm, PZC 2 respectively 7) with an efficiency of more than 99,99 % could be achieved, depending on the pH conditions. Modification of the highly active, porous ceramic surfaces was achieved by incorporation of nanosized inorganic particles composed of zirconium oxide, yttrium oxide, magnesium oxide or copper oxide. Oxide based ceramic granular materials and CNT nanofibers were applied recently for virus filtration, after modification of the nanostructured surface by copper oxide.

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P. Szekeres, Z.Németh, K.Schrantz, K.Németh, M.Schabikowski, J.Traber, W.Pronk, K.Hernádi, T.Graule, ACS Omega, 2018, 3, 446-454.

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K. Domagala, C. Jacquin, M. Borlaf, B. Sinnet, T. Julian, D. Kata, T. Graule, Water Research 179 (2020) 115879.

K.Domagała, J.Bell, S.Yüzbasi, B.Sinnet, D.Kata, T.Graule; RSC Adv., 2021, 11, 31547.

## Invited presentation:

# Design and fabrication of proton-conducting ceramic membranes for H2 separation

Elisa Mercadelli[1], Angela Gondolini[1], Andrea Bartoletti[1], Sonia Escolástico[2], José Serra[2], Alessandra Sanson[1]

[1] *CNR-ISTEC, Faenza, Italy*

[2] *Instituto de Tecnología Química (Universitat Politècnica de València-Consejo Superior de Investigaciones Científícas), Valencia, Spain*

## Abstract:

$BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$ - $Gd_{0.2}Ce_{0.8}O_{2-\delta}$ (BCZY-GDC) is currently one of the most investigated composites as ceramic membranes for $H_2$ separation and membrane reactors. One of the most appealing features for all-ceramic devices is their good chemical stability, especially in sulphur and $CO_2$-rich atmosphere with respect to the other systems. These peculiar characteristics make these systems very promising candidates for process intensification thanks to the possibility to directly integrate the membranes into high temperature reforming or gasification plants. For practical application, the design and production of an asymmetric configuration (i.e. thin membrane supported onto a thicker porous substrate) is crucial to improve the separation performance. In particular, the microstructure engineering of the porous support is a key-strategy to decrease its mass transfer resistance allowing the operation at high flow streams that would enable to reach industrial target. This work will present for the first time the possibility to exploit the ice-templating method to obtain membrane supports with well-organized and aligned porosity for hydrogen separation application. All the processing steps to obtain a defect free dense/porous structure will be deeply considered and analysed. The results will demonstrate that a high-performance device can be obtained only if each single step of the production process is carefully considered and optimized.

## Acknowledgements:

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## Invited presentation:

# Advanced ceramics for green hydrogen production and environmental technology

Alexander Michaelis

*Fraunhofer Institute of Ceramic Technologies and Systems, IKTS, Dresden, Germany*

## Abstract:

Advanced ceramic materials offer enormous potential for innovations in the fields of efficient energy conversion and storage as well as environmental technology. Specific examples for the development of fuel cell, battery, electrolysis as well as ceramic membrane systems are presented.

In the case of fuel cells we focus on ceramic high temperature SOFC (solid oxide fuel cell) technology for combined heat and power applications. SOFC systems can also be operated in the reverse SOE (solid oxide electrolysis) mode for hydrogen generation. A big advantage compared to other electrolysis systems is the possibility to use these SOE systems for co-electrolysis, i.e $CO_2$ can actively be removed from the environment for the generation of syngas ($H_2$ + CO). By the Fischer Tropsch processes this syngas can be transferred to e-fuels, higher alcohols, and waxes. For this, we present a fully integrated co-electrolysis Fischer Tropsch System.

For illustration of the potential of advanced ceramic materials in environmental technology, ceramic membrane systems are discussed. Ceramic membranes can be used for micro-, ultra- or nano- filtration of liquids.

Invited presentation:

# Controlled Nanoconfinement of Polyimide Networks in Mesoporous $\gamma$-Alumina Membranes for the Molecular Separation of Organic Dyes

Nikos Kyriakou[1], Louis Winnubst[1], Sissi De Beer[2], Martin Drobek[3], Arian Nijmeijer[1], Marie-Alix Pizzoccaro-Zilamy[1]

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[2] *Sustainable Polymer Chemistry Group, Department of Molecules &Materials, MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands*

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## Abstract:

Surface modification of micro/mesoporous inorganic supports by covalent attachment of molecules, short polymer chains, and polymeric network provides the opportunity to prepare hybrid systems with controllable pore surface properties. Such control offers the possibility to design hybrid inorganic-based membranes in the NF or UF range which could be used for the recovery of organic solvents, separation of biomass mixtures, and $CO_2$/light gas separation. These systems are conventionally prepared by the direct attachment of pre-synthesized molecules or polymer brushes composed of a reactive linking group able to react with the surface group of the inorganic substrate. This approach, however, is intrinsically limited to the availability of functionalized molecules/polymers and thus unable to precisely tune the pore size and surface properties.

Here, we will present a simple nanofabrication approach that allows the controlled nanoconfinement, growth, and covalent attachment of polyimide (PI) networks inside the mesopores of $\gamma$-alumina layers. The attachment of the PI network on the $\gamma$-alumina layer was initiated via different pre-functionalization steps that play a pivotal role in inducing the in-situ polymerization reaction at the pore entrance and/or at the inner pore surface. The nanoconfinement was found to be limited to maximal the 1.5 µm thick $\gamma$-alumina supporting layer and the resulting hybrid PI/ceramic membranes showed stable performance in a variety of solvents.

These results open novel directions for fine-tuning the separation performance of ceramic membranes for gas separation and solvent nanofiltration applications.

# Ca1-xSrxMnO3-δ perovskites for redox-operation-based thermochemical applications

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## Abstract:

Perovskites offer great versatility in redox reactions due to the large number of cation combinations and their tunable thermodynamic characteristics, being thus well suited for thermochemical $H_2O$ and $CO_2$ splitting cycles, air separation and heat storage applications. However, besides thermodynamics, structural integrity and resilience become important factors for composition as well as usable shape selection i.e. monolithic porous bodies, granules or pellets. Systematic studies on the effects of doping Ca-Mn perovskites with other cations on cyclic redox operation-relevant properties like oxygen uptake/release, concomitant heat effects, phase stability and thermochemical expansion/contraction by thermogravimetry/differential scanning calorimetry, dilatometry, porosimetry and in-situ high-temperature x-ray diffraction were performed under a wide range of temperature and oxygen partial pressures, to correlate such characteristics to possible phase transformations and dimensional changes. It was demonstrated that such perovskite compositions are characterized by complete reversibility of not only oxygen uptake/release but of any dimensional changes due to thermochemical expansion/contraction. The latter is associated with crystal phase transitions during reduction/oxidation, that can be further "fine-tuned" by proper doping with Sr, that also has a beneficial effect on the mechanical strength of the final object. These characteristics, together with low cost, earth abundance, environmentally benign character of constituting elements and amenability of shaping into a variety of sturdy granulated, reticulated, extruded or 3-D-printed porous structures, render such perovskite compositions extremely attractive for large-scale exploitation in various thermochemical processes.

## Acknowledgements:

perovskites, calcium manganate, redox oxides, thermochemical expansion, concentrated solar energy

# Thin films of metal carbides as effective catalyst materials

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## Abstract:

Transition metal carbides have been known for years as ceramic materials with interesting properties such as high hardness, toughness, and heat resistance (higher than 3000°C), to mention the most important [1]. Furthermore, their electronic structure, similar to that of noble metals, opens up a wide range of applications as catalytically active materials [2]. Due to the poor sinterability of powders [3], it is an interesting alternative to obtain such kinds of materials as thin film.

In this work, tungsten carbide containing thin films were prepared by plasma-enhanced chemical vapor deposition (PECVD) from the $W(CO)_6$ precursor. The chemical structure and morphology were analyzed according to different plasma deposition parameters such as generated plasma power, deposition time and temperature, flow rate of the precursor and carrier gas. The surface analysis of the as-deposited films before and after catalytic process was carried out by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) in terms of their microstructure and molecular composition. Furthermore, X-ray diffraction (XRD) was performed to determine the phase composition. The catalytic behavior of the samples in the $CO_2$ hydrogenation reactions was investigated in a tubular reactor at temperature range up to 600°C using gas chromatography (GC) to analyze gaseous products.

It was found that plasma parameters influenced the thin film composition. Besides a mixture of different tungsten carbide phases, tungsten oxides were also found in the deposited films. Catalytic tests have shown that the deposited films exhibit catalytic activity in $CO_2$ hydrogenation reactions. The role of tungsten carbide in this process will be discussed in the presentation.

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## Acknowledgements:

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# Additive Manufacturing Of Ceramic Nanocomposite Fuel Cells

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## Abstract:

Additive manufacturing has the potential to revolutionize the fabrication of ceramic nanocomposite fuel cells (CNFCs). A systematic study on the fabrication of CNFCs through extrusion-based 3D printing resulted in high performance devices. It was found that the temperature of the sintering step after printing the function layers of CNFCs has a large impact on the electrochemical performance of the cells. We optimized all the processing steps involved in the fabrication of the cells to achieve an excellent performance of the single-layer cells (230 mW/cm$^2$). We have developed robust ceramic nanocomposite materials with a high ionic conductivity (0.5 S/cm at 550$^o$C) through freeze-dried assisted Pechini method. Together with efficient catalyst materials, we achieved an outstanding performance of 1.1 W/cm$^2$ at 550$^o$C. We envision a performance of >2W/cm$^2$ at 550$^o$C with the help of our robust nanocomposite materials and their fabrication through digital printing. With the help of the state-of-art electrochemical (electrochemical impedance spectroscopy and current-voltage measurements), spectroscopic (X-ray diffraction, Raman, energy dispersive X-ray) and microscopic (high resolution transmission electron microscopy, scanning electron microscopy) characterization techniques, we perform systematic study to understand the mechanisms in the cells. Effect of engineering parameters such as porosity, cell thickness and cell composition are systematically studied to optimize the cell performance. Finally, stability of the catalytic materials was investigated to understand their degradation mechanisms.

## Acknowledgements:

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# Development of geopolymer network and following influence on conductivity properties

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## Abstract:

Alkali-activated aluminosilicates or so-called geopolymers (GP) have well cross-linked, 3D, fully polymerized aluminosilicate networks. In terms of pores, following properties could vary, and the most studied cations are potassium, sodium and even lithium. GPs are nowadays enforced as alternatives to concrete materials since their preparation minimally contributes to the energy and environmental problems worldwide. In particular, GPs give rise to new approach that could also boost energy savings. A particularly neat contribution in the overlapping fields of construction and energy materials could arise from the production of GP in the form of a paste that can be further developed into thin films. Such conductive and transparent thin-films could broaden the range of applicability in photovoltaic devices from horizontal mounting only to vertical mounting as well. In this work, we focus on chemical and (micro)structural changes occurring during the mullite-based geopolymer curing. Several factors influence changes, such as Al-to-Si ratio in the precursors and curing temperature. With this in mind, we study the conditions behind the geopolymerisation to obtain optimized samples characterised by XRD, DTA-TGA, FTIR, SEM and IS. Particular attention was paid to the NMR study of the evolution of the GP system as a function of curing temperature. Obtained results allowed a better understanding of the influence of chemical composition and homogeneity of constituents on the following structural, microstructural and electrical characteristics of studied samples. We have also demonstrated an interesting development involving a shift from relatively porous bulk to thin-film configuration, in order to spread the applicability of geopolymers for vertical facade photovoltaic systems.

## Acknowledgements:

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# The effect of manganese dioxide on dielectric properties of 0.3BT – 0.1BMT – 0.6BF composite

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## Abstract:

In the last few decades there has been a growing interest in lead free piezoelectric materials. The main driving force is limitations due to environmental concern. PZT is the most commercially viable piezoelectric material due to its high piezoelectric constant, ability to operate in a wide temperature range. Unfortunately, it is lead-containing, thus falls under the restriction of RoHS. In our presentation we have investigated the effect of small amount (0.05%) of manganese dioxide in 0.3BT – 0.1BMT-0.6BF to dielectric and piezoelectric properties.

From broadband dielectric data we have observed that conductivity of a sample which contains manganese dioxide has decreased. This could be attributed to the fact that manganese dioxide impurities tent to accumulate in defected areas thus decreasing the amount of free charge carriers. Furthermore dielectric relaxation which is related to domain wall motion was fitted using Cole – Cole law. Here we observed that alfa parameter which describes the width of the relaxation decreases for the sample with manganese dioxide. Also, similarly, from Arrhenius fits we have observed decrease in activation energy. And lastly from piezoelectric measurements we have observed improved piezoelectric properties for sample with manganese dioxide.

# Material design and optimization of ternary silicon oxycarbide/graphite/tin nanocomposite ceramics for anodes in Li-ion batteries

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## Abstract:

In this work we present characterization and electrochemical performance of various ternary silicon oxycarbide/graphite/tin (SiOC/C/Sn) nanocomposites as anodes for lithium-ion batteries. In binary SiOC/Sn composites, tin nanoparticles may be produced in situ via carbothermal reduction of $SnO_2$ to metallic Sn, which consumes free carbon from the SiOC ceramic phase, thereby limiting the carbon content in the final ceramic nanocomposite. Therefore, to avoid drawbacks with carbon depletion, we used graphite as a substitute during the synthesis of precursors. The ternary composites were synthesized from liquid precursors and flake graphite using ultrasound-assisted hydrosilylation method, and pyrolysis at 1000°C in Ar atmosphere. The role of the graphitic component is to ensure good electric conductivity and softness of the material, which are crucial for long term stability during alloying-dealloying processes. The presented approach allows to increase the content of tin precursor from 40 wt% to 60 wt% without losing the electrochemical stability of the final material. The charge/discharge capacity (at 372 mA $g^{-1}$ current rate) of the tailored SiOC/C/Sn composite is about 100 mAh $g^{-1}$ higher with regard to the binary SiOC/Sn composite. The ternary composites, however, are more sensitive to high current rates (above 372 mA $g^{-1}$) compared to the binary one, due to the presence of graphitic carbon.

## Acknowledgements:

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# Synthesis method as a factor controlling phase composition and ionic conductivity of Na3Zr2Si2PO12 NASICON – Towards improved electrolyte for sodium-metal solid state battery

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## Abstract:

Recently, electrical energy storage gain importance, due to the exploding share of renewable energy sources and electric vehicles. Currently, cutting-edge technology are Li-ion batteries, however, for large scale application their high cost and low energy density are unsatisfactory, therefore new solutions are sought. One of the most promising are all-solid-state sodium metal batteries (Na-ASSB), which offer low cost and high energy density. The key element of the Na-ASSB is a solid state electrolyte, providing a high $Na^+$ conductivity, an impenetrable barrier for growth of sodium dendrites, and low charge transfer resistance at the electrolyte/electrode interface.

This work discusses the influence of the synthesis method on porosity, phase composition and conductivity of the $Na_3Zr_2Si_2PO_{12}$ (NZSP) ceramic electrolyte with the NaSICON structure. The effects of thermal modification of the electrolyte surface on the charge transfer resistance between the electrolyte and the sodium electrode are also reported.

A solid state and sol-gel methods (alkoxide-based and Pechini), were applied to fabrication of sinters. The influence of the synthesis time and temperature, as well as sodium excess on relative density and phase composition was investigated by means of X-ray diffraction and Raman spectroscopy. The morphology and conductivity of the obtained samples were characterized using scanning electron microscopy and impedance spectroscopy.

The effect of surface modifications on contact with sodium metal, charge transfer resistance and electrolyte stability were measured in symmetrical Na|NZSP|Na cells. Among investigated factors are heat treatment, surface polishing, as well as impregnation with transition metal ions.

## Acknowledgements:

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# Functional steel/composite ceramics layered systems for interconnects applied in electrochemical energy conversion devices

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## Abstract:

In order for a solid oxide electrolyzer cell (SOECs) to operate with high efficiency, its operating temperature needs to exceed 1073K. However, such conditions are associated with certain issues – most notably the high-temperature corrosion of metallic interconnects, one of the essential components of an electrolyzer. The interconnect serves several roles – it allows single cells to be connected and form stacks, ensures that the entire construction is sufficiently rigid, enables the flow of electric current through the stack, and transports reaction gases to the anode and cathode via channels located on both of its sides. Interconnects are currently made of high-chromium ferritic steels, since the latter are compatible with the ceramic components of an electrolyzer (anode, cathode, and electrolyte) in terms of their thermal expansion coefficients. During oxidation, a scale with two layers – an inner layer composed of $Cr_2O_3$ and an outer layer consisting of the $MnCr_2O_4$ spinel – forms on this type of steel. The outer layer inhibits the formation of volatile chromium(VI) compounds to a minor degree. Such compounds trigger a particularly undesirable effect referred to as "electrode poisoning", causing the devices to lose some of its energy efficiency. In order to prevent both the formation of volatile chromium compounds and the gradual increase in the internal resistance of the electrolyzer and the associated decrease in its power output, protective-conducting layers can be deposited directly on the surface of an interconnect. In the presented study, the Crofer 22 APU ferritic steel manufactured by the German company ThyssenKrupp VDM was surface-modified with $Gd_2O_3$ nanoparticles and coated with a contact layer based on spinel or a spinel/perovskite composite. The objective was to determine if such modifications would improve oxidation resistance and area-specific resistance and protect the cathode material. The investigations conducted to obtain the required data included high-temperature oxidation studies, measurements of area-specific resistance, and fuel cell tests showing the electrochemical performance and Cr contamination of electrodes. The results provided exceedingly valuable insight.

## Acknowledgements:

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# Efficient oxygen separation from air using manganates RMnO3+d

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## Abstract:

The hyper stoichiometric, hexagonal manganates $RMnO_{3+d}$ promise major advantages in the processes of efficient oxygen separation from air for uses in energy production and in several vital industries. The critical feature of these materials is the ability to reversibly incorporate large amounts of oxygen into the crystal structure on cooling ($T_{ox}$) and release it on heating ($T_{red}$) without destroying the structural framework of metal ions. Unfortunately, this simple process to economically utilize waste heat at low temperatures near 250 °C takes place mostly in pure oxygen for an inexpensive R = Y. The substitutions of larger, but expensive Rare Earths makes process possible in air which is indispensable for industrial applications. Since our discovery of $RMnO_{3+d}$, we have studied the correlations between the four found crystal structures, the microstructure and the oxygen content dependence on the temperature, oxygen partial pressure, the kind and amount of R, and the synthesis conditions. We will show that the mean radius of R plays a decisive role in terms of the thermodynamics and kinetics of reactivity with oxygen. The best properties for application in air were found at the border of structural stability between the hexagonal- and perovskite-type phases. The characteristic temperatures $T_{ox}$ and $T_{red}$, the speed of oxidation/reduction reaction and the amount of produced oxygen can be adjusted to the available process conditions. Based on the comprehensive studies of the physicochemical properties, the best compositions found to date contain small amounts of Pr and Ce in addition to Y. Use of 1 tone of the optimized compound could produce over 100 $m^3$ of pure oxygen in one day.

## Acknowledgements:

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# Preparation of solid electrolyte thick films for Li batteries by aerosol deposition method

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## Abstract:

Replacement of conventional liquid electrolyte by solid ones is today the ultimate goal for Li-battery research. Ceramic ionic conductor can display conductivities as high as the one of liquid electrolytes but form poor electrode/electrolyte interfaces and are difficult to process. Indeed, the preparation of ceramic components usually requires sintering at quite high temperature. It is quite challenging to produce dense layers with a thickness of 20-30 µm while keeping the integrity of the material (no Li loss, no reactivity with the atmosphere…). The aerosol deposition method (ADM) developed by Akedo in the 1990's is a unique technique able to produce dense ceramic films at room temperature, sticking well to the substrate, with a high deposition rate and at a low cost. This coating method is based on the collision of submicron ceramic particles with a substrate. This study is devoted to the preparation of LATP ($Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$) thick films by ADM on various substrates (stainless steel, Pt…). LATP was chosen because of its good ionic conductivity and its good chemical stability towards atmosphere. A suitable powder for ADM process was sprayed on various substrates and ADM parameters were optimized to obtain good quality coatings. Finally, the resulting coatings were characterized in order to determine their thickness, roughness, density and adhesion properties. Impedance spectroscopy measurements were leaded as a function of temperature to determine activation energy and ionic conductivity. The ADM technique is expected to help in room temperature manufacturing of all-solid-state battery by insuring a strong anchoring between layers.

# Innovative architectural oxygen electrodes for solid oxide cells using electrostatic spray deposition

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## Abstract:

Solid oxide cells are efficient electrochemical systems for electrical power generation in fuel cell mode (SOFC) and hydrogen production in electrolysis mode (SOEC). To design novel optimized oxygen electrodes with improved mixed ionic-electronic properties, it is of high importance to control the electrode microstructure and composition to obtain large surface areas. Indeed, these properties are essential to increase the number of active sites for the oxygen reduction reaction and to enhance the ionic transfer at the electrode/electrolyte interface. Here, we report recent advances in the design of the state-of-the-art $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [1], $La_{2-x}Pr_xNiO_{4+\delta}$ (LPNO) [2] with $0 \leq x \leq 2$, and $Pr_6O_{11}$ [3] oxygen electrodes with grain size and porosity at the nanometre length scales. These active functional layers are fabricated using electrostatic spray deposition (ESD), a unique bottom-up method capable of depositing films with original morphologies by a nano-texturing approach. This talk will show our latest electrochemical performance results of these innovative oxygen electrodes investigating the role of the nanostructure and the electrode/electrolyte interface. The correlation between microstructure, composition, grain size, interfaces, and electrochemical properties is discussed in detail for the different investigated oxygen electrodes.

## Acknowledgements:

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# Alginate-derived activated carbon hybridized with NiMn2O4 for use in supercapacitors

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## Abstract:

Transition metal oxides (TMOs) are promising materials because of their specific properties enabling their application in energy solutions, such as their pseudocapacitive behavior enabling utilization as electrode materials in supercapacitors. Activated carbon is a material well known as an electric double layer capacitor (EDLC). Bringing together the two different capacitor materials- TMOs as pseudocapacitors and carbon materials as EDL capacitors is the goal for generating future generation supercapacitors.

Nickel manganite is a material of interest because of various oxidation states of manganese which provide its reactivity in oxidoreduction reactions, enhancing the pseudocapacitive behavior. Herein, we synthesized nano-sized nickel manganite by a sol-gel combustion synthesis process using glycine as fuel and subsequent calcination process. The structure and morphology of synthesized material was investigated via XRD, FESEM, and FTIR spectroscopy. Specific surface area and was determined from measured nitrogen adsorption/desorption isotherms. Activated carbon was obtained by pyrolytic carbonization of alginate hydrogel in nitrogen atmosphere and activation with KOH. The material was combined with synthesized $NiMn_2O_4$ nanopowder and tested as supercapacitor electrode. The second alternative was incorporating $NiMn_2O_4$ powder into alginate hydrogel, followed by pyrolysis in nitrogen atmosphere to obtain a $NiMn_2O_4$-activated carbon composite. The obtained materials were electrochemically characterized with cyclic voltammetry (LV) and galvanostatic chronopotentiometry to get galvanostatic charge-discharge curves. We calculated high specific capacitance values ranging to several hundred F/g, showing our hybrid material is a promising electrode in a supercapacitor system.

# Synthesis and characterization of Nano TiO2/Expanded Perlite applied to the photocatalytic degradation of 4-nitrophenol

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## Abstract:

In this study, a novel core-shell material, comprised of nanoscale > titanium dioxide (TiO2), supported by expanded perlite (EP), is introduced. While $TiO_2$, is a well- established photocatalyst for the degradation of numerous organic pollutants, it requires a microfiltration process in order to be separated from the aqueous media, thus limiting its potential. On the other hand, EP, due to its ability to adsorb aqueous pollutants it allows the decrease of the pollutant's concentration in the aqueous media, however, the pollutant remains entrapped in the porous interior of EP leading to secondary pollution. As a result, further treatment is required for the purification of EP. In order to overcome barriers and exploit the

> nanoscale photocatalyst as well as the adsorptive substrate, the synthesis of perlite supported $TiO_2$ is proposed. To this end, polymeric templated $TiO_2$ is synthesized by employing a dendritic polymer, hyperbranched polyethylenimine, and immobilized on EP. The characterization of this material includes SEM, XRD, FT-IR and BET analysis. The photocatalytic properties are assessed spectroscopically (UV-vis spectroscopy) under solar light through a model reaction, the reduction of 4-nitrophenol to 4 aminoph nol with excess sodium borohydride. The results obtained from this analysis verify the complete degradation of 4-aminophenol in 70 min while the photocatalyst can be reused without being purified for a second photocatalytic cycle with an almost 48% degradation efficacy.

## Acknowledgements:

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# Scalable manufacturing of ceramic components for oxygen separation in industrial processes

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## Abstract:

The improvement of energy efficiency in industry is a matter of pivotal importance for the upcoming ecological transition. In this context, Oxygen Transport Membranes (OTMs) are considered a promising technology for the industrial processes where pure oxygen is needed. Compared to the conventional technologies, OTMs can separate high purity $O_2$ with lower energy losses and improved efficiency.

Single-phase OTMs are ceramic structures made of mixed ionic-electronic conductors, that are usually perovskite oxides available in form of powders. The development of scalable manufacturing processes to realize membrane components is essential to enable the large-scale application of OTM technology and facilitate the market penetration.

This work describes the optimized manufacturing route of planar OTM elements ready to be integrated in a module for $O_2$ separation in industry. The elements are obtained from commercial $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ powders and consist in a multi-layered structure with internal channels for the operation in 4-end mode, where the permeated oxygen is collected by a sweep gas flowing in the channels. In view of a technological transfer, we used industrially attractive techniques. The external faces of the element are tape-casted asymmetric membranes, consisting of a 15 µm dense layer supported on a porous substrate (porosity ~35 vol%). The inner porous layers are thick foils also manufactured by tape casting and punched with the desired channeled layout. Membranes and interlayers are joined by lamination.

Thanks to the accurate control of every process step, including co-firing, we obtained 60x60 mm elements with remarkable reproducibility. The whole manufacturing is very flexible and can be adapted to different component dimensions, layouts, and materials.

## Acknowledgements:

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# Polymer-Derived Ceramic materials for novel ultrahigh-temperature latent-heat thermal energy storage devices

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## Abstract:

There is a renewed interest in returning astronauts to the Moon and establishing a sustainable human exploration capability on its surface. One of the greatest challenges is the energy storage for reducing the potential complexity and mass of a stand-alone power system. Due to the prohibitive cost in transerring materials from Earth, the assessment of In-Situ Resources Utilization approaches for energy production/storage, is crucial. Thermal Energy Storage using Phase Change Materials (PCMs), is one of the options: solid-liquid and liquid-solid phase transitions are “capitalized” to rake and release enthalpy (i.e. latent heat). However, the presence of a phase transition requires specific devices able to confine and retain the PCM in a molten state. These “shape stabilizers” include containers, vessels and porous matrixes. In addition, the efficiency increases with the increasing of the temperature.

Taking into account such requirements, a new generation of materials suitable for proficient latent heat thermal energy storage devices at UHT (up to 2000°C), have been investigated for the first time and presented in this paper. Specifically, the capability of new UHT Polymer Derived Ceramics (PDCs), such as SiOC with tailored microstructure as housing systems for liquid Si as PCM, has been tested. Wetting experiments by the classical sessile drop method and by dispensed drop, have been performed. 3D-printed SiOC architectures have been also infiltrated by liquid Si and their microstructural stability tested under thermal-cycling. Microstructural characterization of the as Si/SiOC composites has been performed by Optical and SEM/EDS microscope as well as a preliminary thermo-mechanical analysis have been performed, discussed and related to the operating conditions.

# Improved performance of Ni-rich NMC using a chemically activated coating process

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## Abstract:

To improve the electrochemical performance of cathode active materials (CAM) and suppress the dissolution of metal ions, the electrode surface is modified by coating with solid ion conducting materials. A coating layer can prevent the active material from direct contact with electrolyte. Also, this protective layer can address the safety concerns originated from flammable organic electrolytes in large-scale batteries by acting as non-flammable solid-state electrolytes (SSE). $LiNbO_3$, LATP, LLTO etc. could play such a hybrid role effectively. Especially, $LiNbO_3$ is well-known to have a very good structural stability, a high room-temperature lithium ionic (~ $10^{-2}$ mS/cm) and low electronic (~ $10^{-8}$ mS/cm) conductivity. The Ni-rich layered NMC oxides, $LiNi_xMn_yCo_zO_2$ with $x+y+z=1$ and $x>0.6$, are widely used as cathode materials in the batteries of electric vehicles. Using a chemically activated coating process, a series of NMC622 and NMC811 materials were coated with $LiNbO_3$, resulting in particles with very homogeneous and stable coating layers. The structure of the obtained active materials was investigated using SEM, TEM, XRD, EDX and XPS spectroscopy, and the electrochemical properties of the prepared cathodes were probed by charge-discharge studies. It was shown that the crystallinity and calcination temperature of the coating material play an important role and have to be carefully and individually selected. In addition, $LiNbO_3$ displays ionic conductivity not only in the crystalline form, but also in amorphous one. At a low calcination temperature, the amorphous type with more vacancies for lithium ion diffusion and transfer can be obtained. In the meantime, reactions with CAMs at the crystallization temperature of $LiNbO_3$ can be avoided.

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# Self-healing binder adaption to silicon-graphite blended anodes

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## Abstract:

Lithium-ion batteries with radically improved energy density and power capability are highly desirable for more demanding applications such as powering of electric vehicles. Silicon (Si) is one of the most promising anode material due to its high specific capacity ($Li^+$ storage capacity is 3579 mAh/g for $Li_{15}S_{i4}$ at room temperature). The major disadvantage is the pulverization and losing of the electrical contact during cycling because of the huge expansion of Si particles up to 300% and their surface cracking. To mitigate these adverse effects, the co-utilization of silicon and graphite has been investigated for a long time. Such blended electrodes exhibit lower irreversible-charge losses during the formation of the passivation layer and maintain a better electronic contact than pure Si electrodes. However, the binders and additives of anodes have also an essential influence on the performance and capacity fading. To increase the columbic efficiency and obtain better stability, self-healing binders based on alginate-derivatives or synthetic polymers can be adapted to Si-C blended anodes. The systematic and statistical investigation approach was implemented in this work. Electrodes were prepared by using 20:80 Si/C weight ratio. Water-based slurries were prepared and casted on copper foil and dried at 100°C under 150 mbar vacuum. The dried electrodes were punched in circular electrodes of 18 mm radius and assembled in argon filled glove box. Galvanostatic charge-discharge tests were carried out between 0.01 and 1.5 V vs. Li/Li+ potential window at different current densities. Solid electrolyte interphase formation and lithation-delithation peaks were investigated by using differential capacity (dQ/dV) values.

## Acknowledgements:

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# Laser Sintering of Li6.6La3Zr1.6Ta0.4O12 Solid Electrolyte

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## Abstract:

Energy conversion and storage applications are the key technologies for e-mobility. Besides developing suitable materials, alternative approaches for microstructural design[1] and manufacturing technologies[2,3] are of great importance to meet the requirements regarding performance, safety and durability. In this context, additive manufacturing techniques have gained significant attention to fabricate complex components with specified microstructures and almost unlimited freedom of design[4]. In the field of batteries, the future potential is currently attributed to solid-state batteries (SSBs) as they offer the potential to provide a higher energy density, safety and stability compared to Lithium-Ion-Batteries[5]. However, the manufacturing of SSBs remains a major challenge. Therefore, in this study, we investigated the laser-powder interaction using the different lasers in the NIR and MIR spectrum range by varying the process parameters such as laser power, scan speed, and track overlap to optimize the sintering process of $Li_{6.6}La_3Zr_{1.6}Ta_{0.4}O_{12}$ (LLZTO) solid electrolyte for SSBs. Phase and microstructural analyses were performed by XRD and SEM techniques, respectively. NIR laser radiation shows an insufficient absorption into the LLZTO; however, MIR laser technology seems to be promising for sintering LLZTO.

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## Acknowledgements:

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# Lowering the processing temperature while maintaining performance of barium cerium zirconates using the cold sintering process

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## Abstract:

Proton conducting perovskite ($ABO_3$) ceramics based on yttrium doped barium cerium zirconate ($BaZr_{1-x}Ce_xY_{0.1}O_{3-\delta}$ BZCY) have a great potential for intermediate temperature energy conversion applications like proton conduction fuel cells and electrolyzers (PCFC/PCEC) as well as membrane reactors. Especially the zirconium rich composition $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$ (BZCY72) combines high chemical stability against $CO_2$ atmosphere and a good total conductivity. However, the refractory nature of barium zirconates materials requires high sintering temperatures, the application of sintering aids (NiO or ZnO) or reaction based sintering methods like solid state reactive sintering (SSRS) to achieve sufficient relative densities. In the present study we develop a novel processing route for the proton conducting material BZCY72 using the cold sintering process (CSP) and an optimized post thermal treatment, which enabled us to limit the maximal processing temperature to 1300 °C. The electrochemical properties were characterized by impedance spectroscopy matching the performance of conventionally processed BZCY72 membranes sintered at significantly higher temperatures (1600°C). The structure and chemistry at the grain boundaries of cold and conventionally processed BZCY72 were characterized by transmission electron microscopy and correlated to the electrochemical properties. Our work introduces a new pathway for processing of barium zirconates at intermediate temperatures, while maintaining electrochemical performance, chemical robustness and relative densities of state-of-the-art sintered membranes.

# 3D printing as an economical and efficient method for fabricating solid oxide cell (SOC) stacks sealings

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## Abstract:

SOC are gaining a lot of attention worldwide as an alternative way of generating electricity. This is due to their high efficiency and ultra-low emissions when fed by fuels with low $CO_2$ footprint. The need for reliable sealing preventing mixing of oxidizer and fuel during SOC operation requires specially designed sealing composition as well as development of adequate shaping technique. Common method for fabrication of such gaskets relies on tape casting which allows to obtain highly uniform layer of casted material. Beside wide-spread use this method has number of drawbacks such as large amount of waste material, complexity and number of taken steps. The aforementionted disadvantages might be overcome by the use of 3D printing method, which is waste-free, more efficient and includes fewer fabrication steps when compared to tape casting.

Presented study was focused on the development of the glass paste suitable for robocasting. A number of compositions were prepared, consisting of different solvent:plasticizer:binder ratios. Moreover, two different binders were tested. The pastes with different amount of solid phase were prepared and applied in the 3D printing process after evaluation of their rheological properties. Both, simple and complex shapes were printed on different substructures to investigate the preferable conditions of the shaping process, which resulted in the most utilitarian composition. Finally, application of the printed glass seals was verified in stacks during operation under standardized conditions in frame of long-term tests. The developed method allowed obtaining high quality seals suitable for the SOC stack. Moreover, it seems to be a promising solution in terms of the ease of scaling-up and decreasing the cost of stacks production in large scale.

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# Translucent/transparent spinel phosphors for solid state lighting and photocatalytic applications

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## Abstract:

Translucent MgAlON and transparent $MgAl_2O_4$ spinel ceramics doped with both transition and rare-earth metals have been prepared. A systematic study was performed to develop a processing methodology for elimination of microstructural defects in sintered samples and improving optical transparency. The green pellets were prepared from freeze granulated and dried powder mixtures by uniaxial and cold isostatic pressing using 400 MPa pressure. The oxide $MgAl_2O_4$ spinels were sintered in air at 1550°C and subsequently HIP-ed at 1550°C for 5 h in 200 MPa Ar gas. A similar process, but at 1800°C was used for the preparation of MgAlON ceramics. The optical real in-line transmittance (RIT) of polished $MgAl_2O_4$ specimens was 95% of the theoretical value.

A series of translucent MgAlON phosphors doped with different cations were prepared and emitted a blue ($Eu^{2+}$), yellowish ($Ce^{3+}$) red ($Yb^{3+}$), and dark red ($Er^{3+}$) light. Some of the phosphors excited by green light emitted dark-red light (715-720 nm).

Titania nanotubes (TNTs) were prepared on spinel substrates by anodization of Ti layer, previously deposited on their surface. The photocatalytic properties of TNTs on spinel substrates were studied by following the degradation of bisphenol A and rhodamine B under UVA irradiation. A promising results have been obtained for the photocatalytic applications of TNTs on transparent/translucent spinel substrate.

## Acknowledgements:

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# High power factor in isovalently substituted Ca3Co4O9 ceramic through a rapid preparation method

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## Abstract:

Since the discovery of the first Co-oxide based ceramic with high thermoelectric (TE) properties [1], many works have been performed in this family to find new materials displaying TE properties. However, these bulk materials possess relatively low TE performances and, as a consequence, many works are performed to increase their TE properties, evaluated through the dimensionless Figure-of-Merit, ZT (=$S^2T/r\ k$, where S, T, r, and k are Seebeck coefficient, absolute temperature, electrical resistivity and thermal conductivity, respectively). In this expression, $S^2/r$ is called power factor (PF).

The improvement of properties is usually performed in two main directions. The first one exploits their anisotropic properties, by aligning the grains along the current flow direction techniques [2,3] to decrease electrical resistivity. The second approach uses cation substitution to tune up ZT [3].

In this work, a combination of both approaches will be performed by isovalently substituting Ca by Sr in $Ca_3Co_4O_9$ ceramic material produced by attrition milling to increase reactivity of precursors. After precursors preparation, materials will be subjected to hot-uniaxial pressing to produce highly dense materials with improved grain orientation. Consequently, electrical conductivity will be improved, without drastic modification of Seebeck coefficient increasing, in an important manner, PF values in a very short processing time.

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# Enhanced performance of high-voltage batteries by the coating of spinel LiNi0.5Mn1.5O4 with different Li-containing oxides

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## Abstract:

$LiAlO_2$,[1] $LiNbO_3$,[2] $Li_{0.35}La_{0.55}TiO_3$ (LLTO)[3] oxide- and $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP)[4] phosphate-coated spinels $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) were prepared by a new method. The structure of the obtained active materials was investigated using SEM, TEM, XRD, EDX and XPS spectroscopy, and the electrochemical properties of the prepared cathodes were probed by the charge-discharge studies. The morphology of the coating material on the surface and the degree of coverage of the coated particles were investigated by the SEM, which shows at low temperatures a fully dense and homogeneous coating on the surface of active material, but at high temperatures – a coating-dependent morphology. XRD studies of the $LiNbO_3$-coated LNMO samples with different $LiNbO_3$ concentrations and treated at various temperatures (between 300 and 800 °C) reveal no expansion or contraction of the unit cell, indicating the absence of foreign ions diffusion into the structure of LNMO. In contrast, the LLTO oxide- and LATP phosphate-coated spinels, treated at the same conditions, show clear evidence of La/Ti and Al/Ti ions doping, respectively. However, the capacity retention tests of all coated materials show a significant improvement of the electrochemical properties associated with the nature of the coating layer. The results also reveal that the coated materials exhibit enhanced reversibility and stability compared to the pristine and, although all coatings show good protection properties, the synthetic procedures and treatment conditions have to be selected individually for every experiment.

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# Ceramic supports with highly dense and aligned pores for molten-carbonate based CO2 separation membranes

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## Abstract:

Composite molten salt-ceramic membranes are innovative devices for high temperature $CO_2$ separation with high selectivity. The membrane performance depends on intensive material properties (ionic and electronic conductivity of the phases) and on its geometry (thickness) and microstructure (pore volume, size, connectivity and tortuosity factor). Ceramic production processes that allow controlling pore size, alignment and connectivity are needed for optimum performance.

The microstructural characteristics of directionally solidified fibrilar eutectics are appealing. Selective dissolution of the minority phase provides a ceramic support with a high density of aligned pores, with pore diameter in the micron range and a high specific surface. Here we report on the first gas separation membrane using a porous ceramic matrix obtained from a magnesium-stabilised zirconia (MgSZ) – MgO fibrilar eutectic. The porous matrix consists of highly aligned, ~1 μm diameter pores, with 21% porosity and all pores aligned within 10°. The finished membrane showed a high $CO_2$ permeability of $1.41x10^{-10}$ $mol.m^{-1}.s^{-1}.Pa^{-1}$ at 815 °C, among the highest reported for supported molten-carbonate membranes. We suggest that the high permeability is attributable to the excellent pore characteristics resulting from directional solidification.

In a further step, we study eutectics of the systems YSZ – MgO and $Ce_xZr_{1-x}O_2$ – MgO, with a consistently stable fibrilar microstructure. The mixed-valent Ce element also aims to add an electronic contribution to the support conductivity, which is known to enhance the $CO_2$ and $O_2$ permeability. Composition, microstructure, structural and ion conducting properties of these families are discussed in relation to their expected performance in $CO_2$-selective membranes.

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# Deep eutectic solvents as possible electrolytes for Al-ion cells

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## Abstract:

The growing importance of renewable energy sources forces the development of new electrochemical energy storage technologies. Lithium-ion (LIBs) batteries currently dominate the battery market. However, due to the scarcity of lithium supplies in the Earth's crust, the limited avaibility of other components (such as Co) further uses of Li-ion technology may be troublesome. Aluminum is an example of alternative to lithium, as a high energy density transporter with low cost due to its common occurrence on Earth.

The primary challenge with today's aluminum-ion batteries (AIBs) are cathode materials that would allow for the long-term use of these systems. Transition metal oxides, metal sulfides, and carbon materials are among the studied materials. Another challenge for sufficient Al-ion cells is a suitable electrolyte that would allow for transportation of aluminum ions between electrodes and also would be non-toxic, low cost and eco-friendly.

The goal of this study was to test different ceramic $WO_3$-carbon composites as cathode materials that could be successfully used with electrolytes based on Deep Eutectic Solvents (DES). DES used as an electrolyte were prepared from polyhydroxyalkanoates (PHA) monomers, choline chloride and aluminium chloride. The impact of processing parameters on the physicochemical properties of prepared $WO_3$-based materials and the performance of Al-ion electrochemical cells made with these materials was studied. Characteristics for manufactured Al-ion cells were investigated using measurements of Open Circuit Potential (OCP), Cyclic Voltamperometry (CV), and Galvanostatic Charge/Discharge curves (GDC). The findings of the EIS and electrochemical properties research have been analyzed and correlated with the materials' structure and microstructure.

## Acknowledgements:

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# The influence of sintering method on electrical properties of BaCeO3-based composite protonic conductors

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## Abstract:

$BaCeO_3$-based compounds represent the group of intermediate temperature ceramic protonic conductors. Barium cerium oxide exhibit relatively the highest protonic conductivity in this group of conductors crystallizing in perovskite structure, especially if it is acceptor-doped. One of the disadvantages of such materials is poor chemical stability in the presence of $CO_2$ and $H_2O$ vapour which brings this material into the disintegration that gives the affect to the regression of mechanical or electrical properties. The way to improve these properties is formation of solid solutions, doping with elements from lanthanides group and/or modification of the grain boundaries which has the dominant impact on the total electrical conductivity by the formation of composite materials.

In this work, the modification has been done by the formation of composite materials. The modifier Ba-Ce-Y-Si-P-O prepared by sol-gel method was introduced into the host material; $BaCe_{0.9}Y_{0.1}O_3$ by mechanical homogenization, compacted in the pellet die and then sintered using two different methods: free-sintering and Spark Plasma Sintering (SPS) at controlled conditions. Obtained materials were characterized and investigated X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques. The electrical properties were determined using Electrochemical Impedance Spectroscopy (EIS) technique as a function of gas atmosphere and temperature. Based on the obtained results the influence of chemical composition and sintering method on phase composition, structure, microstructure and the electrical properties for prepared materials was determined and discussed.

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# Suppression of interfacial reactions in lithia-based cathodes for lithium ion batteries

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## Abstract:

Lithia ($Li_2O$)-based cathodes are considered promising alternatives to commercial cathodes because of their high capacity owing to the anionic redox reaction. The capacity of most cathodes is based on the cationic redox reaction induced by heavy transition metals in the structure, whereas that of lithia-based cathodes is based on the anionic redox reaction related to oxygen, which is lighter in weight. However, charged lithia-based cathodes containing $Li_2O_2$ and superoxo species are highly reactive to electrolytes, which deteriorates the cathode's electrochemical performance during cycling. So, the most difficult challenge in using these cathodes is controlling the interfacial reactions derived from the reactive lithia-based cathodes. In this study, the suppression of undesirable interfacial reactions is focused. Various approaches were used to reduce the interfacial reactions between cathode and electrolyte/binder, which results in the enhanced electrochemical performance such as increased available capacity and improved cyclic performance.

# The influence of preparation conditions and microstructure of hydrothermally derived MnO2 electrode materials on electrochemical performance of pseudocapacitors

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## Abstract:

Supercapacitors are electrochemical devices that can store electrical energy and provide higher power density than commonly known reversible batteries (Li-poly, Li-ion). Different charge storage mechanisms can be considered and among them, in the case of pseudocapacitors, a redox reaction can be involved supporting typically valid adsorption and intercalation processes. The properties of electrode materials can have a strong influence on the capacitance by the charge and size of ions interacting with the electrode surface.

In this work, the pseudocapacitors based on graphite foil/manganese oxide powder electrodes, Celgard™ separator foil, and different electrolytes were manufactured and tested. Different $MnO_2$ powders were prepared using the hydrothermal method and then used for capacitor electrode formation using the doctor blade method.

X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) were used to characterize the obtained powders, while Cyclic Voltammetry (CV) Galvanostatic Charge/Discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS) were used to determine the electrochemical properties of constructed prototype supercapacitors. Obtained electrochemical results were related to the physicochemical properties of $MnO_2$-derived materials used for electrode construction. The obtained results were discussed in detail in terms of structure, microstructure, and electrical properties of $MnO_2$ materials used for electrode formation.

## Acknowledgements:

This work has been supported by program “Excellence initiative – research university” for the AGH University of Science and Technology, grant No. 501.696.7996.

# TiO2 nanotubes on translucent spinel substrate: degradation of different pollutants under UVA irradiation in water

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## Abstract:

In the frame of the work titania nanotubes were deposited on spinel ceramic substrate by anodization of Ti layer, previously deposited by magnetron sputtering, in an ethylene glycol electrolyte. After annealing at 450 °C, the titatania nanotubes were characterized by XRD and SEM in order to investigate the crystalline phase composition and the morphology of the prepared samples. The photocatalytic properties of layers were studied by following the degradation of bisphenol A and rhodamine B under UVA irradiation. To the best of our knowledge, it is the first time that $TiO_2$, in the form of nanotubes, are deposited on transparent spinel for photocatalytic applications. The results are encouraging and further studies are carried out in order to improve the photocatalytic process.

## Acknowledgements:

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# Phase relationships, electrical transport properties and redox behavior of oxides in the PrVO4-Ca2V2O7 system for SOFC applications

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## Abstract:

Rare-earth and alkaline-earth vanadates attract attention as prospective materials for electrochemical applications, in particular, as redox-reversible components for fuel electrodes of solid oxide fuel cells (SOFC). An essential advantage of (Ln,A)$VO_x$-derived components of SOFC anodes is their anticipated resistance to carbon deposition and sulfur-containing impurities, which is critical for hydrocarbon- and biogas-fueled SOFCs. The present work was focused on the oxides of the $PrVO_4$-$Ca_2V_2O_7$ system as fuel electrode precursors, with an emphasis on phase formation, redox and thermomechanical behavior, and electrical properties.

$PrVO_4$, $Ca_2V_2O_7$ and the ceramics with the nominal composition $Pr_{1-x}Ca_xVO_{4-\delta}$ ($x = 0.02$-$0.20$) were prepared by the conventional solid-state route. Ceramics samples were sintered at 1000°C for $Ca_2V_2O_7$ and 1300°C for other materials. XRD demonstrated the formation of phase-pure $Pr_{1-x}Ca_xVO_{4-\delta}$ solid solutions with the tetragonal zircon-type structure for up to 5 at.% of calcium in Pr sublattice. At the same time, SEM/EDS suggest a lower solubility indicated by the presence of Ca-V-O phase impurities. Doping by calcium increases mixed ionic-electronic conductivity of Pr(Ca)$VO_4$ ceramics under oxidizing conditions. The electronic contribution is p-type and decreases with reducing $p(O_2)$. The reduction of $Pr_{1-x}Ca_xVO_{4-\delta}$ ceramics in a 10%$H_2$-$N_2$ atmosphere at 800°C leads to phase separation and formation of perovskite-like $PrVO_3$ and $CaVO_3$ phases. The redox behavior of $PrVO_4$-$Ca_2V_2O_7$ ceramics on isothermal cycling between air and 10%$H_2$-$N_2$ was studied by impedance spectroscopy, thermogravimetry, dilatometry and post-mortem XRD analysis.

## Acknowledgements:

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# Formation mechanism of organosilica layers towards periodic porosity

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## Abstract:

Membrane-based molecular separation processes like nanofiltration (NF) are used more and more in the industry, by virtue of their low-energy consumption and high throughput. The specific industrial application of organic solvent NF demands a robust membrane that can endure continuous exposure to organic solvents at high temperatures. Ceramic membranes NF with a molecular weight cutoff (MWCO) of 200—1000 Da are a perfect candidate for such demanding separation conditions, thanks to their chemical, mechanical and thermal stability. Among the current NF ceramic membranes, organosilica membranes, prepared via sol-gel methods, contain organically-bridged siloxanes making them suitable to filter organic solvents at high temperatures thanks to their high hydrothermal stability, and organophilic surface properties. Nevertheless, these membranes still suffer from permeability and selectivity limitations due to the formation of a tortuous and random porous network. To overcome this issue, this work focuses on the synthesis of a new generation of organosilica membranes with a periodic porosity via a modified Stöber growth pore approach. Hereby, periodic porosity refers to a controlled pore structure made of pores vertically aligned and uniformly distributed directly on top of porous ceramic supports. Thanks to a series of specific techniques, such as HR-SEM and GISAXS, we demonstrated that controlled sol-gel conditions enable the formation of organosilica layers directly on top of macropores. The influence of the pore diameter of the ceramic support on the organosilica membranes formation was evidenced through permporometry and MWCO measurements.

# New ceramic heating elements based on zirconium carbide

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## Abstract:

Ceramic heating elements have been well established in industry for a number of decades. Particularly silicon carbide and molybdenum disiliced are favorably used for heating application in high temperatures under air atmosphere. Refractory metals are preferred for heating devices in high vacuum atmospheres. This is attributed to the very low evaporation pressure of tungsten or molybdenum at temperatures > 1500 °C. On the other hand, these metals show rather low electrical resistance and high manufacture costs.

Zirconium carbide may act as a reasonable technical alternative to tungsten or molybdenum heaters. The vacuum pressure of ZrC is close to that of tungsten and lower than that of molybdenum. ZrC is stable up to 2500°C at least and the melting temperature reaches > 3500 °C.

During recent years IKTS developed a technology which opens an economic technology to produce ZrC ceramics by pressurless sintering technology. First demonstrator heating elements were manufactured up to a length of 250 mm and 20 mm diameter. Heating tests under vacuum show promising results which are close to that of tungsten heating elements. Moreover, the electrical resistance of ZrC is one order of magnitude higher than that of tungsten and the thermal conductivity is considerably lower. These properties enable a much better energy efficiency of heating processes. First results for the validation the feasibility of ZrC heaters in praxis will be shown.

## Acknowledgements:

This project was funded by German BMBF 03VP05870

# Substrate-induced modification of microstructure and thermoelectric properties in Sr-doped Ca3Co4O9 thick films

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## Abstract:

$Ca_3Co_4O_9$ ceramic material is one of the most promising p-type thermoelectric oxides. It can work at high temperatures without degradation or oxidation due to its high thermal and chemical stability. These properties allow the exploitation of high temperature waste heat sources. Moreover, the use in form of thick films is very promising in practical applications due to their low costs and relatively high performance.

In this work, thick films of Sr-doped $Ca_3Co_4O_9$ thermoelectric ceramics have been prepared through the dip-coating technique. The effect of the amount of solid in the suspensions has been determined by using two different powders content (22, and 29 vol.%) to produce different coatings on $Al_2O_3$ polycrystalline substrates. The resulting coating thickness has been determined from [1] using the values of powder density, the surface tension, viscosity of the suspension at 100 $s^{-1}$, as well as the withdrawal speed. Moreover, the effect of substrate has also been investigated using $Al_2O_3$ monocrystalline substrates. After drying the coatings they were sintered at 900 °C for 24 h with a final furnace cooling, and characterized through surface XRD, and SEM observations in the transversal direction to evaluate microstructure and thickness of the sintered coating. These results will be related with the final thermoelectric performances determined through the power factor, PF ($S^2/r$).

[1] T. Schneller, R. Waser, M. Kosec, D. Payne (Eds.), Chemical Solution Deposition of Functional Oxide Thin Films, Springer-Verlag, Wien, 2013.

## Acknowledgements:

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# Novel electrolyte for composite CO2 separation membranes

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## Abstract:

In the last decade composite $CO_2$ separation membranes consisting of a molten salt (net carbonate-ion conductor) within an oxide skeleton (oxide-ion conductor), showed promising efficiency results. These membranes may possess multiple charge carriers, depending on the molten phase and environment characteristics.

In membranes using ceria-based electrolytes (e.g., Gd-doped, CGO), oxide-ion transport is rate limiting. Accordingly, any improvement in $O^{=}$ transfer will drastically improve the membrane performance. The main aim of this work is to test the role of molten nitrates (Na and K, KNN) in $CO_2$-separation membranes. Possible improvements in comparison with standard carbonates molten phase (Na, Li and K, KNLC) include lower impregnation temperature, higher contact angle and, as result, better impregnation and higher stability.

Fourier-transform infrared spectroscopy and $NO_3^-$-selective electrodes were used to monitor the conversion of nitrates into carbonates at different temperatures, in $CO_2/N_2$ atmosphere. The membrane $CO_2$ separation performance was measured in a home-made setup. The composition of the feed ($N_2$:$CO_2$=1:1) and sweep (Ar) streams was the same for all experiments with a flow rate 20 $ml.min^{-1}$. Nitrogen was used also as marker to detect any leak in the system. The measurements were performed in the 450-700 °C temperature range, with 25 °C steps. The nitrates-based membranes show up to 60% higher performance in comparison with standard KNLC-based ones. Probable active chemical species and performance improvement mechanisms are discussed in the frame of this work.

## Acknowledgements:

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# Thorough understanding of degradation in composite CO2 separation membranes

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## Abstract:

The electrochemical separation of carbon dioxide using mixed oxide-molten carbonate ionic conducting composite membranes is recently gaining popularity due to feasibility to operate directly at source site. The membrane works on a counter flow of $CO_3^{=}$ ions in molten phase and $O^{=}$ in solid oxides. Despite the earlier work focused solely on increasing separation capability, the real causes of degradation were scarcely studied. Thus, the current study exploits the causes behind the degradation of membranes after long-term $CO_2$-seperation, using composites of totally different molten phase content and oxide microstructures.

$Ce_{0.9}Gd_{0.1}O_{1.95}(CGO)_{1-X}$-$LiNaCO_3(NLC)_X$ (X = 0.2, 0.4 vol.%) composites were prepared in two-steps. The consolidation of 40 and 20 vol.% porous CGO skeletons, respectively sintered at 850 and 1000 °C, was followed by impregnation of molten carbonates at 800 °C. The pre- and post-mortem microstructural, electrochemical analysis were performed on all membranes tested for $CO_2$-separation stability and/or analogy feed and sweep atmospheric conditions, using XRD, SEM, and EIS.

Both composite membranes with respectively 20 and 40 vol.% of NLC were tested for $CO_2$-separation stability at 650 °C for 250 h. The best stability (≥90% of initial performance) was found in membranes of higher ceramic fraction (i.e., 20 vol.% NLC), whereas the opposite results was found in membranes with higher fraction of NLC. The EIS of composites tested in $CO_2$-separation stability and/or aging in analogue sweep and feed conditions, and a fresh batch, were used to inspect degradation and likely microstructural and compositional causes. The changes in elemental composition at feed and sweep sides of composite membranes were also analysed in and compared with fresh CGO powder.

## Acknowledgements:

This work was funded by project CICECO-Aveiro Institute of Materials (FCT Ref. UID/CTM/50011/2019), financed by national (Portugal) funds through the FCT/MCTES, and when applicable co-financed by FEDER under the COMPETE 2020 Program. Specific support (AJ) provided by national funds (OE), through FCT, IP, in the scope of the framework contract foreseen in the numbers 4, 5, and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19. M.S. acknowledges the support of the FCT–2020.00625.CEECIND grant.

# Investigation and characterization of SrTiO3 thin films for high temperature solar cells

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## Abstract:

The pressing issue of climate change along with the continuously increasing demand for energy, makes the search for sustainable energy sources a priority. A well-known approach is harvesting solar energy by transferring it directly to electrical energy in photo-voltaic cells. Commonly, this is done around room temperature e.g., by Si-based solar cells. However, also high temperature solid oxide solar cells got increased attention over the last years. For devices, where heat is produced during operation, solid oxide solar cells are promising candidates and they might find an application in powering e.g., small sensors for the internet of things (IoT) in the future.

In this study, high temperature solid oxide solar cells, based on $SrTiO_3$ thin films are investigated. The preparation of multi-layer systems, consisting of counter electrode (LSC, LSM), UV-absorber (undoped STO) and UV- transparent top electrode (LSCr), was performed by pulsed laser deposition. Systematic variations of laser frequency, laser fluence and deposition time were conducted. The set of samples are investigated by means of impedance spectroscopy, voltage and current measurements in dark mode (UV off) and illuminated mode (UV on). Impedance spectra are used to gain mechanistic insights into the processes, occurring during UV illumination. Resulting photo-voltages are in the range of a few 100mV, and are discussed in terms of reproducibility and cycle stability. Furthermore, thin film results are compared to already reported bulk STO solar cells in terms of space charge behavior and identification of relevant processes.

# Molten metal – zinc oxide composites for high temperature thermal energy storage

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## Abstract:

Thermal energy storage is at the leading edge of various applications, including waste heat recovery, solar storage and zero-energy buildings. Through a reversible solid-liquid phase transition, phase change materials (PCMs) can be utilized to store heat. PCMs provide high energy storage capacity at constant temperature. The volume change during the phase transition, on the other hand, causes inconsistency in crystallization and leakage, increasing the system's complexity and shortening the life of such materials. These shortcomings can be diminished by impregnation in a porous matrix or encapsulation with an inert shell, yielding shape-stabilized PCMs which maintain their macroscopic shape during phase change.

Here, the synthesis and properties of Bi-ZnO nanocomposites were investigated in order to obtain shape-stabilized phase change materials. ZnO was prepared by sol-gel method and various amounts of Bi were added to the solution. The physico-chemical and thermal energy storage properties of the samples were determined through various characterization techniques. The thermal energy storage and shape-stability was assessed by Differential Scanning Calorimetry (DSC) coupled with in situ Optical Microscopy (OM) while the thermal stability was determined through Thermogravimetric analyses (TGA). The structure and phase composition was analysed through Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD). The samples morphology was assessed through and Scanning and Transmission Electron Microscopy (SEM, TEM). Thermal reliability was determined after 50 consecutive heating cooling cycles. The Bi-ZnO materials have good thermal energy storage, high reliability and shape stability, being able to function as high temperature PCMs.

## Acknowledgements:

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# Optimizing ReBa0.5Sr0.5CoCuO5+δ double perovskite oxides for application as oxygen electrodes for Solid Oxide Cells

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## Abstract:

Cobaltite-based $ReBaCo_2O_{5+\delta}$ (Re: rare-earth element) oxides are known for their high mixed ionic-electronic conductivity and excellent electrocatalytic activity. Along with the appropriate thermomechanical characteristics, these properties allow using them as the electrode materials in Solid Oxide Fuel Cells and Solid Oxide Electrolyser Cells. However, their rather high thermal expansion coefficient, connected with the toxicity of barium and cobalt, hinder the practical application. It has been shown that a partial substitution at the A- and B- sites allows for modifying the properties, including the crystal structure, oxygen content, conductivity, as well as electrocatalytic activity.

We propose $ReBa_{0.5}Sr_{0.5}CoCuO_{5+\delta}$ (Re = Y, La, Pr, Nd, Sm, Gd) double-perovskite oxides, in which half of barium and cobalt was replaced by strontium and copper, respectively. The synthesized oxides were investigated regarding their basic physicochemical properties, as well as electrochemical characteristics when used as the oxygen electrodes in reversible Solid Oxide Cells. Additionally, ab initio calculations were performed, to evaluate the formation energy of the oxygen vacancies. In the series, high total conductivity, exceeding 70 S $cm^{-1}$ at high temperatures, and relatively low thermal expansion coefficient values on the order of $13\text{-}15 \cdot 10^{-6}$ $K^{-1}$ were measured. The manufactured electrodes delivered high power densities, with best values exceeding 650 mW $cm^{-2}$ at 750 °C. This corresponds to the very low electrode polarization resistance, with the lowest values on the order of 0.03 Ω $cm^2$ at 800 °C, being stable over 100 hours. Furthermore, the work discusses the selection of the best oxygen electrode material for the electrode-supported Solid Oxide Cells.

## Acknowledgements:

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# Towards viable solid-state batteries: electrochemical studies and amplifying fabrication for a silicate-based Na superionic conductor

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## Abstract:

All-solid-state sodium batteries (ASSNBs), which combine the benefits of high safety and low cost, are expected to be an alternative or complementary storage technology to lithium ion batteries. Herein, we developed an aqueous tape casting technique for the continuous fabrication of ceramic sheets made of silicate-based $Na_5YSi_4O_{12}$ (NYS) $Na^+$ ion superionic conductor for the first time. After sintering, the ceramics showed a total conductivity of 1.0 mS $cm^{-1}$ at room-temperature, low total activation energy of 0.30 eV, and wide electrochemical window of over 8 V. The critical current density of NYS tape against Na-metal electrodes can reach 2.2 mA $cm^{-2}$ and the galvanostatic cycling time is over 280 h under 0.8 mA $cm^{-2}$ and 0.8 mAh $cm^{-2}$. The obtained tape has high crystalline purity, dense microstructure, favorable mechanical properties (hardness H of 2 GPa and elastic modulus E of 45 GPa). This work not only highlights the potential of the scarcely studied silicate-based NYS ionic conductor as a functional separator, but also presents a cost-efficient and eco-friendly continuous fabrication using the aqueous tape casting technique, thus being expected to boost the practical application of NYS as solid-state electrolyte in ASSNBs. A further step towards ASSNBs is also on the way.

## Acknowledgements:

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# Sr0.7Ce0.3MnO3-$\delta$ as anode material for fuel-assisted solid oxide electrolysis cells

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## Abstract:

Long-term degradation remains the main issue for the viability of solid oxide electrolysis cell (SOEC) technology as a practical hydrogen production system. The principle of the so-called fuel-assisted electrolysis cell is to supply the low-grade fuel to the anode where it can react with oxygen, thus bringing down the oxygen chemical potential at the electrolyte/anode interface and improving its stability. The present work is aimed at the evaluation of $Sr_{0.7}Ce_{0.3}MnO_{3-\delta}$ perovskite for potential application as an anode in fuel-assisted SOEC.

$Sr_{0.7}Ce_{0.3}MnO_{3-\delta}$ was synthesized by the glycine-nitrate technique with repeated calcinations at 900-1300°C to obtain phase-pure perovskite material. Ceramic samples were sintered in air at 1450°C. The oxide exhibits negligible variations of oxygen content under oxidizing conditions while reducing p($O_2$) below $10^{-4}$ atm at 750-900°C results in oxygen losses and reduction of Mn cations. The low-p($O_2$) stability boundary of the perovskite phase at 800°C corresponds to $\sim 3\times10^{-17}$ atm. $Sr_{0.7}Ce_{0.3}MnO_{3-\delta}$ shows good thermomechanical compatibility with solid electrolytes under oxidizing conditions; however, reduction at operation temperatures (800°C) leads to undesirable chemical expansion. The electrical conductivity of $Sr_{0.7}Ce_{0.3}MnO_3$ ceramics is p-type electronic and decreases with reducing p($O_2$) but still exceeds 40 S/cm under anticipated oxygen electrode operation conditions. The electrochemical activity of $Sr_{0.7}Ce_{0.3}MnO_3$ electrodes was evaluated in contact with YSZ solid electrolyte as a function of relevant parameters. The best performance was obtained for the cells with a CGO buffer layer and $Sr_{0.7}Ce_{0.3}MnO_3$ electrodes infiltrated with $PrO_y$ (load of ~ 30 wt.%) that can show anodic overpotentials of ~50 mV under 400 mA/cm$^2$ at 800°C in air.

## Acknowledgements:

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# Virus retention of porous and granular Al2O3 modified with MgAl2O4 for drinking water production

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## Abstract:

Safe and readily available drinking water is one of the major requirements for a healthy life. Poor water quality rapidly affects many individual lives and threatens public health by carrying pathogens and pollutants. In 2017, 2.2 billion people did not have access to a safely managed drinking-water service, and the situation hardly improved ever since. One of the main strategies to address problems associated with waterborne diseases worldwide is to apply on-site water treatment systems, i.e. point-of-use (POU) or household water treatment (HWT) technologies, to remove or lower microorganism contents in water prior to consumption. Ceramic filters are hereby of particular interest, owing to their properties that render them particularly suitable for regeneration processes combined with long service life without degradation. Common ceramic filters are able to reliably remove large-sized microorganisms such as protozoa and bacteria, but they struggle with virus removal, owing to their small size (i.e. ~25 nm). However, modifications of the filter surface has shown that virus removal can be achieved through intermolecular surface forces. In this study, we developed ceramic filters made from $MgAl_2O_4$ nanoparticles distributed within a granular porous $Al_2O_3$ by spray granulation. These granular materials have a positive charge of a large pH range and were tested in filtration experiments with MS2 and fr bacteriophages to determine their virus retention performance. It was found that $MgAl_2O_4$-modified $Al_2O_3$ granules show promising adsorption properties, reaching a $\log_{10}$ reduction of 5 and 7 for MS2 and fr bacteriophages, respectively, after 2 L of filtration without any degradation in phase composition and morphology.

## Acknowledgements:

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# Synthesis and characterization of Ba(Fe,Zr,Ni)O3 perovskites for potential application in electrochemical NOx decomposition

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## Abstract:

Emissions of nitrogen oxides remain a significant problem associated with the use of fuel-efficient lean combustion in transportation (diesel engines) and the passivation of catalytic converters by excess oxygen in exhaust gasses. One possible way to achieve high-efficiency $NO_x$ conversion is electrochemical reduction under anodic polarization in symmetrical solid oxide cells. Recent research was focused on improving efficiency in the presence of 1-15 vol.% oxygen: seeking for $NO_x$ selective electrodes based on mixed-conducting transition metal oxides, impregnations with basic components (BaO, $BaCO_3$, $K_2O$) to enhance adsorption of acidic $NO_x$ or pre-oxidation of NO to $NO_2$ which is more readily adsorbed on the electrode surface. The present work is focused on the synthesis of Ba-rich $Ba(Fe,Zr,Ni)O_3$ perovskites and characterization of their electrical properties, phase stability, and thermomechanical behavior with the aim to assess the prospects of their use as electrocatalysts for $NO_x$ elimination.

$Ba(Fe_{1-x-y}Ni_xZr_y)O_{3-\delta}$ ($x = 0.05–0.5$, $y = 0–0.4$) ceramics were synthesized by glycine-nitrate combustion technique. Single-phase perovskites with a minor NiO impurity were found to form only for prevailing Fe content and with the total Ni and Zr content $x+y \leq 0.3$ at 1100°C. Sintering at $T \geq 1200$°C leads to segregation of secondary phases. The electrical conductivity of single-phase ceramics is moderate and reaches 3.5 S/cm at 400-500°C; this may limit electrochemical performance. The perovskite phase is demonstrated to be stable in reducing conditions down to $pO_2 \sim 10^{-16}$ atm. The dilatometric studies show unusual and nonlinear behavior of thermal expansion coefficients, with the absolute values varying in the range of 15-50 ppm/K at 250-950°C.

## Acknowledgements:

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# Polymer-derived silicon-based aerogels as shape stabilizers for thermal energy storage

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## Abstract:

In the last years, thermal energy storage (TES) has gained wide interest within the frame of daily and seasonal energy management and optimization. One of the main challenge in this topic is the confinement of phase change materials with high thermochemical energy or latent heat of crystallization to preserve their thermal characteristics over continuative use. Porous scaffolds are by far the best solution, and we are reporting, for the first time, the use of ceramic aerogels derived from pre-ceramic polymers (PDCs). The synthesis of novel silicon-based PDCs aerogels for TES will be discussed together with a characterization of their chemistry and the evaluation of the thermal performances. Two of the most promising inorganic salts for medium temperature ($T<400°C$) TES applications have been loaded in the ceramic aerogels. In particular, we selected $MgSO_4 \cdot 7H_2O$ and $NaNO_3$ as thermochemical and latent heat storage salts, respectively. For these two applications, which require mechanically and chemically strong materials able to bear hydration and crystallization stresses, we synthesized novel amorphous Si-O-C and Si-N aerogels obtained through the pyrolysis of pre-ceramic polymers. The Si-N/$NaNO_3$ composite exhibits an excellent energy storage efficiency of 82%, while the Si-O-C/$MgSO_4$ one is able to store 59.1 %wt of anhydrous salt and presents fast hydration/dehydration abilities. Both composites have limited salt leakage, and good stability to thermal cycling. Such a novelty in the TES field could pave the way towards new functional aerogels as shape stabilizers for PCMs storage solutions.

# Composite glass-zirconia sealing for SOC technology

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## Abstract:

Solid oxide cell technology is gaining high interest due to the high efficiency of energy or hydrogen generation seen as an environmentally friendly process of no greenhouse gas emission. Both applications require further development in the field of materials crucial for joining the cells in the stacks. One of them is sealing that separates anodic and cathodic compartments of the stacks, protecting the system from mixing of hydrogen and air in continuous operation at 600-800°C. Most common is the use of specially designed glass of a matching TEC value. It bonds the adjacent elements permanently forming a rigid seal. However, this can be troublesome to implement in some SOC stack designs due to the low mechanical strength of the softened glass, thus hybrid or composite gaskets are often required.

The aim of the research was to study the characteristics of SOFC-dedicated composite glass-zirconia seals based on commercial glass powder with zirconia grains as an infill and define the influence of the zirconia grain size on the properties of the seals. Sample gaskets composed with the use of different $ZrO_2$ powders of nano and micro grain size were fabricated by tape casting and used for joining two Crofer 22APU pieces following the sealing procedure adequate for the SOC stack. The cross sections of so prepared samples were analysed by SEM/EDS to study the adhesion and density of the seal. The compression of the seals was calculated on the basis of the thickness differences before and after the thermal treatment. Thermocycling tests were performed from cold restart additionally to investigate the reliability of the joints. It appears that $ZrO_2$ infill in the glass matrix can decrease the compression rate of the gasket allowing the same level of gas-tightness as the glass seal.

## Acknowledgements:

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# Symposium H: Ceramics and Glasses for Healthcare, Bioceramics and Optical Ceramics, Bio-Electroceramics

Invited presentation:

# Ceramic biomaterials: from traditional technologies to novel applications

Katalin Balázsi, Csaba Balázsi

*Centre for Energy Research, ELKH, Budapest, Hungary*

**Abstract:**

The 400 000 artificial hip joint operations made every year in the word and there are 25 000 000 people with a total hip replacement. The wear and risk of the implant loosening increases so that after 10 years 10-20% of the implants have to be renewed. Biomaterials used for implant should possess some important properties in order to long-term usage in the body without rejection. The biocompatibility, mechanical, chemical and surface properties play a key role in the creation of sufficient and long term functional replacements. New fundamental research outcomes with industrial perspectives are given for understanding the applications of ceramics in load-bearing and low-load-bearing bioimplants with directions for future developments. Nowadays, Si3N4 is a new bioceramic with extremely good mechanical properties. Hydroxyapatite (HA) is a widely used bioceramic in implantology considering its high bioactivity. A bioactive coating (HA) on the bioinert ceramic implant's surface (Si3N4) could help avoid the rejection from the body in the critical early few days after the operation. The preparation of bioceramics will be showed from traditional technologies to novel applications. The main trends and fundamental scientific problems will be discussed.

## Invited presentation:

# Mesoporous nanoparticles doped with ions with potential therapeutic effect: synthesis and characterization

Nurshen Mutlu[1], Fatih Kurtuldu[1], Zuzana Neščáková[1], Kai Zheng[2], Aldo R. Boccaccini[3], Dušan Galusek[1]

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[3] *Institute of Biomaterials, Friedrich Alexander University Erlangen-Nuremberg, Erlangen-Nuremberg, Germany*

## Abstract:

Mesoporous bioactive glass nanoparticles (MBGNPs) are attracting significant attention as suitable materials for multifunctional biomedical applications, as suitable vehicles for drug delivery, and controlled release of ions with potential therapeutic effect. In the present work, we report on our activities in the preparation and characterization of mesoporous nanoparticles in the system CaO-$SiO_2$, doped with various amounts of metallic ions, such as Ce, Ga, and Zn. Various methods of dopant incorporation are examined, and the influence of synthesis conditions on morphology, pore structure, specific surface, and solubility of the nanoparticles is evaluated. Ce- and Ga- doped systems exhibit bioactivity in-vitro, documented by precipitation of phosphate phases upon immersion in a simulated body fluid. The Zn-doping inhibits the formation of hydroxycarbonate apatite (HCAp). The Ce-MBGNPs are non-cytotoxic toward pre-osteoblast MC3T3-E1 cells in direct contact with nanoparticles up to a concentration of 100 µg/mL. The nanoparticles decrease the release of nitric oxide, indicating the anti-inflammatory response tested with lipopolysaccharides (LPS)-induced proinflammatory RAW 264.7 macrophage cells. Ce- and Ga-containing MBGNPs show antibacterial activity against S. aureus and E. coli without exhibiting cytotoxicity towards MG-63 osteoblast-like cells. Zn-MBGNs improve the differentiation of the MG-63 osteoblast-like cells, also showing a higher ability to adsorb proteins than their undoped counterparts. Due to their advantageous morphological and physiochemical properties, the prepared nanoparticles show promise as bioactive fillers in a variety of applications including bone regeneration and wound healing.

## Acknowledgements:

This paper is a part of dissemination activities of the project FunGlass. This project has received funding from the European Union´s Horizon 2020 research and innovation programme under grant agreement No 739566. Financial support of this work by the grants SAS-MOST JRP 2015/6, and VEGA 2/0028/21 is gratefully acknowledged.

Invited presentation:

# 3D printing of different types of ceramics for modern medical engineering

Johannes Homa, Daniel Bomze, Martin Schwentenwein

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## Abstract:

Additive manufacturing (3D printing) has become an integral part of modern medical engineering. Patient-specific medical devices based on titanium or cobalt-chromium-molybdenum alloys as well as auxiliary tools such as cutting or drilling guides made of plastics are currently on their way to becoming clinical standard. High-performance ceramics and bioresorbable ceramics are also gaining more and more interest in medical engineering due to their unique material properties and lithography-based ceramic manufacturing (LCM) is a very promising approach to shape different ceramic materials in very high precision.

This contribution will focus on 2 use cases. On the one hand, this will be bioresorbable scaffolds from tricalcium phosphate and hydroxyapatite and show the achievable resolution and reproducibility showing that the proposed approach is a suitable technique to produce biomimetic scaffolds of bioresorbable ceramics. Here, highly porous scaffolds could be produced with a minimum feature resolution around 150 µm for struts and pores, as well as with a relative standard deviation of well below 3% even for very small features. In addition, basic mechanical and biological testing was performed and the obtained results underline the good suitability for the usage of such structures as scaffolds in non-load bearing applications.

On the other hand, the production workflow of 3D printed lithium disilicate dental restorations will be presented based on a clinical case. The fit of the prostheses and aesthetic results were evaluated and the 3D printed material was analyzed regarding its leachability, cytotoxicity, and residual carbon content, and the data was compared to conventional CAD/CAM manufactured lithium disilicate.

Invited presentation:

# Advanced shaping approaches for the production of transparent ceramics and ceramic laser gain media

Jan Hostaša[1], Valentina Biasini[1], Laura Esposito[1], Andreana Piancastelli[1], Francesco Picelli[1], Guido Toci[2], Barbara Patrizi[2], Matteo Vannini[2]

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[2] *CNR INO, National Research Council, National Institute of Optics, Sesto Fiorentino, Italy*

## Abstract:

Transparent ceramics have been in the spotlight as advanced optical ceramic materials for the last two decades, in particular with rare earth doping for applications in photonics, and even more so with the wider use of compact diode-pumped lasers. The advantage of ceramic technology over that of single crystals is strongly related to the shaping possibilities given by the wide range of processing techniques. In the case of uniformly doped laser rods, even to-date, single crystals remain the material of choice, but their technology lacks the flexibility in terms of shapes and even more in compositional variation. Different studies have shown the advantages of dopant gradients or the introduction of multiple dopants into one component. And where single crystals require expensive, and not always reliable bonding processes, ceramics can be produced in one piece by different methods. The present work illustrates the various approaches applied in the shaping of transparent ceramics with structured dopant distribution for lasers. In particular, planar and channel laser waveguides composed of doped and dopant-free parts (Yb:YAG – YAG) were produced without the requirement of complex post-processing after a vacuum sintering step. The optical and laser performance is shown.

## Acknowledgements:

The authors gratefully acknowledge the support from the Italian Ministry of Defence under PNRM Contract No. 8731 of 04/12/2019 (CeMiLAP2).

## Invited presentation:

# ATZ bioceramics for medical instruments a comparison from CNC to LCM production

Claudia Ortmann[1], Thomas Oberbach[1], Jan Mokros[1], Martin Liebelt[1], Eric Schwarzer-Fischer[2], Nadine Lorenz[2], Maria Reichel[2]

[1] *Mathys Orthopaedie GmbH, Moersdorf, Germany*

[2] *Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden, Germany*

## Abstract:

Alumina and YTZP ceramics have been established in joint arthroplasty since the 1970s and 1980s. Zirconia-rich dispersion ceramics of alumina and YTZP have also been known for decades for high strength, high fracture toughness and low wear rates. ATZ (alumina toughened zirconia) is used as joint implant by Mathys since 2007. New efforts were made to use ATZ for production of a surgical cutting tool.

This paper summarizes the initial investigations on standard ceramic manufacturing (CNC) compared to LCM (lithography-based ceramic manufacturing) of a ceramic cutting tool. The product development began with the formulation of clinical requirements and the design suitable for ceramic part and manufacturing process. After defining the requirements for the ATZ-ceramic based on standards (ISO 13356, ISO 6474-2), suited raw materials were defined and the slurry development for the LCM process was started. A debinding process and thermal treatment - sintering and HIP - were elaborated. High purity and elimination of any porosity are mandatory for clinical use. The whole process was accompanied by the determination of properties such as microstructure, density after the thermal processes and geometry.

From appropriate raw materials meeting chemical requirements a suitable ATZ slurry was prepared. It was used to produce green parts. By adjusting debinding and thermal processes sinter densities of about 99,00 % theoretical density were reached. The microstructure could be adjusted that grain sizes for $Al_2O_3$ in the range between (0.39 - 0.41) µm and for YTZP in the range between (0.38 - 0.46) µm were produced.

First cutting tools made of ATZ ceramic were successfully realized with conventional CNC production and LCM.

## Acknowledgements:

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## Invited presentation:

# Bio-inspired scaffolds based on silicon-wollastonite and multi-substituted hydroxyapatite-chitosan hydrogel

Antonia Ressler[1], Nikhil Kamboj[2], Anamarija Rogina[1], Marica Ivanković[1], Irina Hussainova[2], Hrvoje Ivanković[1]

[1] *Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb, Croatia*

[2] *Tallinn University of Technology, Department of Mechanical and Industrial Engineering, Tallinn, Estonia*

## Abstract:

The scaffolds, which morphologically and physiologically mimic natural bone, are of high demand for regenerative medicine. To address this challenge, bioactive porous silicon/wollastonite (Si/W) scaffold was fabricated by additive manufacturing through the selective laser melting approach with a pore size of 400 μm, previously designed by using CAD. To increase biocompatibility and osteogenic properties of Si/W scaffolds, hydrogel based on multi-substituted hydroxyapatite (HAp) and biopolymer chitosan (CS/HAp) was incorporated into Si/W by impregnation and freeze-gelation method. HAp phase was obtained by wet precipitation method from biogenic source (cuttlefish bone) as a precursor of $Ca^{2+}$ ions and was additionally substituted with 1.25 mol% of $Sr^{2+}$, $Mg^{2+}$, $Zn^{2+}$ and $SeO_3^{2-}$ ions. The CS/HAp have shown a highly porous structure, with very well interconnected pores and homogeneously dispersed HAp, and high stability during 28 days in the degradation medium. Biological characterization in static and dynamic conditions by using human mesenchymal cells indicated that ionic substitutions have a beneficial effect on cells and tissues. SC/HAp have shown an increase in expression of osteogenesis-related markers, increased phosphate deposits and bone tissue formation. Therefore, SC/HAp was a good candidate to be incorporated in the Si/W scaffold to increase regenerative properties. The composite scaffolds were analysed by X-ray diffraction analysis, Fourier-transform infrared spectroscopy, scanning electron microscope, elemental mapping and compression test. By the combination of Si/W and CS/HAp, the biocompatibility of Si/W was enhanced, while the mechanical properties of SC/HAp were improved.

## Acknowledgements:

The authors are grateful for the JECS Trust for funding the visit of Dr. Antonia Ressler to Tallinn University of Technology (Contract No. 2020259). The L'Oreal-UNESCO Foundation 'For Women in Science', European Regional Development Fund (grant KK.01.1.1.07.0014.) and Estonian Research Council (grant PRG643) are gratefully acknowledged.

# Sinter-Crystallization of Nepheline Glasses for Dental Application

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## Abstract:

Glass-ceramics are used in dentistry to create biocompatible lifelike dental restorations, such as crowns, bridges, and veneers and is the closest material option to natural dentition. Layering methods of glass-ceramics in powder forms into tooth shape then sintering result in aesthetically pleasant dental restorative materials. However, existing glass-ceramics options for such dental application have significant limitations, they are prone to chipping or delamination compared to metal alloys and zirconia which influence the clinical decision, workflow, manufacturing processes, acceptance and accessibility of treatment options by patients. $TiO_2$ is known to play a key role in the controlled crystallization of ''bulk processed nepheline glasses''. The aim of this study was to investigate the effect of adding $TiO_2$ to a nepheline glass system made for powder processing to develop glass-ceramics for dental applications via sinter-crystallization route. Three novel glass compositions based on the nepheline system were synthesized using the melt-quench method. Glasses were designed to contain 3.0 molar % $TiO_2$, 6 molar % $TiO_2$ and one glass made free of $TiO_2$. Experimental glasses were ground into fine powders and then heat-treated at identical crystallization schedules then characterized using DSC, XRD, SEM and Dilatometry. The addition of $TiO_2$ hindered the densification process during the sinter-crystallization heat treatment. $TiO_2$ free glass was found to sinter crystallize into a desirable material. In this study, the use of 3 molar % $TiO_2$ and less was found to be effective in controlling the thermal properties without hindering the densification process during sinter- crystallization.

# Synthesis of bioactive materials based on Zn3(PO4)2 –Ca5(PO4)3F – CaAl2Si2O8 system for dentistry applications

Mastura Aripova, Tatyana Nam, Zebo Babakhanova

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## Abstract:

Never before has the situation been more important to have a dental material that can bond reliably to tooth structure, can potentially reduce biofilm formation and can also inhibit dental diseases as well as protect the tooth and aesthetic aspects. Getting own material, which would answer all demands is actual problem in medical materials in Uzbekistan.

Our investigation is aimed to create a new modern Glass-Ionomer Cement made from new composition of glasses in $Zn_3(PO_4)_2$ –$Ca_5(PO_4)_3F$ –$CaAl_2Si_2O_8$ system and liquid, as well as technological parameters, analysis of its physical and chemical properties, biological compatibility to living tissue.

Based on the results obtained in the study of the diagram of the $Zn_3(PO_4)_2$ –$Ca_5(PO_4)_3F$ –$CaAl_2Si_2O_8$ system, the area of glass formation was determined. To do this, we synthesized glasses in this system. Originally, thermal treatment of 36 of $Zn_3(PO_4)_2$ –$Ca_5(PO_4)_3F$ –$CaAl_2Si_2O_8$ system glasses was conducted. The glasses were prepared by fusion of these components in a ceramic crucible, with fusion temperature of 1450 °C. After melting and allowing the mixture to become thoroughly homogeneous at an elevated temperature, the melt was cooled rapidly by pouring it directly into water. This resulted in the formation of a glass frit consisting of large pieces of glass. It was then ground to a fine powder of 20–50 μm.

First, it was determined, that melting temperature increases with fluoride content reduction. Furthemore, dependence between glasses transparency was identified. Some show a degree of phase separation that leads to an opaque appearance, whereas others have no visible phase separation and are clear in appearance.As a result, clear glasses are more common for the system, which fit for obtaining materials with necessary aesthetic characteristics. However, opaque and phase-separated glasses could be appropriate to get stronger cements than clear glasses.

Working up scientific and technological base of synthesis GIC presents scientific and practical interest, which will help to obtain material with projected and managed properties. In view of their demonstrated properties, they can be developed even further to become an increasingly useful group of materials to assist with overcoming the problems of dental desease managment.

# The effect of TPMS design and pores size on biological and mechanical properties of Calcium Phosphate bone graft

Islam Bouakaz[1], Ehsan Sadeghian[2], Liesbet Geris[2], Gregory Nolens[3], David Grossin[4]

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[4] *Institut national polytechnique de Toulouse, Toulouse, France*

## Abstract:

Hydroxyapatite is one of the most used ceramics for bone filling due to its strong similarity with the bone minerals. The porosity of these materials was deeply studied because of its impact on bone regeneration. Ideally bone implant needs highly porous scaffolds, high pores interconnectivity and optimal sizing. These factors allow cells migration leading to an increase of the bone regeneration. Besides these morphological properties, the mechanical properties of the implants need to be comparable to the bone's one and depend on the load applied on this implant. Since increasing porosity decreases these mechanical properties, combining high mechanical properties and sufficient porosity can be achieved by generating specific internal design of the implant. Recent developments in ceramic 3D printing allow such complex design that meets these standards.

This work concerns the design and evaluation of the influence of macro-porosity and wall thickness on three different TPMS (Triply Periodic Minimal Surfaces). Compression and bending specimens of these latter were printed using Hydroxyapatite by direct light processing (DLP) stereolithography (SLA), then thermally treated for debinding and sintering.

To study the effect of pore size and wall thickness on the mechanical properties of these lattices' structures, three different pores sizes and wall thicknesses were applied for each structure.

The potential issue of TPMS additive manufacturing, dynamic and static in vitro results will be also presented.

The results allowed a better understanding of the mechanical and biological behaviours of these TPMS as well as the influence of pores sizes and wall thickness on their compression and bending resistance.

## Acknowledgements:

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# Development of nanocomposite ceramics (MgO/Y2O3) for infrared window applications

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## Abstract:

Transparent ceramics are materials of choice for high temperature infrared (IR) windows. Those windows are especially used for aerospace applications. Alumina, AlON and spinel-type ceramics have been developed for the 3-5 µm atmospheric transparency band. Nevertheless, these compounds show a degradation of their optical properties (transparency and emissivity) at high temperature (around 1000°C) limiting their use in that wavelength range.

MgO and $Y_2O_3$ have a broader transparency window up to 9 µm and they stay highly transparent in the 3-5 µm range even at high temperature but their thermomechanical resistance is weak. The aim of this study is to combine these compounds into a nanocomposite ceramic. The nanostructure would permit to keep a good IR transparency and increase its mechanical resistance (Harris et al. – 2013). Thus, to reach such properties, porosity ratio must be close to zero ($< 0,1$ %) and the average grain size must stay as small as possible ($< 200$ nm).

During this study, we processed MgO-$Y_2O_3$ nanocomposite ceramics by the sol-gel route for power synthesis. Then, sintering has been processed by natural sintering or the Spark Plasma Sintering techniques. Improvement of the ceramic quality (using a post-HIP) and sintering modelling are in progress. Finally, microstructural (MEB, EBSD, and Porosity), optical (transmission) and thermomechanical characterisations have been carried out.

Pellets with different nanostructures were obtained. Some pellets have their porosity ratio lower than 0,5 % and a medium average grain size smaller than 200 nm. A good transparency in the mid-infrared, up to 70 % for à thickness of 1 mm, is obtained for the most dense and homogenous samples.

## Acknowledgements:

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# Sanitization of different porcelain stoneware tiles after bacterial contamination

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## Abstract:

To fight COVID-19, the WHO advises disinfecting high-touching surfaces of indoor spaces, many of them made of ceramics. Albeit antibacterial ceramics are available, their use would mean to replace existing surfaces. Yet, antibacterial ceramics are more expensive than regular ones, which limits their widespread use. In this work, by an in-house protocol, we assessed different sanitization procedures on two kinds of porcelain stoneware tiles, one easy (E) and one hard (H) to clean, after contamination by Staphylococcus aureus ATCC 6538P. The tiles were industrially prepared and contaminated either as-prepared or after pre-treatment with bovine serum albumin (BSA), to mimic "clean" and "dirty" conditions. After 24h of contact with S. aureus, the tiles were sanitized by rinsing with PBS (positive controls) or treated with sponge rags soaked with either PBS or 0.2% NaOCl (to mimic standard surface cleaning practice). After complete detachment by ultrasound cleaning, the residual bacterial cells were assessed by CFU assay. Our data show that the treatment with NaOCl caused a drop of about 1.7 log with respect to positive controls in both materials, when pre-treated with BSA. Differently, the cleaning procedure on as-prepared tiles was much more effective on the E material (4.5 log drop) than on H material (3.1 log drop). Overall, these data highlight that on tiles treated with BSA the effectiveness of sanitization does not differ irrespective of the material tested, whereas on clean surfaces, bacteria adhere better to the H material, from where they are also removed less effectively. In conclusion, both the sanitization procedure and the surface of the porcelain stoneware tiles may greatly affect bacterial removal/persistence, in turn conditioning "indoor" contamination.

## Acknowledgements:

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# Ceramic 3D printing with adjustable multi-scale porosities

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## Abstract:

Camphene has been used as a porogen for its dendritic structures and sublimable property through crystallization of liquid camphene. In the existing freeze-casting method, the camphene is liquefied by heating (~60oC) and crystallized by cooling after shaping process. In this study, to prevent the problems of the existing method and for the application of photocurable 3D printing, various microscale porosities could be achieved under desired temperature via camphene/photopolymers solution system based DLP printing technique where camphene and two photopolymers with different solubilities. In this way, efficient manufacture of ceramics with adjusted multi-scale pore structures (nano, micro, and macro-sacle) that can be applied to multiple fields is possible via 3D printing technique, camphene loading, and sintering condition.

## Acknowledgements:

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# Influence of ceramic slurry composition on the physicochemical properties of bioceramic scaffolds

Ewelina Cichoń, Szymon Skibiński, Joanna Czechowska, Piotr Pańtak, Anna Ślósarczyk, Aneta Zima

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## Abstract:

According to the literature, organic additives used in ceramic slurries influence the final properties of scaffolds obtained by the foam replica method. This study focuses mainly on surfactant additives, which lower the surface tension of solvent and the interfacial tension between the liquid and the grain surface of the ceramic powder.

Seven different ceramic slurry compositions were prepared from calcined (in 900 °C) β-tricalcium phosphate (β-TCP) powder. The amount of β-TCP powder was 73 wt.%. Slurries varied in the amount of dispersant - Dispex A40 and binder - methylcellulose. Moreover, nonionic surfactants: Tween 20, Tween 80 or Tetronic 90R4 were used as slurry modifiers. Polyurethane sponges were immersed in the prepared suspensions. The coated sponges were dried at 60 °C and then sintered at 1200 °C.

Study revealed that nonionic surfactants did not have a positive impact on the microstructure and porosity of the scaffolds. The materials obtained from the ceramic slurries without methylcellulose and with polysorbates (Tween 20, Tween 80) possessed lower compressive strength (4.8 ± 1.2 and 4.1 ± 1.1 MPa, respectively) if compared with the reference material (5.8 ± 1.7 MPa). The presence of Tetronic 90R4 in the slurry along with methylcellulose slightly improved the mechanical properties of the scaffolds (up to 6.7 ± 1.8 MPa) but reduced their porosity. The most favourable physicochemical properties possessed scaffolds based on the slurry, containing Dispex A40 and methylcellulose. They were characterised by the highest open porosity (55.7 %vol.), homogeneous microstructure and satisfactory compressive strength (5.8 ± 1.7 MPa).

## Acknowledgements:

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# Structure and microstructure of PDMS-borosilicate hybrid materials produced by sol-gel for biomedical applications

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## Abstract:

A promising group of biomaterials for bone tissue engineering is hybrid materials based on the PDMS-$SiO_2$-CaO system. They take advantage of the synergy between inorganic silica domains, based on sol-gel bioactie glass composition, and organic polydimethylsiloxane domains. Since, calcium (Ca) and boron (B) ions are known to stimulate bone regeneraion and angiogenesis, they appear as an interesting alternative to vascular growth factors. Its combination in the hybrids system, prepared by sol-gel, is a novelty and a challenge. Thus, the main purposes of this work were to produce a bioactive and biocompatible hybrid material based on PDMS-$SiO_2$-$B_2O_3$-CaO system, capable of releasing Ca and B; and to achieve a better understanding of the relantioship among Ca and B ions, material's structure, and microstructure. Different monolithic materials were obtained with distinct structures and microstructures, at low temperatures without phase-separation. The structure was evaluated by Fourier transform infrared (FTIR) spectrometry and solid-state nuclear magnetic resonance (NMR) techniques, which confirmed the formation of hybrid bonds (Si-O-Si) between organic (PDMS) and silica inorganic precursors (TEOS), and borosiloxane bonds (B-O-Si). The $^{11}B$ NMR results showed that the presence of CaO modifier changes boron's coordination from trigonal ($BO_3$) to tetrahedral ($BO_4$). Scanning electron microscopy (SEM) micrographs and $N_2$ isotherms revelead that the incorporation of boron changes the material's microstruture by increasing the macroporosity and decreasing the specific surface area. In vito bioactivity tests, by soaking the materials in simulated body fluid (SBF), demonstrated the materials ability to form a calcium-phosphate layer on its surface and a release of therapeutic ions.

## Acknowledgements:

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# Biomicroconcretes containing hydroxyapatite/chitosan hybrid granules for bone tissue regeneration

Joanna Czechowska[1], Ewelina Cichoń[1], Anna Belcarz[2], Piotr Pańtak[1], Szymon Skibiński[1], Anna Ślósarczyk[1], Aneta Zima[1]

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## Abstract:

Biocompatibility, bioactivity, adequate mechanical properties, ease of handling, and antibacterial properties play a key role in the success of bone grafts. Recently, self-setting calcium phosphate cements (CPCs) enriched with granules and microspheres, i.e. biomicroconcretes, have gained much attention. Our study aimed to obtain and examine non-modified and silicon-modified $\alpha$ tricalcium phosphate ($\alpha$ TCP) based materials composed of hydroxyapatite/chitosan hybrid granules containing metal nanoparticles (AuNPs, AgNPs).

The XRD and FT-IR analysis showed that the biomicroconcretes were composed of two crystalline phases: $\alpha$ tricalcium phosphate and hydroxyapatite. SEM and TEM studies revealed good adhesion at the granule/matrix interface. The introduction of silicon and AuNPs led to a favorable shortening of the setting process. The compressive strength of the biomicroconcretes was sufficient for non-load bearing applications.

The in vitro tests in SBF revealed a high bioactive potential of materials, especially for those simultaneously modified with AuNPs and silicon. All biomaterials with AuNPs exhibit antimicrobial activity against S.epidermidis, S. aureus, and E. coli. Metal nanoparticles and silicon have been proven to be effective modifiers of biomicroconcretes. Further biological studies are needed.

## Acknowledgements:

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# Elaboration of 3D bioceramic scaffolds mimicking human bone architecture

Paul Danty[1], Emeline Renaudie[1], Fanny Leborgne[2], Vincent Pateloup[1], Patricia Pascaud-Mathieu[1], Valéry Valle[2], Eric Champion[1]

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## Abstract:

When a bone defect larger than a natural reparation occurs, the patient needs an implant. Design of such bone substitute gives a challenge in terms of biocompatibility, mechanical stress, three-dimensional complex geometries and interconnected multiscale porosity. 3D printing technology and more specifically stereolithography (SLA) meets requirements to shape bone tissue engineering (BTE) scaffold. Hydroxyapatite (HA) was a great candidate to this printing because of its composition close to mineral bone. The main objective of this study is to elaborate bioceramic scaffolds mimicking human bone architecture especially trabecular bone by additive manufacturing.

Several samples of human tibial bones of 1 $cm^3$ were collected during cadaver dissection and scanned by XR microtomography, with a resolution around 15 micrometers, to generate 3D model database. The 3D model was next sliced with a thickness of 100µm and printed with SLA device after optimization of machine parameters. Green parts were then sintered to obtain dense ceramic scaffolds.

Several characterizations were realized throughout the process in order to control 3D fabrication and characterize the properties of these substitutes. Firstly, comparative study between 3D model and the green part was performed in order to verify the macro-porosity between both models. Secondly, different thermal cycles were studied to optimize the sintering with regard to the thinness of the walls of the architecture and the targeted micro-porosity necessary for cell development. Finally, cell culture was performed on bone substrates to investigate proliferation, adhesion and attachment of human bone cells.

Synthetic HA scaffolds mimicking human bone architecture for BTE could be efficiently developed by additive manufacturing.

## Acknowledgements:

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# Modification of the surface layer of silicon nitride using oxyacetylene flame

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## Abstract:

The aim of the work was to develop a bioactive surface on silicon nitride ($Si_3N_4$) using an oxyacetylene flame treatment. The dense $Si_3N_4$-based materials with the sintering additives, such as $CaSiO_3$ and $CaSiO_3$-$Y_2O_3$, were sintered within the temperature range of 1600 °C - 1750 °C using spark plasma sintering in order to optimize their mechanical properties. The densities and mechanical properties, such as Young modulus, hardness, strength, and fracture toughness, were determined to identify the sintering conditions resulting in the best combination of mechanical properties. The samples were then treated using an oxyacetylene flame to develop a bioactive layer on the outer surfaces of $Si_3N_4$. In addition, the effect of other parameters, including nozzle distance, temperature, and flame exposure time on the thickness, topography, and chemical composition of the formed layer was investigated. The formation of the hydroxyapatite mineral coating was studied in a simulated body fluid (SBF). The concentrations of ions in the SBF after soaking were determined to prove the formation of hydroxyapatite. In vitro testing of Human pulmonary fibroblast cells, MRC5 was used to test potential cytotoxicity and cell viability. The preliminary results showed that the use of oxyacetylene flame generated positive cell growth in the bioceramic surface of the $Si_3N_4$-$CaSiO_3$ material, producing around 93% of cell viability. As a result, oxyacetylene flames treatment can be used to create a bioactive surface in silicon nitride based materials.

## Acknowledgements:

This work was supported by the Slovak Grant Agency APVV-18-0542, VEGA Project No. 2/0116/22, and JRP SAV-TUBITAK project No. 546676.

# YAG-based transparent ceramics: study of nanopowders synthesis by batch or continuous co-precipitation.

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## Abstract:

In this study, YAG ($Y_3Al_5O_{12}$) nanopowders has been synthetized by a reverse co-precipitation synthesis method with two designs of reactors (batch or continuous). In the batch reactor method, the effects of parameters like the concentration of metallic ions, the nature of the counter-ions, the precipitating agent used, the temperature, the pH and the maturation time have been studied in regards to the structural and morphological characteristics of the powders. Results show that the temperature and nature of the counter-ions were able to control the precipitation kinetics of $Y^{3+}$ and $Al^{3+}$ and thus have a strong effect on the stoichiometry and on the morphology of the powder. As a result, it was found that the precipitation of pure YAG phase in the form of isotropic nanoparticles is possible with AHC (Ammonium Hydrogen Carbonate) as precipitant and at 60°C. Nanopowders characteristics obtained by o-precipitation in a continuous reactor were compared to the previous ones and correlated to precipitation parameters. Finally, the effect of the powder's morphology on their sintering ability was investigated in order to produce fully dense and transparent ceramics.

## Acknowledgements:

The authors gratefully acknowledges the financial support from the National Research Agency under the Investments for the future program with the reference ANR-10-LABX-0074-01 Sigma-LIM.

# Investigation of the microwave sintering of carbonated hydroxyapatite

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## Abstract:

With improved solubility and biodegradation rate, carbonated hydroxyapatites (CHA) are promising bioceramics for filling bone defect compared to unsubstituted hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$). Carbonate ions in the HA lattice can substitute either for $OH^-$ through thermal treatment under $CO_2$-rich atmosphere to form A-type CHA ($C_AHA$) or for $PO_4^{3-}$ through synthesis by wet precipitation to form B-type CHA ($C_BHA$).

Controlling the amount and location of $CO_3^{2-}$ as well as the microstructure, which affect the biodegradation, depends on the fabrication process and remains challenging. The sintering of $C_BHA$ is usually achieved through resistive sintering under a $CO_2$-rich atmosphere to prevent thermal decomposition. This atmosphere causes an enrichement of A-type $CO_3^{2-}$ known to hinder densification. Sufficient consolidation thus requires high temperature or longer dwell time which may be accompanied by thermal decomposition or grain growth. To overcome these limitations, we investigate the microwave (MW) sintering which allow faster processing time.

In this work, the sintering of $C_BHA$ containing 0.8 mol.% of $CO_3^{2-}$ was studied in a MW multimode cavity under air. Pellets starting from $C_BHA$ alone or from $C_BHA$ mixed with carbon powder to generate in-situ a $CO_2$-rich atmosphere were considered. Sintering were performed at 900 °C and 1000 °C with different ramps and dwell times. Final densities were ranged between 70 and 85 % of theoretical density. From XRD and FTIR results, it was not possible to sinter a pure $C_BHA$. With carbon, substitution of A-type $CO_3^{2-}$ appeared. The presence of carbon was thus effective for generating a $CO_2$-rich atmosphere but insufficient, in our conditions, to avoid the decomposition. Further studies are under progress to optimize the sintering condition.

## Acknowledgements:

We acknowledge David Marchat for providing the powder, Christophe Meunier for assistance on MW sintering, Maryline Mondon for help on SEM, Olivier Valfort for aid on XRD analysis and Laetitia Vielle for support on FTIR and thermal analysis , all from Mines Saint Etienne.

# Co and Zn co-doped bioactive glasses: comparison between standard sol-gel method and sol-gel combined with solvent evaporation-induced self-assembly (EISA) synthesis

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## Abstract:

Silicate bioactive glasses (BGs) are one of the most attractive biomaterials for bone tissue engineering that can be used as effective carriers for therapeutic ions because of their ability to incorporate a large variety of elements and their controllable dissolution properties in physiological environment. Cobalt (Co) is known to upregulate vascular endothelial growth factor (VEGF) secretion, inducing angiogenesis. In turn, zinc (Zn) shows osteogenic, antibacterial and anti-inflammatory properties. The combination of these two therapeutic ions would give multifunctional BGs. Sol-gel-derived BGs possess highly bioactive properties because of their porous microstructure and unique surface chemistry which accelerate hydroxyapatite formation. However, the combination of sol-gel technique with EISA process allows for obtaining BGs with outstanding surface area and ordered mesoporous structure, providing high reactivity in physiological fluids.

The Co- and Co/Zn-doped BGs from the basic $SiO_2$–CaO–$P_2O_5$ system were synthetised using standard sol-gel method and sol-gel coupled with EISA technique. BGs were evaluated in terms of structural (WAXS, FTIR) and textural (TEM, BET) properties. Furthermore, the materials were incubated in simulated body fluid (SBF) for 14 days. SEM and FTIR methods were used to assess calcium phosphate-forming ability, while ICP-OES technique was used to evaluate changes in the concentration of the ions in SBF.

The results indicated that synthesis technique and doping with therapeutic ions affect structural and textural properties. This gives the possibility to obtain BGs differing in bioactivity as well as release kinetics of therapeutic ions, and thus biological activity.

## Acknowledgements:

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# Glass-ceramics from glass powders and reactive silicone binders: from sealants to additive manufacturing

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## Abstract:

A target glass-ceramic system may be processed by means of a novel technique, relying on the reaction of glass powders with silicone polymers. Instead of the parent glass, a 'silica-defective variant' is considered. A fundamental feature is the fact that the silicone polymer act as binders for glass powders from room temperature up to the firing temperature, at which, operating in air, they convert into silica. The interaction between 'silica-defective' glass powders and binder-derived silica allows for the recovery of the original stoichiometry. The overall process has important advantages when glass powders lead to glass-ceramics, by sinter-crystallization, after the burn-out of organic binders. The shape of components may be lost simply by sliding of particles before the activation of viscous flow. Silicones, besides providing an extended binding action up to the maximum firing temperature, stabilize the shapes during sintering. Otherwise, a significant viscous flow of softened glass is prevented by the formation of a rigid silica skeleton, from the transformation of the silicone binder. After successful preliminary applications to glass-ceramic sealants for SOFC, we will present an extension to glass-ceramic scaffolds, for tissue engineering applications, manufactured by the application of advanced additive manufacturing technologies. We will show that reactions in nitrogen enable the transformation of silicone binders into silica and pyrolytic carbon, in turn leading, by reaction with glass powders, to novel glass-ceramic/C composites.

## Acknowledgements:

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under the H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 project FunGlass (Centre for Functional and Surface Functionalized Glass), grant agreement No. 739566.

# Bioactive ions doped carbonated hydroxyapatite-biopolymer composite coatings for orthopaedic implants

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## Abstract:

Bioactive ions (Mg, Sr, Zn) doped carbonated hydroxyapatite powders (dHAp) have been prepared by wet chemical precipitation method. The bioactive ions were incorporated into the HAp matrix by co-precipitation from solution containing the appropriate amount of gluconate and chloride salts of different ions. The ion doping had significant effect on the morphology and crystallinity of calcium phosphate particles. Owing to the ion addition, the crystallinity of particles noticeably decreased. Particle aggregations have been observed after the chemical precipitation. The as-prepared dHAp powders have also been incorporated into biopolymer matrices, such as cellulose acetate (CA) and polycaprolactone (PCL). It has been shown that the dHAp particles can be successfully incorporated into the CA and PCL polymer films. The dHAp loaded biopolymer coatings have been prepared by solution casting technique onto implant materials. The attachment of the layer onto the surface significantly improved compared to the dHAp powder coating. On the other hand, the bioceramic powder addition to the polymer solution can improve the biocompatibility of implant materials, providing appropriate environment to bone cell adhesion and growth.

## Acknowledgements:

This work was supported by the National Research, Development and Innovation Office – NKFIH OTKA-PD 131934.

# Mechanochemical synthesis and cold sintering of mussel shell-derived hydroxyapatite nano-powders for biomedical applications

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## Abstract:

Sustainability and energy management are two pillars of the circular economy philosophy and can find tangible fulfilment in the reduction of natural resources consumption and in the development of limited energy-consuming processes. In this scenario, our work is focused on the production of nano-hydroxyapatite powder from food industry waste, mussel shells, and on the consolidation of such powder with a low energy-demanding route, i.e. cold sintering process. Hydroxyapatite (HA) was synthesized at room temperature by mechanochemical synthesis, mixing phosphoric acid solution with discarded mussel shells, as a biogenic source of calcium carbonate. The as-synthesized powder was characterized by x-ray diffraction (XRD), Fourier-transformed infrared (FTIR) and inductively coupled plasma optical emission spectroscopy (ICP-EOS), field emission scanning electron microscopy (FE-SEM), thermogravimetric and differential thermal analyses (TGA-DTA). Nano-hydroxyapatite was then consolidated by cold sintering at 200°C in about 15 min. The applied pressure ranged from 300 to 600 MPa and different solvents were mixed with the ceramic powder to investigate the densification mechanisms. Sintered pellets were investigated by XRD, SEM and densimetry. A final relative density up to 82% was achieved. Sintered bodies were also characterized from a mechanical and biological point of view, in light of their application as scaffold for bone tissue regeneration. Promising results in terms of flexural strength were obtained. The preliminary in vitro assessment revealed good cell viability and faster adhesion of human bone marrow-derived mesenchymal stem cells (hBM-MSCs) on mussel shells HA in comparison to commercial hydroxyapatite.

## Acknowledgements:

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# Development of Yb2O3-based ceramics for indirect production of 177Lu used in targeted radionuclide therapies.

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## Abstract:

The demand for targeted radionuclide therapies (TRT) increases worldwide with surging numbers of cancerogenic cases. There is a growing concern that the availability of such medical isotopes may not be sufficient in the long term.

In particular, the $^{177}$Lu is identified as an important example of a medical isotope to be at risk for future shortages. The challenges of its production routes, as well as the limited accessibility to nuclear research facilities need to be therefore addressed and debated. In this work we discuss the distinctive aspects of forming ceramic targets based on $Yb_2O_3$, as this material possesses sufficient chemical and thermal stability under reactor irradiation to obtain the $^{177}$Lu radionuclide.

The study comprises the $Yb_2O_3$ powder to be initially doped with aluminum isopropoxide prior to formation of cylinders with diameter below 1.7 mm. Consequently, the grain-growth and creation of a new phase $Yb_4Al_2O_9$/ $Yb_3Al_5O_{12}$ between formed $Al_2O_3$ and $Yb_2O_3$ during sintering at 1750 °C in air atmosphere improves the densification and leads to increase of Vicker's hardness and mechanical stability of such manufactured targets. The stability of $Al_2O_3$-doped $Yb_2O_3$ targets is tested via impact test through 12 meters long steel tube having two arc points, while the system is pressurized with $N_2$ gas up to 10 bar. Twenty-five specimens are shot through the pipe to simulate the activation route as in the nuclear reactor with 100 % success rate of such an impact test. The post processing of the solid material takes place in autoclaved system at 260 °C, 40 bar and acidic mixture of $H_2O/HCl/HNO_3$ until the complete dissolution is achieved, usually no longer than 26 minutes. Thus, allowing the newly created radionuclide to be extracted and further used for medical purposes.

# The effect of boron oxide doping on the properties of alkali-free bioactive glasses designed for the production of microfibers for bone regeneration

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## Abstract:

In this work, we investigated the effect of boron oxide addition on the properties of alkali-free bioactive glasses. Our main objective was to obtain new glass compositions with enhanced thermal properties that are suitable for the fabrication of glass microfibers for bone regeneration. For this purpose, a new series of alkali-free bioactive glasses based on FastOs® composition was synthesized by partially replacing silicon dioxide network – former with boron trioxide network – former, while using calcium oxide as a charge compensator to maintain the network connectivity of all glasses on a similar level. Glass bars were prepared by the standard melt quenching technique. All the samples were characterized in terms of their structure (NMR, FTIR, XRD) and thermal properties (DSC and dilatometric measurements). In the next step, glass fibers were obtained using the classic drawing technique. The apatite-forming ability of obtained fibers was evaluated by immersion in simulated body fluids (SBF). Glass samples with a moderate amount of $B_2O_3$ demonstrated improved thermal stability which resulted in better performance during the fiber drawing process. The correlations between properties and structure were established with the reference to the configurational entropy calculated for the synthesized glasses. Immersion tests in SBF showed the significant formation of hydroxycarbonate apatite (HcA), similar to that of FastOS® glass which should provide efficient integration between bone and the glass. As a result, presented glass fibers may be considered as promising materials to produce wool-like material for bone implants or as reinforcing components in biopolymer/glass composites.

## Acknowledgements:

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# Preparation, phase separation and porosity analysis of an alkali resistant glass composition for biomedical applications

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## Abstract:

This work reports crystallization and phase separation of an alkali resistant glass composition in the $Na_2O$–$CaO$–$Al_2O_3$–$B_2O_3$–$SiO_2$ system with addition different amounts of $Mo_2O_3$, $ZrO_2$ and $TiO_2$. At first, based on the previous studies, the base composition was selected and then glass specimens prepared by melting of raw pure materials and above-mentioned additives in an alumina crucible at 1400$^0$C For 3 hrs. and casting in a metal mold. Additives were added in constant values of 2.5 and 3.5 mole%. XRD analysis carried out to ensure that no crystalline phases are formed. Then heat treatment was performed in temperature intervals of 620, 650, 680 and 710°C. SEM was used to phase separation study, the samples were imaged using electron microscopy (SEM).The tendency of crystallization decreased with increasing the amount of $ZrO_2$ due to increase in viscosity. By increasing the amount of $TiO_2$ in the mother glass, phase separation was achieved and crystallization occurred in samples containing molybdenum oxide. In the next step, the acid leaching process of phase separated glasses was performed. Porosity analyzes and measurement of specific surface area of BET were performed on acid leached samples. The results show that the highest porosity volume was related to the samples containing zirconium oxide with three steps acid washing and the sample containing $Mo_2O_3$ with two steps acid washing. The lowest was obtained in samples containing titanium oxide and samples containing $ZrO_2$ with two acid washing steps. Based on the specific surface results, the highest specific surface area was obtained for the sample containing zirconium oxide with three acid washing steps (23.78 $m^2$ / g) and the lowest for the sample containing zirconium oxide with two acid washing steps (2.27 $m^2$ / g).

# Influence of laser engraving on alumina-zirconia composites

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## Abstract:

Laser technology is used for different applications such as joining and cutting as well as structuring and marking of surfaces.

Orthopedic implants are marked by laser engraving to ensure product traceability according to ISO13485.

In this study the influence of a solid-state laser on surface properties of two alumina-zirconia composites (ATZ; ZTA) is analyzed. The laser was used to mark the ceramic. A good visibility and readability as well as no negative influence on the properties and application performance of the ceramic is indispensable.

Both ceramics were lasered in two different states: as green and sintered body. Different laser parameters were used. The laser engraving was done by two commercially available marking stations with solid-state lasers made of Nd:YAG and Nd:$YVO_4$.

The laser engravings were analyzed regarding the macrostructure (LSM), phase content (XRD), and microstructure (SEM, FIB-Tomography, EDS, TEM) and chemistry (XPS, EDS).

In the lasered zone the color changed from white to brown-black. The higher the zirconia content and the higher the energy density the darker the color. Higher energy density also led to deeper engravings. Phase analysis showed a change in XRD pattern at the (101) tetragonal peak of the zirconia which might be linked to a lattice deformation or presence of a solid solution layer. SEM and FIB-tomography analyses showed a formation of slight surface cracks. Just below the surface a kind of solid solution layer of Al-Zr-O was detected. XPS revealed probably changes in oxidation state and formation of vacancies.

In the study the influence of the changes at the surface is discussed regarding the mechanical properties and ageing resistance.

## Acknowledgements:

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# The effect of sintering temperature on material properties of 3D printed hydroxyapatite scaffolds.

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## Abstract:

The viability and development in use of additive manufacturing (AM) technologies is manifested today in its successful certification, accreditation, and implementation into various production series. For utilization of easily available extrusion technology such as Fused Fillament Fabrication the application variables include beyond others: objects production size and topology optimisation, nozzle material extrusion limitations, printing operation parameters and final object quality control. The AM has without dispute high potential for production of personalized bone replacements with suitable interconnected porosity in a synthetic bone substitute.[1] For medical applications, the availability of suitable biomaterial with physiologically relevant physical, chemical, and biomimetic properties is crucial. The tuning of hydroxyapatite properties as the main mineral component of human bones may initiate tissue extracellular matrices with biochemical signalling for osteogenic cells, to effect synergy and osteoconductive processes for rapid bone healing.[2]

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## Acknowledgements:

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# Photocurable 3D plotting technique for microporous shell / hollow core hydroxyapatite scaffolds using core-shell feedrod

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## Abstract:

The present study demonstrates the manufacturing of macroporous hydroxyapatite (HA) scaffolds, comprised of microporous hollow filaments with high shape retention, by photocuring-assisted 3D plotting using a feedrod comprised of a photocurable HA shell and a carbon black (CB) core. The 3D porous HA scaffold was fabricated by photocuring assisted 3D plotting. After heat treatment, these sintered scaffolds have pores consisting of micropores by camphene/camphor crystal, macropores by CB core and filament gap. The porosity was adjusted by different filament gaps [0.5 and 1.0 mm] and camphene/camphor vol.% [50 and 60vol.%]. The 4 types of sintered scaffolds have overall porosity of 50.7~64.6 % and 74.3 ~ 79.3 %, respectively. The mechanical properties of two types of scaffolds with porosity of 74.3 ~ 79.3 % were exhibited reasonably high compressive strengths (2.36 - 3.58 MPa) and modulus (68–86 MPa). The ceramic scaffold and various ceramic architecture without supporter were created using photocuring-assisted 3D plotting.

## Acknowledgements:

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# Production of high translucent 5Y PSZ dental applications with high strength using DLP technique

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## Abstract:

Bio-ceramics such as alumina, calcium phosphate and zirconia have been employed in medical and dental industry due to their distinctive characteristics. Especially for the ceramic prostheses in dental applications, zirconia ceramics have been widely used since they have exhibited extraordinary performances in terms of the mechanical and biological properties. In addition, zirconia ceramics present great optical properties to satisfy translucency of restorations in anterior and posterior teeth for aesthetic purpose. In this work, due to the increasing aesthetic demands, 5Y-PSZ (5 mol% yttria partially stabilized zirconia) was used to enhance the transmittance for modifying natural teeth. DLP (Digital Light Processing) which is one of the novel additive manufacturing technique is introduced to fabricate the dental crowns elaboratively using high solid loading slurries which maintain the stability of homogeneous composition. The predetermined amounts of slurry were extruded through the nozzle and tape casting was followed by photocuring. After debinding and sintering procedure, dental crowns, which exhibited excellent mechanical properties and aesthetics at the same time, were fabricated precisely based DLP technique., As a result, this research demonstrates additive manufacturing technique for producing dental applications, which can be utilized in clinical usage.

## Acknowledgements:

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# Characterization and Environmental-friendly preparation of Calcium-Silicates

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## Abstract:

The most distinguished calcium silicate system properties are lightweight, low thermal conductivity, and excellent bioactivity, biodegradability, and biocompatibility, which could make them applicable in different areas as an anticaking agent in the food industry, ceramic, glass, electrical, building industry, and dentistry. Their biological characteristics promote them as promising materials for bioapplications such as bone repairing, tissue engineering, drug carrier, and dental restoration. These applications are accompanied by the formation of an apatite layer on the surface upon implantation when it is connected to biological fluids; that helps in bonding with the surrounding tissues. However, the biological behaviors can be affected and controlled by different parameters such the fabrication method, the composition, the precursors, the sintering temperatures and so on. Therefore, the aim of the presented study were to investigate the effect of $CaO/SiO_2$ on the composition and recycle the natural wastes as an alternative source for the starting materials.

In our work, calcium silicates were successfully prepared using an eco-friendly natural source represented in chicken eggshells, upon the heat treatment in the air at 900 °C for 7-12 hours, the reaction of the extraction of calcium oxide (CaO) will occur. Whereas the silica ($SiO_2$) has been prepared by ball milling starting from silica gel by intensive ball milling for 3 hours in dry conditions. Different ratios have been produced, pressed in dry conditions, and sintered at 800 °C for 1 hour. Extensive analytical tools were used to determine the composition-structure-property relationships.

## Acknowledgements:

I would like to thank Stipendium Hungaricum scholarship

# Fabrication of compositionally graded zirconia products with high translucency using digital light processing (DLP) technique

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## Abstract:

Zirconia ceramics, due to its excellent mechanical properties along with reasonably high translucency and biocompatibility, have gained popularity in dental prosthetics. One of the widely used method for fabricating zirconia prosthetics was utilizing dental CAD/CAM technique, nonetheless, was claimed to have several issues while machining. Meanwhile, additive manufacturing with zirconia arose as promising substitute to manufacture dental prostheses, however, most of previous studies utilized single source of material for fabrication. Usage of single material within fabrication was a challenge to meet the needs for more aesthetically satisfying prostheses, which mimics the gradient hue transition of natural teeth. Thus, this article aims to present novel additive manufacturing method with functionally graded material (FGM) concept for fabricating compositionally graded zirconia products via digital light processing (DLP) technique, with comprehensive evaluation of 3D printed zirconia products to be utilized in clinical applications.

Two differently shaded (A0 and A3 shade) zirconia suspensions with 50 vol% solid content were prepared, while maintaining printable rheological and photo-curing properties. By controlling the extrusion ratio of both suspensions through static mixer which is attached to custom-built DLP 3D printer, solidified layers of slurries in functionally graded manner at stacking direction was additively manufactured, hence, compositionally graded zirconia products were fabricated. Compositionally graded zirconia products showed linear shade and translucency transition, along with 3-point flexural strength of 702 MPa, followed by in-vitro assessment of marginal fit which was evaluated as 41.3 μm. The results of this research regarding the compositionally graded zirconia product demonstrates novel additive manufacturing method for fabricating functionally graded objects, as well as showing high possibility of 3D printed products to be adopted in clinical usage.

## Acknowledgements:

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# Local controlled “Cancerthermia” for treating cancer diseases

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## Abstract:

Creation of innovative technology of local controlled cancerthermia for treating patients. Innovation is in the following: thin piece of cloth impregnated in 42-45°C warm water and then squeezed is placed over the cancerous site.A thermopad of 45°C temperature, of the size:25x18 cm isapplied on the material till the material is dried. This is done for preliminary precursor treating of patient’s skin, for opening pores, in order the heat that is emitted from thermopad penetrated deeper in the diseased section and acted efficiently on cancer cells for their necrosis, to prepare the organism for cancerthermia. Then the temperature on the apparatus should be reduced to 43°C and the séance should be continued according to prescription,up to approximately 40-70 minutes,it depends on the reaction of the patient and the disease to cancerthermia. The result obtained by such technology becomes apparent after 7-8 séances, instead of 10-12.Besides, the cases were studied in dynamics by MRT and method of morphological study, cancer necrosis and correlation of tumor mass and necrotic sections. Innovative method and high anti-blastoma technological result was proved at the Kutaisi Oncology Clinical Center “Saroveli”, wheretherapeutic apparatus created by us at the Georgian Technical University, Institute of Bionanoceramic and Nano-composite Technology for treating by the method of locally controlled cancerthermia was tested. The Clinic received high results after treating of internal organs:Stomach, liver, Kungs and Ovaries, absolutely all, about 300 cancer patients with 3d and 4th stage.Treatment of patients is continued and the results are positive in all patients.Principally new methodology and technology of high anti-blastoma effect were.

# Surface modification of boron-rich boron carbide as a potential carrier in Boron Neutron Capture Therapy

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## Abstract:

Boron Neutron Capture Therapy (BNCT) is bimodal radiotherapy used in the treatment of a patient diagnosed with cancer, which localization in the human body makes them inoperable. The therapy is based on the nuclear reaction between neutrons and compounds containing isotope $^{10}B$ where alpha particles are produced. An important issue in BNCT is to obtain a high selectivity of boron supply and its appropriate concentrations in cancer cells.

The main goalof the research was to determine the impact of surface modification of boron carbide powder because before introducing $B_4C$ into the organism, its surface should be appropriately modified by carbohydrates and amino acids covering.

The boron carbide surface was functionalized with amino acids and saccharides. Boron carbide was obtained by direct synthesis from elements. Then it was subjected to the process of grinding, rinsing, and centrifuging. Next, its specific surface area was subsequently calculated and modified with amino acids and carbohydrates. Samples before and after modification were tested for particle size and changes in the Zeta potential. Changes in morphology were observed using a scanning electric microscopy.

The conducted experiment confirmed that the surface of boron carbide nanoparticles can be modified with the use of appropriate polysaccharides. The results obtained in the research shows appropriate selection of the saccharide and functional groups present in the saccharide affects the size of the particles after modification, as well as the modification itself.

# Synthesis and surface modification of boron carbide (B4C) nanopowders as a boron deliver agent in Boron Neutron Capture Therapy

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## Abstract:

Boron carbide, because of its properties is highly valuable structural material. Materials in the form of dense, polycrystalline samples are characterized by high melting point, extreme hardness, relatively low density and high chemical resistance. Such properties are favorable for $B_4C$ applications such as the production of components resistant to abrasion in ball mills, nozzles, parts of machinery and equipment or as parts of anti-ballistic armor. Recently, boron carbide was newly applied in medical applications, as a carrier in BNCT. BNCT therapy is about the "introduction" of boron compounds into tumor cells and then irradiating them with low energy epithermal neutrons. In that case, radiation-induced during the decay of nuclei $^{11}B$ is safe for the body and has a "therapeutic" range, comparable to the size of the cell.

The work aimed to study the interaction between boron-rich boron carbide nanoparticles and selected tumor and immune phagocytic cells. Experiments were performed to investigate the feasibility of the application of $B_4C$ nanoparticles as a boron carrier in BNCT. The another problem undertaken during the research was the functionalization of the nanoparticles surface of $B_4C$.

The synthesis of $B_4C$ nanopowders was carried out using direct synthesis from element. In the second stage of the research, the cytotoxicity of $B_4C$ and its influence on cell viability were determined. Moreover, the metabolic activity of the cells was assessed based on the nitric oxide release level and the total amount of protein. In the course of the work, the potential interaction of $B_4C$ nanoparticles with the tumor environment in the context of boron-neutron therapy was also checked, and attempts were made to functionalize the obtained particles with the use of "cell carriers".

# Synthesis and magneto-optical properties of rare-earth co-doped Y2O3

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## Abstract:

Alternative materials for Faraday devices used in the visible and near infrared range, $Y_2O_3$ transparent ceramics were prepared by modified arc plasma melting. Procedure of synthesis is the conducting of the proceedings in the Polish Patent Office. The synthesized ceramics were doped with two different rare earth elements. The influences of the high paramagnetic ions on the morphologies and magneto-optical properties of $Y_2O_3$ polycrystals were characterized. The $Dy_2O_3$ transparent ceramic sample prepared by modified arc plasma melting, presents the high optical quality and large size of diameter. The values of in-line transmittance of the optimal ceramic specimen with the thickness of 1.0 mm are 75.3% at 530 nm and 85.9% at 850 nm. The Verdet constant of $Y_2O_3$ ceramics was measured over 2000 ± 10 deg/(T·m) at 433 nm and 700 ± 10 deg/(T·m) at 433 nm. Temperature dependence of the Verdet constant was studied. Figure of merit for magnetoδoptical media was calculated. The obtained results indicate the potential use of suitable magnetic-optical devices in high-power laser systems and telecommunications applications.

These materials were synthesized within the Sonata grand financed by the National Science Center and are development during Tango A grant financed by the National Centre for Research and Development. We invited to co-operation and develop our materials.

## Acknowledgment

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# Lithography-based additive manufacturing of short fiber reinforced alumina

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## Abstract:

There are various reasons why patients suffering from health issues need a bone replacement. One approach providing these replacements to patients, who are in need of one, is by personalized implants. Using additive manufacturing to print these implants has the advantage of processing individual and complex parts directly from a CAD model.

One attractive material for bone replacements is alumina. It is one of the most studied bioceramics, which can be used for articulating components in hip prosthesis and is a promising material for dental implants. It is characterized by excellent physical and chemical properties like high abrasion- and excellent corrosion resistance compared to metallic alloys. Nevertheless, structural ceramics like alumina have one disadvantage. They show a brittle behavior. Using fiber reinforcements their fracture toughness can be increased, leading to favorable mechanical properties for applications in biomedical engineering.

This work aims to present the advancements of processing of fiber reinforced alumina by lithography-based ceramic manufacturing (LCM). The feasibility of incorporating short fibers into the ceramic slurry to create ceramic matrix composites (CMCs) is shown. Processing short fiber CMCs using LCM is a three-step process. First, the slurry has to be prepared. This is a very challenging step as the fibers tend to agglomerate. Second, green bodies are generated using the energy of light. Third, the green bodies are thermally post processed to gain densified CMCs objects, whose mechanical properties are measured.

# Compressive strength and effective elastic constants of bone tissue engineering scaffolds with regular and shifted primitive cubic base cell

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## Abstract:

Additive manufacturing allows controlling the structure of tissue engineering scaffolds through digital design. The aim is to develop a network of pores suitable for bone ingrowth, having mechanical properties, strength and stiffness, similar to bone to guaranty structural support and prevent stress shielding. Therefore, the present work reports on the mechanical properties of scaffolds with regular and shifted primitive cubic base cell built by direct ink writing. Pores smaller than the strand diameter generated scaffolds with superior mechanical behaviour in the longitudinal than in the transverse direction and vice versa. Shifted and regular scaffolds showed similarly mechanical properties in the transverse direction, but in the longitudinal direction the shifted scaffolds, having the advantage of a more tortuous pore network, were weaker because shifted layers induced bending stresses. Thus, other designs have to be considered to improve both tortuosity and strength at the same time. Other geometrical features and printing accuracy had a relevant effect too. For example, the contact radius at the joints of perpendicular strands and errors in the layer alignment impaired the strength and stiffness by increasing the stress concentration and inducing extra bending stresses, respectively. Whereas, deflections of the strands increased the effective transverse stiffness of the shifted scaffolds, thus increasing the related compressive strength. The response of the other scaffold configurations was only slightly altered. In summary, these experimental and numerical results show that the alignment of the scaffold at the implantation site should be carefully selected to guaranty optimal stress distribution acting in the material.

## Acknowledgements:

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic (LTAIN19112).

# Nanostructured Si-based bioactive glass coatings by electrostatic spray deposition technique

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## Abstract:

In 1969, Dr. Larry Hench created a 4-component glass, nowadays known as 45S5® [1]. Since then, Bioglasses (BG) are the subject of intensive investigation as a bone replacement material. However, due to brittleness and poor mechanical properties, BG direct clinical applications are limited to non-load-bearing implants. Nevertheless, BG can be employed as coatings on metallic substrates, to combine their biological performance with the mechanical strength of metals.

To the best of our knowledge, the fabrication of BG-coatings by electrostatic spray deposition (ESD) technique was never assessed before. ESD is a low-cost method that allows the deposition of films with controlled chemical composition and microstructures by a nanotexturing approach. In previous work, by coupling the sol-gel method with ESD, we have obtained single-phase nanocrystalline hydroxyapatite coatings in one step [2]. This study focuses on ESD manufacturing of BG coatings belonging to the $SiO_2$-$CaO$-$P_2O_5$ system on Ti6Al4V substrates. Amorphous coatings with optimized S85, S75, and S58 compositions have been obtained [3]. Innovative microstructures were optimized by varying ESD parameters, ranging from porous coral-like to more compacted cauliflower-type. Their bioactivity was assessed by immersion assays in simulated body fluid and will be discussed versus compositions and microstructures.

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# Bioactive glass-based composite scaffolds incorporating gelatin/ manganese doped mesoporous bioactive glass nanoparticles for bone tissue regeneration

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## Abstract:

This study successfully prepared 45S5 BG-based composite scaffolds using a foam replica approach. The scaffolds were coated with Mn-doped mesoporous bioactive glass nanoparticels (Mn-MBGNs) and gelatin by impregnating the 3D structures with Mn-MBGNs (15 wt./vol %) and gelatin (5 wt./vol %) in ethanol and water solutions, respectively. The synthesized scaffolds were characterized in relation to morphology, porosity, mechanical stability, bioactivity, and cell biology behavior using osteoblast-like (MG-63) cells. Results revealed that the gelatin coating improved the compressive strength of 45S5 BG scaffolds. The coatings were confirmed by EDX (by the presence of Mn peaks) and FTIR spectra (by amide groups), respectively. All scaffolds exhibited high pore interconnectivity and bioactivity upon immersion in SBF (e.g., formation of HA layer after three days in SBF). Preliminary cell culture results obtained using both direct and indirect approaches indicated the non-toxicity of the scaffolds toward MG-63 cells. Results revealed the attachment and proliferation of the cells on the surfaces of the struts. However, gelatin/Mn-MBGNs coated 45S5 scaffolds showed better cell attachment and cell proliferation on scaffold's surface in contrast to uncoated scaffolds. It is proposed that the dual release of gelatin and Mn ions plays a positive role in cell attachment and proliferation and the quantitative evaluation of this effect remains an exciting topic for further research.

# Multifunctional injectable inks for extrusion-based additive manufacturing techniques

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## Abstract:

An implanted calcium phosphate (CaP) based scaffold that smartly combines mutually therapy functions of drug-eluting, hyperthermia and bone regeneration will bring lots of benefits not offered by the conventional medical practice. Several studies have been reported that the magnetic behaviour in bioceramics contributed to the significant growth of bone-derived cells, proliferation, and osteogenic differentiation, due to the mechanical stimulation regulated through the external magnetic field. This is frequently obtained by the incorporation of magnetic nanoparticles in polymeric matrices of non-magnetic CaP which may be associated with potentially long-term toxic effects. The addition of biomolecules in CaP-based materials obtained by conventional methods and/or by recent additive manufacturing (3D printing) techniques is commonly done after sintering step (high temperatures), by long impregnation procedures and diminutive precision regarding the amount that is adsorbed.

Accordingly, the present work reported, for the first time, new extrudable composite inks, based on a natural polymeric matrix loaded with intrinsic magnetic CaP-based bioceramics for additive manufacturing. Customizable 3D multifunctional structures with interconnected porous, similar to the natural chemical composition of bone and scaled to the intended defect, can be constructed. These structures are able to respond to an external magnetic field and simultaneously heat when subjected to an alternating magnetic field, being a promising alternative to treat healing bone defects and localized cancer by hyperthermia. Sintering step was eliminated and the mechanical integrity of the scaffolds was attained by the composite crosslinking capacity and the high concentration of bioceramic particles.

## Acknowledgements:

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# Influence of various liquid phases on properties of α-TCP based bioactive bone cements

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## Abstract:

The increased prevalence of bone disease requires development of new bone substitutes. An important group of these biomaterials are calcium phosphate cements (CPCs), which are characterised by bioactivity and chemical composition similar to inorganic part of natural bone. CPCs consist of a solid phase and a liquid phase which, when mixed, form a plastic paste with self-setting properties.

In this study, the influence of the liquid phase on the physicochemical and biological properties of CPCs was investigated. The solid phase of the developed cements composed of highly reactive α-TCP powder. As liquid phases mixtures of 5 wt% citrus pectin (CP) with 2 wt% disodium hydrogen phosphate ($Na_2HPO_4$) aqueous solutions in various ratios (1:0, 1:1, 0:1) were used. Phase composition, setting times (ST), compressive strength and microstructure of the obtained materials were investigated.

Studies have shown that the obtained biomaterials were characterized by unique properties due to the various liquid phase compositions. CP provides materials with better injectability whereas $Na_2HPO_4$ enables cementitious pastes to set. Setting times of investigated CPCs were in the range of 6-14 ± 1 min (initial ST) and 13-30 ± 1 min (final ST). The compressive strength of the studied materials ranged from 8.4 MPa to 13.8 MPa and was similar to that of a cancellous bone. The combination of CP and $Na_2HPO_4$ in a liquid phase allowed to obtain materials characterised by both self-setting and surgical handiness.

The developed bone substitutes can be prosperous self-setting materials for bone defects' filling. Preliminary in vitro tests in simulated body fluid demonstrated the bioactive potential of obtained CPCs and paves the way for further in vitro and in vivo studies.

## Acknowledgements:

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# In vivo assessment on calcium phosphate and titania scaffolds prepared via freeze-casting

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## Abstract:

Bioceramic materials used for bone regeneration are considered to be biocompatible and bioactive. However, scaffolds used for the regenerative process must also exhibit other essential properties, such as high porosity and sufficient mechanical stability at the same time. Freeze-casting of bioceramic materials allows the preparation of highly porous structures with high mechanical stability. The aim of our study was to characterize the mechanical stability and biological properties of calcium phosphate (CaP) and titania scaffolds.

Bioceramic scaffolds based on CaPs and titania were freeze-cast using liquid nitrogen as a cooling medium. Oriented lamellar microstructure was prepared by controlled ice growth in one direction. Sintered scaffolds were tested for flexural strength by the three-point bending test. Bioactivity was tested via simulated body fluid (SBF), and biocompatibility was tested in vivo with a subcutaneous-implantation rat model.

The scaffolds showed high relative porosity ~70 %, with interlamellar spaces 10–20 μm. The flexural strength ranged from 10 to 17 MPa, indicating sufficiently high mechanical stability. The SBF testing revealed low bioactivity of titania scaffolds which surface did not show any significant changes. By contrast, the CaP scaffolds exhibited high bioactivity with a fully grown apatite layer after 21 days. The biocompatibility of scaffolds was evaluated six weeks after the subcutaneous implantation. A thin fibroblastic tissue covered all the samples attaching them to the subcutaneous tissue. No inflammation or pathological response in the surrounding tissue was observed, also the blood counts did not show any significant changes compared to the sham-operated control group.

## Acknowledgements:

CzechNanoLab project LM2018110 funded by MEYS CR is gratefully acknowledged for the financial support of the measurements/sample fabrication at CEITEC Nano Research Infrastructure.

# YAG-based transparent ceramics: comparison between HIP and SPS post-sintering treatments

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## Abstract:

YAG-based transparent ceramics are conventionally prepared by vacuum sintering or by a double sintering process, viz. vacuum sintering followed by Hot Isostatic Pressing (HIP). The use of a pressure-assisted process on vacuum pre-sintered ceramics favours the closure of residual porosity, and is therefore suitable for the production of highly transparent ceramics, where pores would otherwise act as light scattering centres. On the other hand, these post-sintering treatments are effective with samples exhibiting a suitable microstructure after vacuum sintering, i.e. no secondary phases and only closed pores with a size smaller that the size of the grains. As an alternative to HIP, a fast post-sintering treatment with Spark Plasma Sintering (SPS) is proposed. In this poster we present a comparison of transparent YAG-based transparent ceramics obtained by vacuum sintering followed by post sintering with HIP and with SPS. Several combinations of vacuum sintering + HIP/SPS conditions were tested on YAG and Yb:YAG samples prepared by reactive sintering of single oxides in order to modify their microstructure, especially grain size and residual porosity. Magnesium oxide (M) or magnesium oxide with TEOS (M+T) were used as sintering aids. SEM and optical microscopy analyses were used to characterise the microstructure of the samples after vacuum sintering and after post-sintering, and to identify correlations between the microstructure and optical properties of transparent YAG ceramics.

## Acknowledgements:

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# Biological evaluation of ZrO2 ceramic scaffolds with biomimetic and nanoparticle coating as drug delivery systems

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## Abstract:

Nowadays, difficulties in the treatment of bone infections often result from the poor distribution of antibiotics in bone tissue [1]. As a result, despite the great availability and variety of antibiotics, bone infections have a high percentage of relapses and remain a challenge for medicine [2]. This study aimed to design a ZrO2 scaffold with a biomimetic calcium phosphate layer (CaP) containing poly(L-lactide-co-glycolide) (PLGA) nanoparticles (NP) loaded with antibacterial drugs. Pressing and sintering methods were used to make a ceramic scaffold. The method of double emulsion with solvent evaporation was used to prepare NP. To introduce NP into the ceramic substrates, we used two methods: (i) the drop-casting, based on placing a drop of NP dispersed in water, on the previously coated substrate by immersion in a 10-times concentrated simulated body fluid (SBF), and (ii) the addition of NP in the SBF during the bioactivation process. The obtained materials were characterized using scanning electron microscopy (SEM) and dynamic light scattering (DLS). Human mesenchymal stem cells (hMSCs) were used for biological evaluation. Proliferation and mineralization were tested by LDH and ALP activity, respectively. Cell viability and morphology were visualized by live/dead staining. The results show that both methods of immobilization of NP were efficient. In vitro tests confirm that the applied modification supports stem cell adhesion, proliferation, and osteogenic differentiation. In summary, the proposed materials have great potential for use in bone tissue regeneration and for the treatment of difficult-to-heal bone infections.

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# Near colourless UV protective glass and coating

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## Abstract:

Ultraviolet radiation can negatively impact food stability, leading to faster decomposition or undesirable changes. For instance, the oxidation of olive oil, caused by UV radiation, translates into a sensation of rancidity affecting consumers' sensory profile. This typically demands the use of opaque dark packaging. However, with the need to win over customers, the visual appeal of the product and the possibility of visually assessing its safety, have nowadays increased importance. Glass, considered in Europe as a good packaging material to fight against climate change, is colorless, food compatible, and transparent. It would be a great opportunity if one could develop a glass that maintains its transparency could additionally protect against UV radiation. In this work, a two-prong approach is explored for the development of a highly transparent UV-shielding material with a neutral color. First, soda-lime glasses were doped with ionic species of recognized UV-shielding capacity, such as V, Mn and Ce. Coatings containing carbon quantum dots prepared by two different routes were deposited via dip-coating on top of those glasses. These coatings have high transparency little color and absorb radiation under 400 nm. The glasses, the coatings, and their combination were evaluated and compared in terms of UV-shielding capacity. Regarding the glass matrices, different amounts and combinations of added ions were tested, and in the coatings, different dip-coating conditions (velocity and number of layers) were examined. The most promising combined conditions (glass + coating) were characterized through UV-Vis spectroscopy, CIELab, ellipsometry and TEM. The best result achieves protection in the UV range (320-400 nm) - 97.6 % superior to commercial green glass beer bottles 54.9 %.

## Acknowledgements:

This work was developed within the scope of CLEVER project Nº POCI 01-0247-FEDER-039699 co-financed by FEDER. The authors also thank the support of CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020. MRFS and PF are thankful to FCT for the PhD grant SFRH/BO/145661/2019 and FCT Investigator grant IF/00300/2015, respectively.

# Optimization of additively manufactured Si/Hydroxyapatite scaffolds by selective laser melting for bone tissue engineering applications

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## Abstract:

Selective laser melting (SLM) method is gaining increasing attention for the fabrication of scaffolds with different architecture for bone tissue engineering applications. The SLM method was used for the fabrication of powder mixtures of silicon (Si) and hydroxyapatite (HAp) to obtain porous scaffolds with a pore size of 400 μm. The used materials were mixtures of HAp/Si with weight ratios of 50/50 and 30/70. The process parameters such as weight percentage of phases, layer thickness, point distance, scanning speed, laser power, and energy density were optimized to obtain desired bioactive phases and mechanical properties of scaffolds. To understand the effect of different phase compositions and fabrication parameters on properties of obtained scaffolds, X-ray diffraction and Rietveld refinement analysis, microstructural evaluation and assessment of mechanical properties were conducted. Fabricated scaffolds with nominally added 50wt% of HAp were composed of Si and pseudowollastonite (PW, $CaSiO_3$), where with a decrease of exposure time and laser current, the weight percentages of the PW phase decreased. In fabricated scaffolds, with nominally added 70wt% of HAp, along with Si and PW, the formation of larnite ($Ca_2SiO_4$) was detected. With a decrease of exposure time and laser current, the weight percentage of obtained calcium silicate phases decreased. The morphology of the scaffolds depends on the process parameters and used powder materials. The scaffolds fabricated with the lowest processing parameters have shown macroporous size and interconnection joint dimensions which are in the best agreement with the obtained CAD design. With a decrease of exposure time and laser current, and an increase of HAp phase, the mechanical properties of fabricated scaffolds decreased.

## Acknowledgements:

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# Effect of ceramic stereolithography processing on the mechanical behavior of ductile ceria-stabilized zirconia-based composites for biomedical applications

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## Abstract:

Ceramics and ceramic composites generally fail catastrophically when stressed, have a slight tendency to deform before rupture and exhibit relatively low tensile strength, toughness and capacity to withstand impact loads. However, due to their high ability to undergo stress-induced tetragonal to monoclinic phase transformation, Ce-TZP-based ceramic composites can provide new materials that exhibit plastic deformation before fracture, excellent resistance to processing flaws and a Weibull modulus close to that of some metals. In this study, we investigated the influence of the ceramic stereolithography (SLA) shaping method on the mechanical behavior of these ceramics.

A ceramic paste compatible with SLA process was developed and 4-point bending bars printed and sintered. We used statistical fracture analysis to characterize the mechanical strength of Ce-TZP-based composites sintered at different temperatures. Failure probability distributions revealed low strength variability. The effect of microstructural features on the shape/size of transformed zones and the ductility degree was also studied. The results showed that similarly to composites obtained by conventional methods (pressing or slip-casting), SLA printed Ce-TZP-based composites can deform plastically and exhibit comparable fracture strength. In the future, medical devices based on Ce-TZP composites with complex architectures, geometries and surfaces and suitable for various patient-specific prosthetic applications could be manufactured by SLA.

# Toughening robocast chitosan/ceramic composite scaffolds with silk fibroin

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## Abstract:

Bioceramic particles and natural polymer blends are widely described in the scaffold's production for bone tissue engineering. Most of the studies explores conventional manufacturing methods where porous interconnectivity is difficult to attain. Robocasting (also called direct-write assembling) is an additive manufacturing technology based on the extrusion and deposition of an ink, layer by layer, allowing to create architectural and compositional 3D porous structures with high precision and reproducibility.

The present work aims the production of composite bioceramic scaffolds by robocasting with mechanical properties comparable to similar sintered CaP-based scaffolds, supressing sintering as post printing process. For this purpose, composite sintered-free scaffolds were developed from inks based on a polymeric matrix comprising chitosan (CH) and silk fibroin (SF) highly loaded with bioceramic particles, whose mechanical strength and rigidity were achieved through the crosslinking of the system. Our findings revealed that SF used to reinforce a CH matrix allows to reach higher mechanical performance reflected in high values for Young's modulus and maximum compressive strength. In addition to the enhanced mechanical properties, the combined natural polymers (CH and SF) mixed with bioceramic particles gave rise to a superior 3D structure provided by low temperature robocasting method, high biocompatibility and superior cellular performance of human osteoblasts cultured on their surfaces. Therefore, the mechanically fine-tuning composite scaffolds present a great potential to be used either as bone substitutes, or in the treatment of bone diseases.

## Acknowledgements:

This work is funded by FEDER funds through the COMPETE 2020 Programme and National Funds through FCT - Portuguese Foundation for Science and Technology under the projects 2BBone with reference POCI-01-0145-FEDER-029940 (PTDC/CTM-CER/29940/2017). The project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement, was also acknowledged. P M C Torres and S M Olhero acknowledge FCT for CEECIND/01891/2017 and CEECIND/03393/2017 contracts, respectively.

# Towards a better compromise between mechanical properties, aging resistance and translucency of Zirconia for dental applications: comparison between sub-micronic and nanometric YSZ with various Yttria contents

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## Abstract:

During the last years, the market of dental Yttria-Stabilized Zirconia (YSZ) has shown a growing interest in the development of grades with higher translucency in order to meet the aesthetic appearance of natural teeth, without compromising mechanical properties and Low Temperature Degradation (LTD) resistance. To decrease scattering due to birefringence inherent to tetragonal structures two main strategies are employed: increasing the $Y_2O_3$ content to have a larger amount of the transparent cubic (c) phase, or decreasing the grain size down to less than 100nm (nano-YSZ) to decrease their scattering cross section.

In this study we compared these two strategies in terms of mechanical properties, LTD resistance and optical properties to find the best compromise. Microstructure, mechanical properties, aging kinetics and translucency of different grades of conventional sub-micron YSZ (3, 4 and 5 mol.%) and nano-YSZ (1.5 and 3 mol.%), provided by Ivoclar Vivadent, were characterized and compared.

In the conventional sub-micron YSZ, the amount of transparent cubic phase increases with the dopant content, at the expense of the transformable t-phase, improving translucency and LTD resistance while decreasing strength and toughness. On the other hand, the decrease of grain size in the nano-YSZ improves the translucency and LTD resistance. Toughness is only slightly decreased in nano-3YSZ, while it is increased in nano-1.5YSZ.

The nano-YSZ offer the best compromise between the desired properties. In particular, the strategy of decreasing the grains size combined with low Y-content provides materials with highly transformable tetragonal nano-grains, capable of high strength, contact damage resistance and toughness, without losing LTD resistance.

# Crystal structure and mechanical properties of yttria-stabilized zirconia for dental applications

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## Abstract:

Yttria-stabilized zirconia (YSZ) is one of the most commonly used commercial dental ceramics. The favorable properties of YSZ for dental use are high mechanical strength, good optical properties, high chemical stability, and biocompatibility. However, improved esthetics and increased lifetime remain essential for the continued research and development of YSZ. The latest development of YSZ for dental use has been the introduction of multi-layered YSZ, where the doping levels of $Y_2O_3$ in $ZrO_2$ vary from the incisal to the gingival area, typically in the range of 3 mol% to 5 mol%. With varying doping levels, the phase fractions of the crystal phases in YSZ, cubic (c), tetragonal (t/t'/t''), and monoclinic (m), will vary. With an increasing amount of $Y_2O_3$ in $ZrO_2$ follows a reduction in strength and increased transmittance. The current knowledge of these layered materials is based mainly on isotropically doped YSZ for dental use. However, we would expect an increased amount of residual strain from the doping gradient after sintering. Furthermore, it is not well understood if the varying doping levels perform worse mechanically than isotropically doped YSZ. In our current work, we take advantage of mechanical testing, light spectroscopy, and x-ray diffraction (XRD) to investigate the relationship between the crystal structure, mechanical properties, and esthetics relevant to the dental industry.

# Borate bioactive glasses: the effect of synthesis method on structural and bioactive properties

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## Abstract:

Bioactive glasses (BGs) are well known for their ability to release therapeutic ions, gradual degradation and the ability to develop hydroxyapatite (HAp) layer in the physiological environment. Silicate BGs have low degradation rate, what recently increased the interest in glasses based on other oxides - for example $B_2O_3$. Due to their lower chemical durability, borate bioglasses can degrade and convert completely to HAp. In addition, boron ions support the regeneration and reconstruction of bone tissue, accelerate the wound healing and increase the proliferation and differentiation of stem cells.

Bioactive glasses with the composition (mol.%) $(40\text{-}x)SiO_2\text{-}xB_2O_3\text{-}54CaO\text{-}6P_2O_5$, where x = 5, 10, 20, and 40, were obtained by sol-gel method and melt-quenching technique. In the case of sol-gel synthesis, two different precursors of $B_2O_3$ were used – boric acid and triethyl borate.

Glasses were characterized in terms of their microstructure and bioactive properties. The morphological, chemical and structural changes after 1-, 3-, 7-, and 14-day incubation in SBF were monitored using SEM/EDX and FTIR methods, while the changes in ion concentration in the solution was analyzed with ICP-OES. The influence of $B_2O_3$ content on the glass structure and their ability to crystallization was monitored with FTIR and XRD.

Based on the conducted research, it was found that the presence of boron in the composition of bioactive glasses caused significant structural changes. Moreover all tested materials had excellent bioactive properties. By changing the chemical composition of bioactive glasses ($SiO_2/B_2O_3$ ratio), we can control their final properties, such as the tendency to crystallization, solubility and bioactivity.

## Acknowledgements:

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# Composite scaffolds based on β tricalcium phosphate and short and medium chain length polyhydroxyalkanoates for bone tissue regeneration

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## Abstract:

Bioceramic scaffolds based on β tricalcium phosphate (βTCP) due to their biocompatibility and bioactivity are commonly used as bone substitutes. However, βTCP scaffolds exhibit low compressive strength and high brittleness. The use of degradable polymers for fabrication of ceramic-polymer composites may, besides improving mechanical properties, open potential applications as platforms for biologically active substances. Polyhydroxyalkanoates (PHAs) are biocompatible and bioresorbable polymers with different physicochemical properties, which have found many applications, mostly in soft tissue replacement.

In this work, βTCP scaffolds prepared by a polyurethane matrix replica method were covered with short and medium chain length PHAs: poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly(3-hydroxyoctanoate) (PHO) respectively. Influence of the polymeric coating on the phase composition, microstructure, porosity, and compressive strength of the obtained materials was determined.

In both cases, XRD and SEM studies confirmed the presence of polymeric layers on βTCP surface. Developed scaffolds possessed a network of interconnected spherical pores with sizes between 100 to 900 μm and had high total porosity (~70 vol%). The compressive strength of the composites was higher (3.9 ± 0.9 MPa and 4.4 ± 0.7 MPa for βTCP/PHBV and βTCP/PHO respectively) when compared to uncoated TCP scaffold (2.9 ± 0.7 MPa). Furthermore, due to the presence of polymeric microfilaments that connected microcracks edges, after the compression test the composites kept their integrity and did not disintegrate.

Obtained ceramic-polymer composites might be promising candidates for bone tissue regeneration in non-load bearing places. However, further in vitro and in vivo studies are necessary.

## Acknowledgements:

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# Highly translucent and strong 3Y-TZP ceramics for dental applications

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## Abstract:

New 3Y-TZP ceramic was prepared by colloidal processing using unique mesoporous nanoparticles with a low $Al_2O_3$ content. Zirconia powder consisted of particles with a size in the range of 50-200 nm. These particles were composed of mesoporous, loosely connected nanocrystallites [1]. Green bodies were prepared by a gel casting method, pre-sintered, machined [2], and sintered at different temperatures. An optimum sintering schedule (1550 °C/2 h) was investigated from the viewpoint of mechanical and optical properties of sintered samples. Grain size of sintered samples varied in the range 150-400 nm. The best translucency achieved 41.1 % (for 1 mm thick glossy-polished sample at wavelength 600 nm). The biaxial strength (ball-on-three-balls test) up to 1180 MPa was determined (for samples with roughness parameters Ra 0.13 μm and Rz 1.16 μm). Other investigations included determination of complex refractive index, XRD, TEM and LTD analyses. Proof of concept was performed via producing a dental crown, three-unit bridge and knee joint for partial knee replacement. The novelty lies in the combination of i) gel casting method using ii) unique powder and obtaining iii) zirconia ceramic with superior properties especially for applications in dentistry.

[1] Liu, L. et al. Self-supported yttria-stabilized zirconia mesocrystals with tunable mesopores prepared by a chemi-thermal process. Journal of Materiomics, 2019, Vol. 5, (3), pp. 350–356. DOI: 10.1016/j.jmat.2019.03.001.

[2] Kastyl, J. et al. Machinability and properties of zirconia ceramics prepared by gelcasting method. Advances in Applied Ceramics, 2019, Vol. 119, (5–6), pp. 252–260). DOI: 10.1080/17436753.2019.1675402.

## Acknowledgements:

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# Structural role of sulfur in the soil active glasses

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## Abstract:

The aim of this study was to determine the role of sulfur in the structure of silicate-phosphate glasses from the $SiO_2$-$P_2O_5$-$K_2O$-MgO system with varying content of glass formers ($SiO_2$, $P_2O_5$) as well as the structure of their sulfur free counterparts has also been investigated. All glasses were synthesized by traditional melting raw materials mixture but sulfur containing glasses obtained under reducing conditions. Such glasses could find application as glassy carriers of sulfur for soil environments which is essential element for plants. Thus, we can try to solve the problem of sulfur deficiency in soil.

The amorphous nature of the samples was verified using XRD analysis. The bulk composition of glasses was confirmed with XRF technique. The homogeneity of the glasses was confirmed by SEM EDS measurements. We employed spectroscopic techniques (MIR, Raman and MAS NMR) to investigate the structure of such sulfur-containing and sulfur-free glasses. This work also referred to the density and molar volume of the glasses.

The addition of sulfur increased the abilities of glasses with higher amounts of $P_2O_5$ to form. The sulfur-bearing glasses were characterized by a lower density value than that of their sulfur-free counterparts. The lower density of the sulfur-doped glasses was probably related to the presence of large sulfur-containing anions in their structure. The addition of sulfur showed changes in the silicate–phosphate networks, making them more polymerized, which was probably related to the concentration of potassium ions in the vicinity of the sulfur ions.

## Acknowledgements:

This work was financed by the National Science Centre, Poland, project number 2018/31/D/ST8/03148.

# Preparation of transparent cerium-rare-earth-elements doped yttrium aluminum garnet (Ce,REE:YAG) ceramics with the aid of freeze granulation

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## Abstract:

The good spectroscopic parameters of Ce:YAG single crystals and the high temperature and mechanical resistance characteristic for yttrium aluminum garnets cause that this material can be widely used in light technology as a material for high power white light source. Still the problem is, that such a source does not have a high enough color rendering index. The solution may be doping with other rare earth elements (REE) or transition metal.

In this presentation, we report, the preparation of transparent Ce:YAG ceramics doped with erbium, holmium, neodymium, praseodymium and chromium by using freeze granulation process and solid state synthesis. Firstly aqueous slurries of pure oxides were prepared through mixing the powders in a planetary mill in water with Duramax B-1000 as a binder, Dolapix CE64 as a dispersing agent and laboratory-prepared octaanion as a source of $Si^{4+}$ ions. Slurries were sprayed into the liquid nitrogen in order to form granules which were immediately afterwards freeze dried. The granulates were pressed (under both uniaxial and isostatic pressure) into 20 mm pellets. The samples were fired up in order to remove organic additives and afterwards sintered under vacuum. The samples were annealed again in the air. Received ceramics were abraded and polished up bilaterally to mirror-like paralel surfaces with 1 mm thickness.

The optical transmission of Ce,REE:YAG ceramics was measured in the range 200÷3000 nm. The samples were subjected to phase analysis by XRD diffraction, surface microstructure analysis by SEM scanning electron microscopy, analysis of the chemical composition of the sample by EDS spectroscopy, and then the photoconversion and absorption properties were examined.

## Acknowledgements:

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# Ferroelectric BaTiO3 coating of beta-titanium alloy – physicochemical properties and human mesenchymal stromal cells response

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## Abstract:

Beta-titanium alloys are promising materials for bone implants due to their advantageous mechanical properties. To enhance the interaction of bone cells with this material, we deposited a ferroelectric $BaTiO_3$ coating on a Ti39Nb (wt.%) alloy by hydrothermal reaction of $TiO_2$ with $Ba(OH)_2$.which was formed by reaction of $BaCl_2$ and NaOH in the autoclave. A Parr hydrothermal reactor with custom made titanium insert (300°C / 48h) was used. The best ferroelectric properties were detected by micro-Raman spectroscopy when Ti39Nb alloy was coated with an interlayer of Ti (cca 5μm) deposited by magnetron sputtering, and it was subsequently in situ oxidized to $TiO_2$ in an $O_2$ atmosphere (500°C / 6h). The Ti interlayer hinders the diffusion of Nb to the $BaTiO_3$ layer during hydrothermal synthesis. In addition to micro-Raman spectroscopy, X-ray diffraction confirmed the presence of tetragonal $BaTiO_3$ in the coating, with crystallite size 80 – 100 μm (some crystallites were larger than ~200 nm). The morphology of the coating was determined by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The composition was confirmed by SEM/Energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy (XPS), as well. Mechanical properties were determined by nanoindentation and roughness measurements. Leaching experiments in a saline solution using XPS revealed that Ba is released from the surface of the coating. Experiments on the cultivation of human mesenchymal stromal cells on bare Ti39Nb samples and those coated with ferroelectric $BaTiO_3$ film indicate that ferroelectric $BaTiO_3$ coating could be promising for improved osseointegration of metallic bone implants.

## Acknowledgements:

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# Production and characterisation of dense Nd: Y2O3 ceramics as a potential candidate for a solid-state laser

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## Abstract:

The aim of this work was production and characterisation of Nd:$Y_2O_3$ dense polycrystal for a potential application as solid-state laser. Proper amounts of fine $Y_2O_3$ and $Nd_2O_3$ (1 at. %) powders were thoroughly mixed and isostatically pressed. Pure $Y_2O_3$ samples were prepared as a reference material. The samples were sintered in air at 1400°C, 1450°C and 1500°C to achieve materials with no open pores. Such samples were post-HIP-ed at 1650°C for 4h, which led to fully dense materials. The materials required Microstructure and chemical composition of the material was investigated using SEM – EDS method. The coefficient of thermal expansion (alpha) as well as the heat transfer coefficient (lambda) of the materials were measured. The emission spectrum of Nd:$Y_2O_3$ in the near infrared region (NIR) was measured. Densification of yttrium oxide was affected (slowed down) by the presence of Nd addition. The SEM/EDS results showed uniform distribution of Nd cations within the material. Its thermal properties and emission spectrum were comparable with that of Nd:YAG material.

## Acknowledgements:

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# LiF as a luminescence component of the oxyfluoride glass and glass-ceramics

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## Abstract:

The physico-chemical properties of glass and glass-ceramics with their variety of composition show that they could be a promising alternative for dosimetry. The materials are investigated due to their application in brachytherapy, radiotherapy, nuclear medicine diagnosis, radioisotope power systems, radiation processing of food, geological and archaeological dating methods.

LiF shows thermoluminescence (TL) and optical stimulated luminescence (OSL) properties which is widely used for the purpose. It is applied for dose analysis of high-energy radiation e.g., alfa and beta radiation. Unfortunately, a content of fluoride in the most used silicate glass is limited to a few percent due to induction of uncontrolled crystallization of the melt. We studied a few glass systems in which it is possible to obtain amorphous materials with higher content of LiF and good luminescent properties. The oxyfluoride glass and glass-ceramics from the LiF-$B_2O_3$-$SiO_2$ system were developed. The stable glass can be produced in the range of 20–40 mol% LiF. The oxyfluoride phosphate glass $50P_2O_5$-(50-x)BaO-xLiF ($x = 0 \div 50$) and borotellurite glass with content of up to 45 mol% LiF glasses were obtained. We studied the thermal stability and ranges of the linear response to the dose of ionizing radiation and the temperature positions of the thermoluminescent peaks depending on the LiF concentration.

## Acknowledgements:

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# Boron carbide nanoparticles as potential carriers in boron-neutron capture therapy – physicochemical characterization

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## Abstract:

Due to the high boron content, boron carbide may be a potential carrier in Boron Neutron Capture Therapy (BNCT). Therefore, the subject of the research were two fractions of boron carbide ($B_4C$) which were synthesized according to the procedure described in Ref. 1. Physicochemical characteristics of $B_4C$ particles comprising the diffusion coefficients, hydrodynamic diameter, electrophoretic mobilities and zeta potentials were initially determined. The particle size distribution were be determined using AFM imaging in air. The topographical analysis of the particle layer images acquired by AFM was be carried out by determining the height profiles and calculating the root mean square roughness (the interface width) using a specialized software. This enables to quantitatively determine the particle shape, the thickness and heterogeneity of the particle layer.

[1] Kozień D, Szermer-Olearnik B, Rapak A, Szczygieł A, Anger-Góra N, Boratyński J, Pajtasz-Piasecka E, Bućko MM, Pędzich Z. Materials. 2021; 14(11):3010.

## Acknowledgements:

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# Symposium I: HT Materials / Refractories / Composites

## Invited presentation:

# Nanocarbon added Silicon Nitrides

Csaba Balázsi, Katalin Balázsi

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## Abstract:

This research explores the use of a variety of carbon nanoparticles to impart electrical, thermal conductivity, good frictional properties to silicon nitride matrices. We used the highly promising types of carbon as carbon nanotubes, exfoliated graphene and carbon black nanograins. A high-efficiency attritor mill has also been used for proper dispersion of second phases in the matrix. The sintered silicon nitride composites retained the mechanical robustness of the original systems. Bending strength as high as 700 MPa was maintained and an electrical conductivity of 10 S/m was achieved in the case of 3 wt% multiwall carbon nanotube addition. Electrically conductive silicon nitride ceramics were realized by using carbon nanophases. Examples of these systems, methods of fabrication, electrical percolation, mechanical, thermal and tribological properties are discussed.

## Acknowledgements:

This research was funded by Hungarian National Research Development and InnovationOffice, grant number NKFI-NN 127723 and NKFI-NNE 129976.

## Invited presentation:

# Deformation and fracture of high - entropy ceramics during micro/nano mechanical testing

Jan Dusza

*IMR SAS, Kosice, Slovakia*

**Abstract:**

The deformation and damage characteristics of different high entropy ceramics – carbides, nitrides, carbonitrides, dual – phase systems, etc, were investigated. Depth-sensing nano-indentation of differently oriented grains and bulk systems has been applied to study the nano/micro hardness and deformation characteristics. Micro-compression tests of micropillars prepared by focused ion beam from oriented facets of grains were studied. During micro-cantilever tests in bending deformation and fracture characteristics of individual grains and grain boundaries have been investigated. The hardness values of differently orientated grains showed significant angle dependence. A strong influence of the grains orientation on compressive yield stress and rupture stress values was found during the micropillar test, too. The active slip systems for individual systems have been recognized. The bending strength of micro-cantilevers was strongly dependent on the character/size of the present fracture origins which were in all cases in nano-metric range. The fracture toughness of the individual grains and grain boundaries were investigated, too.

## Invited presentation:

# Characterization and mechanism of early hydration of high resistant refractory cement systems undoped and doped with foreign elements

Dominika Madej

*AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Ceramics and Refractories, Krakow, Poland*

## Abstract:

Alkaline earth elements have of utmost importance because of the ability to formation of hydraulic phases type $MAl_2O_4$ (M = Ca, Sr, Ba). Hence, aluminates are the mostly studied and used compounds as hydraulic binders designed for unshaped refractory materials, especially calcium monoaluminate, $CaAl_2O_4$. Examination of hydration behaviour of the aluminates type $MAl_2O_4$ discloses different hydration rate but not the nature of hydration, since the reactions of the anhydrous phases with water usually appear to arise by congruent dissolution followed by precipitation of products in the form of hydrated alkaline earth aluminates $(CaO,SrO,BaO)\text{-}Al_2O_3\text{-}H_2O$.

In this work, investigations on the early hydration of cement-bonded refractory composite cements were traced by means of X-ray diffraction (XRD), simultaneous thermal analysis (DSC-TG-EGA-MS), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS), time-resolved electrochemical impedance spectroscopy (TR-EIS). Impedance camera instrument was successfully applied for TR-EIS measurements under nonstationary conditions and record the time-dependent evolution of the Nyquist plots for hydrating cement pastes. New approach to equivalent circuit modelling of the cement-based refractory pastes was implemented to interpret spectra obtained from TR-EIS, assigning electrical responses to the hydration features such as hydration products and microstructure. Moreover, this work deals with the monitoring the hydration process of new cementitious materials and phase changes within the $(CaO,SrO,BaO)\text{-}Al_2O_3\text{-}H_2O$ systems doped with foreign elements through different spectroscopic techniques.

## Acknowledgements:

This project was financed by the National Science Centre, Poland, project numbers 2017/26/D/ST8/00012 and ID: 528544 (Recipient: D. Madej).

## Invited presentation:

# Self-healing zirconia mullite refractory with secondary mullite precipitation inducing crack repair

Jacques Poirier[1], Lizeth Arbelaez Morales[2], Thierry Chotard[2]

[1] *CEMHTI/CNRS UPR 3079, University of Orléans, Orléans, France*

[2] *IRCER UMR 7315, University of Limoges, Limoges, France*

### Abstract:

Design of the microstructures with the ability of crack-healing in service is an attractive challenge for the development of advanced refractories with improved thermal shock resistance and lifetime.

This research addresses the most recent findings of crack-healing in zirconia-mullite composites and discusses the self-healing mechanisms involved.

Mullite zirconia refractory composites are developed from andalusite, zircon and alumina fine powders. These materials show a very interesting behaviour when they are subjected to thermal shock: an increase in the Young modulus and no damage are observed during a subsequent thermal cycling.

The characterisation of the microstructural and thermomechanical behaviour, using different techniques (X-ray Diffraction, SEM, Ultrasonic Echography and Acoustic Emission), make it possible to propose a self-healing scenario.

The role of andalusite is preponderant. The formation of secondary mullite resulting from the reaction between the alumina and the high silica glassy phase acts as a bridge between the phases and thus improves the mechanical properties. This vitreous phase also has a very important effect in the densification of the material by decreasing its porosity.

These innovative sintered zirconia-mullite composites seems promising for use as refractories subjected to severe thermal shocks. These products could be an interesting alternative to alumina-chromium refractories, which are costly and have a negative environmental impact.

However, an excessive amount of glassy phase can significantly affect the mechanical properties. That is why the amount of raw materials proposed for the manufacture of these refractories should be carefully considered.

## Invited presentation:

# Extending carbon fibre ceramic composites from boride to carbide and oxide matrices

Diletta Sciti, Antonio Vinci, Pietro Galizia, Simone Failla, Luca Zoli

*National Research Council of Italy - Institute of Science and Technology for Ceramics, Faenza, Italy*

### Abstract:

Ceramics, oxides and non-oxides, have an extremely interesting combination of properties including refractoriness, strength, hardness and stiffness but in most cases they suffer from catastrophic failure under aggressive conditions. The most common way to reinforce ceramics is through addition of discontinuous secondary phases, such as particles, whiskers and short fibres that usually contribute to a modest increase of the fracture toughness. The incorporation of continuous Carbon fibres allows the achievement of new hybrid composites where both fibre and matrix cooperate synergically in imparting structural properties, damage and environmental tolerance. In addition, fibres can also exert other functions, improving thermal/electrical conductivity and reducing the material weight. By extending the process and concepts recently developed for $ZrB_2$-based ultra-high temperature ceramic composites in the EU C3harme project, we will show preliminary results on the development of reinforced composites based on non-oxides such as ZrC, SiC, $B_4C$, $TiB_2$ and oxides such as $Al_2O_3$ and $ZrO_2$. These composites have in common a similar process including impregnation of carbon fibres with water-based slurries and densification by sintering, the latter not being the typical consolidation technique for CMCs. Basic microstructure and mechanical properties will be illustrated. From preliminary results, carbide- and oxide-based composites displaed a weaker fibre/matrix interface, enabling extensive fibre pull-out and showing a more plastic behavior compared to boride-based composites characterized by a stronger interface and stiffer matrix.

## Invited presentation:

# Taming thermal gradients for an optimal chemical vapor infiltration with the help of modeling

Gerard Vignoles

*U. Bordeaux - CNRS - LCTS, Pessac, France*

### Abstract:

The Chemical Vapor Infiltration (CVI) process is among the most employed ones for the infiltration of matrices in high-performance CMCs. To overcome one of its main drawbacks, which is the possibility of non-uniform infiltration with residual porosity present in the middle of the CMC part, thermal-gradient variations of the process have been proposed in different implementations. Ideally, they aim at creating an infiltration front starting from the bottom of the porous preform and progressing towards its surface. However, in practice, it may be quite difficult to evaluate the magnitude of the thermal gradient necessary for the achievement of this desired infiltration front. Modeling may bring solutions for the design of a successful processing situation. This presentation will review the principles of multi-physics modeling applied to this process, discuss some solution methods and present some application examples given in several practical situations.

Invited presentation:

# Development of 3D-Printing Filament System for Manufacturing of Tailor-Made Refractory Products

Serhii Yaroshevskyi[1], Piotr Malczyk[1], Tilo Zienert[1], Tobias Stenzel[2], Uwe Lohse[2], Christos Aneziris[1]

[1] *TU Bergakademie Freiberg, Institute of Ceramics, Refractories and Composite Materials, Freiberg, Germany*
[2] *XERION BERLIN LABORATORIES GmbH, Berlin, Germany*

## Abstract:

The development of filament system for refractory ceramics and ceramic reinforced Metal Matrix Composites has been done. The elaborated thermally debindable filament binder was based on polyethylene powder with addition of cellulose, stearic acid and lignin sulfonate. The binder was mixed with solid material powder in proportions of 48 vol% to 52 vol%, respectively. Filaments were manufactured by the help of filament extrusion setup aided with winding system.

It is necessary that, the binder system ensures the sufficient form stability of the 3D printed product over the whole temperature range of the thermal treatment. Therefore, to reveal the most favorable binder composition as well as to determine their adequate debinding and sintering procedure the DSC/TG analyses and softening tests of filaments with different binder composition were performed. Selected filaments based on the alumina rich spinel AR78 solid material were manufactured and subsequently printed into casting nozzle form specimens using Xerion Fusion Factory Printer. Sintered nozzle specimens were subjected to thermal shock at 850 °C for 15 min. Afterwards, the impact of the thermal shock on the compression strength of nozzle specimens was investigated. Selected nozzle specimens were scanned by means of computed tomography for examination of their internal structure in the green, sintered as well as thermal shocked states.

The result of the research revealed successful development of filament binder system capable of being debinded and sintered using only thermal treatment while maintaining excellent structure and form stability of the printing products. The developed binder system enables utilization of broad selection of powder formed solid materials from ceramics up to ceramic/metal matrix composites.

## Acknowledgements:

The authors gratefully acknowledge that presented research have been done with financial support of the Federal Ministry for Economic Affairs and Climate Action (BMWi) via Central Innovation Programme for small and medium-sized enterprises (ZIM): project Multimat 1800 °C (founding number ZF4096916AG8).

## Invited presentation:

# Fabrication and selection of high temperature energy storage ceramic materials and refractories for solar thermal systems: microstructure-performance relationship under corrosive atmosphere

Nur Sena Yüzbasi[1], Lukas Geissbühler[2], Thomas Graule[1], Gurdial Blugan[1]

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[2] *Synhelion SA, Lugano, Switzerland*

## Abstract:

Concentrated solar power (CSP) plants convert sunlight into high-temperature heat, which can be used for solar thermochemical fuel production. To operate the deployed thermochemical reactors economically and efficient, stable and continuous operation of the reactors is crucial. Thermal energy storage (TES) allows high-temperature solar energy supply 24/7 and is therefore one of the key technologies to enable economically-viable solar fuel production.

Current CSP plants are under broad industrial development; however, adapted TES materials and systems are still not available specifically for high temperature operations. This study targets the development of cost-effective ceramic-based TES materials that are compatible with the high temperatures (~1200 °C) and can withstand multiple heat charging/discharging cycles using steam as heat transfer fluid. In this context, alumina based high performance ceramic storage materials were fabricated using slip casting. Together with commercially available refractories, the compatibility of selected materials with steam were tested in a high-temperature corrosion setup up to 1’200 °C. Finally, compressive and flexural strength measurements before and after corrosion tests complemented with microstructure imaging were conducted to evaluate the relationship between microstructure and mechanical properties.

## Acknowledgements:

Financial support of Innosuisse Swiss Innovation Agency through 53851.1 IP-EE Project is grate-fully acknowledged.

# Manufacturing and characterisation of fully stabilised hafnia by FAST and natural sintering

Lisa Audouard[1], Aurélie Julian-Jankowiak[2], Jean-François Justin[2], Pierre Bertrand[3], Cécile Langlade[3], Matthieu Garcia[4]

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[3] *ICB, Belfort, France*
[4] *CNES, Toulouse, France*

## Abstract:

CNES has engaged the development of a new green propellant, which induces the study of new combustion chamber materials due to harsh operating conditions. Functionally graded materials (FGM), and especially ceramic/metal FGM demonstrate appropriate behaviour in an ultra-high temperature oxidising environment, associated with good mechanical resistance. Related to the FGM under investigation at Onera, this work is focused on the development of a 3000 K oxides resistant ceramic as EBC/TBC. In our previous studies, hafnia based samples with different doping strategies in terms of compositions have shown a high potential. In particular, high amounts of additives (>33 mol. %) seem to be very promising and are presented in this study.

To complete those results, hafnia samples with different rare earth oxides as $Lu_2O_3$, $Y_2O_3$ and $Gd_2O_3$ are sintered using Field Assisted Sintering Technology (FAST) or natural sintering. XRD analysis revealed the formation of fluorite or rhombohedral phases and allowed the determination of the lattice parameter, depending on the composition. The influence of the temperature and the dwell-time on the final density of the samples is analysed with an iterative approach. For that, the microstructure of each sample is investigated by scanning electron microscopy (grain size, homogeneity, porosity and chemical composition). After that, hardness, Young's modulus and thermal expansion coefficient of each composition are measured. Thus, the relationship between the microstructure, the process and the properties can be established. These results will be useful to better understand the influence of the nature of the rare earth oxide on the stabilisation of hafnia and to select the most appropriate composition.

## Acknowledgements:

The authors would like to acknowledge N. Horezan (ONERA) for EBSD analysis and M. Tsoutsouva (ONERA) for XRD analysis.

# From design to application of porous TiC(N)/SiC(N) Nanocomposites derived from preceramic polymers

Maxime Balestrat, Samuel Bernard

*CNRS-IRCER, Limoges, France*

## Abstract:

Silicon-based non-oxide ceramics (SiC, Si3N4) have great potential for many industrial specifications due to their good mechanical and chemical properties, and also their reliability at room and elevated temperatures. The addition of a second ceramic (nano)phase into silicon carbonitrides leads to materials with versatile, and so tunable, proprieties which offer solutions in many more fields of applications. However, the preparation of these materials is still a challenging task according to the fact that the conventional processes unavoidably lead to size and structure inhomogeneities of the different phases and possible presence of impurities which affect the final properties. The Polymer-Derived Ceramics (PDCs) route offers new preparation opportunities in ceramic sciences. The molecular origin of preceramic polymers, and the possibility to design advanced ceramics in particular forms, play a major role in the preparation of functional ceramics. In this talk, we will present our last results on the modification of polysilazanes with metal-organic species to offer functionalities to TiC(N)/SiC(N) porous nanocomposites obtained after the thermo-chemical conversion of precursors. The characterization of the materials will be done at each step of their elaboration process and their optical properties/selectivity will be evaluated.

## Acknowledgements:

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# Reinforced porous mullite ceramics via sol gel impregnation

Eva Bartonickova[1], Jiri Svec[1], Lucie Galvankova[1], Petr Hruby[1], Jan Koplik[1], Frantisek Soukal[1], David Zemanek[2], Lucie Kersnerova[2], Karel Lang[2]

[1] *Institute of Materials Chemistry, Faculty of Chemistry, Brno University of Technology, Brno, Czech Republic*

[2] *PD Refractories CZ JSC, Velke Opatovice, Czech Republic*

## Abstract:

Nanotechnology has been entered into the refractory industry decades ago; however, there are still some peculiarities that hinder its routine application. Poor mechanical strength is one of them. Here we introduce the fabrication method of mullite porous ceramics using a calcium-free colloidal binding system followed by secondary sol-gel impregnation. The primary foam was prepared from direct foaming of slurry containing colloidal silica, gelling agents, surfactant, micro silica, and reactive aluminas. The foam mixture was cast, de-moulded and dried using a cascade drying procedure. The investigation of mullitization that occurred during the high-temperature treatment was studied by HT-XRD, TG-DTA analysis and heating microscopy. Raman spectroscopy was used to assess the SiO- bonding in a green and fired system. Then the sintering curve consisting of various temperatures combined with relaxation dwells was applied to obtain the highest mechanical properties. The resulting foam (with open porosity, volume density about 400 kg/m$^3$ and mechanical strength about 7 MPa) was further processed by the impregnation step. The applied mullite sol and unreacted alumina gained secondary mullitization during following high-temperature treatment, which enhanced mechanical strength. The secondary mullitization process was also investigated by HT-XRDand TG-DTA analysis. Foam microstructure was observed by an electron scanning microscope. The porosity evolution was studied by mercury intrusion porosimeter and calculated from image analysis.

# The effect of Nano-Iron on phase and microstructural evolution of MgO-C refractories

Hossein Rastegar[1], Mohammad Bavand-Vandchali[2], Farhad Golestani-Fard[3], Ali Nemati[4]

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[2] *Department of Materials Engineering, Science and research university, Tehran, Iran*
[3] *Refracto-Ceramics Consultancy LTD, London, United Kingdom*
[4] *Department of materials science and engineering, Sharif University of Technology, Tehran, Iran*

## Abstract:

In the present study, the effect of Iron Nitrate as catalytic precursor to in situ formation of nano-Fe particles in phenolic resin and microstructural evolution of MgO-C refractories has been investigated. Therefore, various samples according to matrix section formulation of low carbon MgO-C refractories (LCMCR's) with 0 and 6 wt% (Fe/Phenolic resin) were prepared and phase and microstructure changes after coking at temperatures 800-1400ºC studied by XRD and FESEM analyses. Based on attained results, iron nitrate transfer to Fe nano particles with 60-80 nm in diameter during firing in reduced atmosphere. In situ formed Fe nano-particles as catalytic agent promotes graphitization behavior of phenolic resins. Increasing temperature led to a more effective graphitization level. In addition, the different nano crystalline carbon shapes such as onion and bamboo like and carbon nanotubes (CNTs) were in situ formed. Phase and microstructure analysis of LCMCR's samples reveal that different ceramic whiskers such as MgO, $MgAl_2O_4$ spinel, $Al_4C_3$ and AlN formed after coking at 1000 °C and the amount of whiskers phases significantly increased at higher coking temperatures. It was also clarified the presence of Fe nano-particles have effective influence on the formation of gases components and promote ceramic phases formation. Microstructural observation showed the graphitic carbons like carbon nano-tubes (CNTs) and ceramic whiskers mainly formed in the bonding phase between the aggregates according to the V-L-S and V-S growth mechanism.

# Control of the sample temperature profile in pilot-scale Microwave-assisted Chemical Vapor Infiltration reactors by means of multiport/multifrequency excitation

Roberto D'Ambrosio[1], Andrea Cintio[1], Laura Aliotta[2], Vito Gigante[2], Marcel Mallah[3], Steffen Probst[3], Andrea Lazzeri[2], Giuseppe Annino[1]

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## Abstract:

In Chemical Vapor Infiltration (CVI) of Ceramic Matrix Composite (CMC) preforms, the temperature profile in the sample is critical both for the material quality, deposition profile as well as the process efficiency. The use of microwaves (MW) in these processes has a great potential, thanks to the generation of an inverse temperature profile and to the direct release of power in the preform. A common limit of MW-CVI of samples larger than the electromagnetic wavelength, is the limited uniformity of the heating pattern. Possible approaches to mitigate this problem are under investigation in the framework of the European CEM-WAVE project.

In this contribution, the possibility to control and optimize the sample temperature profile in a multiport MW-CVI reactor designed for pilot-scale applications will be discussed. The proposed approach is based on a multifrequency excitation of the reactor by three solid-state sources fully tunable in the ISM band centered around 2.45 GHz. In particular, the rigorous numerical modeling enabling the choice of the most suited excitation frequencies, the practical implementation of the proposed technique, and its experimental validation, based on microwave heating trials up to infiltration temperatures, will be presented.

## Acknowledgements:

The research leading to these results has received funding from the European Union (H2020-NMBP program) under grant agreement no. 958170.

# Additive manufacturing of CMCs by Direct Ink Writing

Filippo Da Rin Betta[1], Giorgia Franchin[1], Paolo Colombo[1], Sarah Ferris[2], Benjamin Baker[2], Charles Footer[2]

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[2] *Qinetiq, Farnborough, United Kingdom*

## Abstract:

Ceramic Matrix Composites (CMCs) is a subgroup of composite and ceramic materials and consists in ceramic fibres included in a ceramic matrix. Although CMCs show an improved mechanical behaviour, the production of complex shapes is fairly difficult; one of the ways to address that is the use of preceramic polymers, polymeric materials that can be converted into ceramics by thermal treatment. This class of material is highly compatible with the Direct Ink Writing (DIW) technology, an Additive Manufactory technique where the part is progressively built by extruding a slurry through a nozzle. Using a slurry as feedstock material enables the fairly simple inclusion of short fibres directly in the feedstock, and moreover the fibres align in the printing direction during the shaping process.

In this work, a commercially available polysilazane was used as polymeric precursor for a silicon carbonitride matrix, and chopped carbon fibres and silicon carbide powders were added as fillers. The shaping process was performed using a commercially available 3D printer (Delta Wasp 2040 Turbo 2), customized to enable a pneumatic extrusion system, according to the geometries generated by Python-based scripts. The samples were pyrolyzed by thermal treatment in inert atmosphere at 1200°C.

# Magnetic Biasing and Magnetocaloric Effect in a Large Temperature Window in Magnetic Composite of Alloy and Oxide

Subhadeep Datta, Manoranjan Kar

*Indian Institute of Technology Patna, Patna, India*

## Abstract:

The structural and magnetic properties have been investigated in the magnetic composites of hard magnet Barium hexaferrite (BHF) and soft magnet Ni-Mn-Sn Heusler alloy (NMS). The lattice parameters of the composite samples remain unaltered from the corresponding parent phases. The composite samples undergo two distinct ferromagnetic (FM) to paramagnetic (PM) and ferrimagnetic to PM phase transitions corresponding to NMS and BHF phases respectively. Magnetic biasing between the hard and soft magnetic phases has been observed in the composites when both the phases are in the FM region i.e., a squeezing in the M-H curve is observed around $H= 0$. The squeezing effect may be used in the magnetic memory device application where an optimum coercivity, high remanent magnetization and high squareness ratio are required. These parameters can be optimized by proper tuning of hard and soft magnetic phases along with the milling time and temperature. On the other hand, the composite sample shows a high magnetocaloric effect (MCE) with a constant high value of magnetic entropy changes in between the two successive magnetic transitions. This gives an advantage with wide working temperature in the MCE application.

# Pressure-less glass-ceramic joining of SiC/SiC nuclear fuel clads for Light Water Reactors

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[2] *Technische Universität Dresden, Dresden, Germany*

## Abstract:

Several materials have been proposed for joining of SiC/SiC components for nuclear light water reactors.

Among them, some Silica-Alumina-Yttria (SAY) glass-ceramics gave promising results as pressure-less joining materials for slurry-based joining technologies suitable for a nuclear environment.

The present work reports on a Silica-Alumina-Yttria (SAY) glass-ceramic pressure-less joining options for SiC-based components; the same SAY glass-ceramic can be been used to join SiC/SiC composites by traditional furnace heating and by localized heating, then coated by Cr layer to protect the joining area from hydrothermal corrosion.

Morphology, micro-structure, mechanical test and autoclave test in pressurized water reactor (PWR) conditions, on SiC/SiC tubes joined to SiC/SiC end-plugs, will be discussed.

## Acknowledgements:

Part of the research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 740415 Project "IL TROVATORE - Innovative Cladding Materials for Advanced Accident-Tolerant Energy Systems".

# High-resolution mass spectrometry-based classification of high-boiling binders used in refractory materials

Julia Doll, Ali Masoudi Alavi, Peter Quirmbach

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## Abstract:

Organic binders for the manufacturing of refractory bricks are complex carbon mixtures. These mixtures contain hundreds of very similar compounds, such as polycyclic aromatic hydrocarbons and their heteroatom derivatives. In addition, the majority of these compounds are characterized by their low volatility and solubility. These aspects lead to the fact that, despite intensive research, the exact chemical composition of such carbon mixtures remains unclear. This study presents an approach for the analysis of complex carbon mixtures using the example of a commercial binder which is needed in refractory industry. In particular, it was shown that high-resolution time-of-flight mass spectrometry (HR-TOFMS) combined with prior sample separation is a powerful tool. Matrix simplification was performed using two-dimensional gas chromatographic separation (GCxGC) for the volatile fraction. The semi-volatile fraction was separated based on different boiling points using a temperature gradient under vacuum. Due to reduced separation efficiency in the semi-volatile fraction, data processing plays an important role. A method for resolution-enhanced data processing was applied, which enabled the detailed visualization of high-resolution mass spectrometric data. The individual compounds could thus be assigned to different substance classes.

## Acknowledgements:

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# Lightweight Alumina-B4C composites for structural and functional applications

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[2] *National Institute of Optics - National Research Council (INO-CNR), Firenze, Italy*

## Abstract:

$Al_2O_3$–$B_4C$ composites with 0, 5, 10, 15, and 50 vol% $B_4C$ additions were consolidated by hot pressing (HP) and pressureless sintering (PLS). The influence of the $B_4C$ additive on the densification behavior, microstructure and mechanical properties of the composites was investigated. Detailed SEM-EDS and XRD studies highlighted differences in microstructures and secondary phase formations. The evolution of the Gibbs free energy at different temperatures and the equilibrium phases were calculated by means of thermodynamic simulations. These analyses showed that formation of Al-B-O gaseous phases was affected by atmospheric conditions (vacuum or Ar flux). Addition of 50 vol% of $B_4C$ promoted an increase of hardness and toughness (~24 GPa and ~5.85 MPa $m^{1/2}$) and a substantial decrease of weight (~18%) compared to monolithic alumina, which could be of interest for armor and other structural applications. Besides, functional applications were considered. The addition of $B_4C$ caused a marked change of colour and increase of solar absorbance. The optical properties of these composites were investigated in view of possible applications as solar receivers in concentrating solar power system.

# Development of new tool materials synthesized from WC-Ti composite powders by HEBM and SPS

Dariusz Garbiec[1], Jakub Wiśniewski[1], Mateusz Marczewski[1], Grzegorz Adamek[2]

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## Abstract:

Several authors have already reported some research on WC-Ti composites. The novelty of the presented research is the use of the combined technologies of high-energy ball milling and spark plasma sintering to obtain cobalt-free new tool materials. This innovative manufacturing route leads to the receipt of a new type of composite materials characterized by high hardness and fracture toughness, with a high application potential. New tool materials were synthesized from WC-Ti composite powders with 5 and 15 wt% titanium. The microstructures and phase compositions of the sintered samples were investigated by SEM and XRD. The Vickers hardness and indentation fracture toughness were also measured. The best values of hardness (>2000 $HV_{10}$) and fracture toughness (>8 $MPa \cdot m^{1/2}$) were achieved with the addition of 5 wt% titanium. No notable carbon uptake from the graphite tool was detected. New graphite tools were designed and the thermal distribution during sintering was modeled by the finite element method for the near-net shape manufacturing of cutting tools.

## Acknowledgements:

This research is part of the InnoHM project that has received funding from the Polish National Centre for Research and Development under grant agreement No. LIDER/20/0071/L-11/19/NCBR/2020.

# Efficient experimentally-based exploration of the High Entropy Alloys as fillers, brazers and coating materials for CMCs: the FCC-CoCrFeMnNi alloy as case study.

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## Abstract:

Currently, aircraft and aerospace industries are focused on developing new and more capable MMCs and CMCs materials reinforced by high-strength continuous fibers. However, limitations exist: costly manufacturing processes, difficulties in producing/assembling large and complex CMCs shapes, integration with dissimilar materials (i.e. metals, ceramics or other composites) and fibers degradation during fabrication processes and in service, mainly at high temperature. Indeed, Cf and SiCf show the tendency to be oxidized/degraded (by releasing CO-SiO) if processed at T above 400°C and 1200°C under oxidizing atmospheres, respectively. Reliable densification and joining of CMCs by liquid assisted processes are crucial for preserving the CMC thermomechanical properties and for saving weight. Both densification and joining reliability are ensured by the microstructures resulting from the interaction phenomena occurring at the metal/fiber interfaces.

Such limitations are forcing to improve the existing options or to explore new materials. High entropy alloys (HEA) are proved to be a new initiative in today era in the field of materials science and engineering. Exhibiting large ductility, key requirement in structural applications in the area of transportation and energy fields, the high demand for HE-alloys (HEA) and feasibility studies on their potential applications, are well justified.

In this work, an experimentally based feasibility study of using successfully HEA alloys as fillers, brazers and coatings for CMCs, is presented. Specifically, the FCC-CoCrFeMnNi alloy was selected as case study to densify and join CMCs based on Cf and the results will be presented as well as the wettability of SiC and C by the selected HEA and related interfacial phenomena.

# Oxidation resistance of Spark Plasma Sintered (SPS) Inconel 625-NbC Metal Matrix Composites (MMC)

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## Abstract:

Oxidation performance evaluation of Spark Plasma Sintered (SPS) Inconel 625-NbC Metal Matrix Composite (MMC) obtained for potential high-temperature applications was the main objective of the presented research project. The manufactured composite material, with reinforcement phase ranging from 5 to 20 wt.% of NbC, was exposed to the elevated temperature of 800°C in the free flow of air simulating a typical work environment. Surface and cross-section studies by SEM are utilized to observe the kinetics of oxidation within the material. EDS qualitative analysis by the elemental mapping is presented in order to initially characterize emerging compounds. Mass gain after 24, 49, and 100 hours of exposition is presented. Microhardness losses of near-surface zones due to corrosion were measured. Two major oxidation mechanisms are found and described, related to the matrix and reinforcement phases respectively. It was revealed that the initial step of oxidation was an important factor in regard to the overall corrosion resistance of the composite. In that regard, DSC/TG measurements are provided to observe temperatures of reaction and mass gain during the rapid stage of oxidation with reference to the slow stage of oxidation. All samples preserved Cr-rich passive layer formation and composites with 5 wt.% of NbC were similar in terms of their oxidation resistance to the reference, pure Inconel 625 alloys.

## Acknowledgements:

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# Wetting, interfacial reaction and joining of monolithic SiC and Cf/SiC composites by ZrSi2 alloy

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## Abstract:

In this work, the wettability and interfacial reaction of molten $ZrSi_2$ alloy on the monolithic SiC and $C_f$/SiC composite surfaces, and joining of SiC ceramics with $ZrSi_2$ filler were investigated. The results show that a significant evaporation of Si from the liquid affected the wetting behavior of the alloy when tested in a vacuum at 1670°C. The better wetting and spreading of the alloy over the SiC surface was observed under argon atmosphere and the wetting angle decreased significantly. The molten alloy reacted with the SiC surfaces to form ZrC reaction layer, while the remaining unreacted $ZrSi_2$ alloy with some free Si was observed in the solidified alloy. Afterwards, the studies were utilized to join SiC and $C_f$/SiC ceramics with $ZrSi_2$ alloy as the filler. The alloy was applied on the joining surfaces of the materials in the form of slurry, then the pressure-less and pressure-assisted joining were performed for the sake of comparison. The thickness of the interlayer was controlled by the weight of the slurry and the effect of different thickness of the interlayer was studied. The phase and microstructure analysis of the joints revealed that due to the formation of the ZrC layer on the interface, the interfacial bonding between the SiC and the interlayer was significantly improved.

## Acknowledgements:

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 798651. This work was also supported by the Slovak Research and Development Agency under the contract no. APVV-17-0328. The support of VEGA 2/0161/22 project and the Joint Mobility Project under the CAS-SAS agreement (SAV-21-04) is also acknowledged.

# Corrosion of MgO-Cr refractory by PbO-rich copper slags by various corrosion methods

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## Abstract:

For decades, magnesia-chromite (MgO-Cr) refractories are indispensable materials for linings in the heating devices of Cu and Pb metallurgy. They contain mainly MgO and up to 50 wt.% $Cr_2O_3$, MgO. However, the formation of chromium (VI) compounds at elevated temperatures requires searching for alternative Cr-free refractories. In order to achieve this, comprehensive knowledge of the chemical resistance of currently used refractories is essential.

The refractory used in the work was a direct-bonded MgO-Cr commercial refractory product. The three chemically different PbO-rich copper slags were applied for the corrosion of MgO-Cr refractory. The corrosion was conducted by: hot stage microscopy, pellet and contact corrosion test. The corrosion results were interpreted by XRD and SEM/EDS. The SEM images of corroded materials were analyzed using developed recognition and object detection algorithms.

In the work, we show that increased PbO content in the slag is responsible for intense microstructure disintegration of the MgO-Cr refractory when compared to $CuO_x$. The general mechanism responsible for corrosion of material is as follows: The PbO-rich copper slag fully infiltrates the refractory through the open pores/cracks. This infiltration directly influences the weakening of magnesia-chromite solid solution direct bonds, and is followed by dissolution of chromite and magnesia grains, and subsequent formation of forsterite – the main new corrosion product that increases the volume of the refractory leading to the material swelling.

Based on: Ludwig M., Śnieżek E., Jastrzębska I., Piwowarczyk A., Wojteczko A., Li Y., Szczerba J., Corrosion of magnesia-chromite refractory by PbO-rich copper slags, Corrosion Science, 2021, Article in Press, doi: 10.1016/j.corsci.2021.109949.

## Acknowledgements:

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# Processing and characterization of binderless WC for high temperature applications

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## Abstract:

Development of fusion power plants is one of the most significant scientific and technological challenges. During the construction of the ITER reactor, the design of the EU DEMO demonstration power plant is undergoing. In order to achieve high efficiency and safe operation in the reactor chamber, it is necessary to provide low-activation materials that will withstand high-heat loads without critical damage over a long period of time. The development of low activation materials, which would withstand the high-heat-loads in the divertor, is also one of the priorities of the European fusion programme. Current research has been focused on the improvement of the tungsten, which has, however, certain limitations. As an alternative, we were studying binderless tungsten carbide (WC). In contrast to metallic tungsten, WC is not subjected to recrystallization at high temperature leading to grain growth and deterioration of mechanical properties. The objective of this study was consolidation of binderless WC without secondary phases and with competitive thermo-mechanical properties.

The WC powders used in this study were commercial powders with various particles' sizes, which were consolidated using Field Assisted Sintering Technique (FAST) varying final temperature (1700, 1900 or 2000 °C), holding time and applied pressure. The phase composition of sintered samples was carefully monitored and adjusted in the case of formation of unwanted phases (in particular $W_2C$). Additionally, room-temperature and high-temperature thermo-mechanical properties were evaluated. Briefly, initial particles' size affects the degree of densification at selected temperature, microstructure of sintered samples and also their thermo-mechanical properties (especially thermal conductivity).

## Acknowledgements:

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# Carbon-bonded alumina refractories reinforced with graphene oxide

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## Abstract:

Carbon-bonded alumina refractories ($Al_2O_3$-C) are very important ceramic materials in the steel industry for their unique mechanical, thermal, and chemical properties. Despite their excellent flexibility and thermal shock performance, carbon-bonded alumina material usually offers poor mechanical strength. Interestingly, nanoscale additives such as multi-walled carbon nanotubes, or boron- and nitrogen-doped graphene have the ability to reinforce $Al_2O_3$-C refractories. In this work, we studied the physical and mechanical properties before and after thermal shock of carbon bonded coarse-grained alumina with the addition of graphene oxide (GO). The coarse alumina aggregate fraction was coated by a viscous graphene oxide suspension prepared by the improved Tour's method, dried in air, and used to prepare dry pressed samples. The physical and mechanical properties like true density, porosity, cold modulus of rupture and Young's modulus before and after thermal shocking were measured. The results showed that the use of GO had a positive impact on the mechanical properties of the graphene-reinforced $Al_2O_3$-C refractories. In addition, the thermal shock only had a minor impact on the Young's modulus and CMOR values of the samples.

## Acknowledgements:

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# High-Temperature Strength of Liquid-Phase Sintered Silicon Carbide Ceramics

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## Abstract:

Silicon carbide is a promising ceramic material for high-temperature structural applications, owing to its high flexural strength and room temperature (RT) strength retention ability at elevated temperatures (≥1500 °C). This study reports the influence of critical factors (grain boundary structure, additive composition, additive content, and microstructure) on the RT strength retention at high temperatures and the high-temperature strength of LPS-SiC ceramics. The results suggest that (1) the minimization of additive content and careful selection of additive composition are crucial for achieving high flexural strength and excellent RT strength retention at ≥1500 °C, and (2) additive compositions without $Al_2O_3$ have great potential to achieve excellent RT strength retention at ≥1500 °C.

## Acknowledgements:

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# Effect of SiC particulates/whiskers reinforcements on properties of spark plasma sintered high entropy borides (Ti0.2Zr0.2Hf0.2Nb0.2Ta0.2)B2 synthesized using boro/carbothermal reduction

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## Abstract:

In recent years, high entropy borides (HEB) gained much attraction due to their superior hardness and oxidation resistance compared to their boride counterparts. SiC is one of the extensively investigated reinforcements in $HfB_2$ and $ZrB_2$ systems, which was reported to improve the densification and fracture toughness of monoliths. Though there were few reports on HEB-SiC system, the effect of SiC morphology and volume fraction on the mechanical and high temperature properties was not systematically investigated till date. In the present study, mixtures of presynthesized HEB $(Ti_{0.2}Zr_{0.2}Hf_{0.2}Nb_{0.2}Ta_{0.2})B_2$ powders and 5 vol.%, 10 vol.%, 15 vol.%, 20 vol.% and 25 vol.% SiC particulates/whiskers were subjected to ball milling followed by Spark Plasma Sintering (SPS) at 1900 °C to obtain highly dense HEB-SiC composites. HEB of this particular composition was synthesized using boro/carbothermal reduction of oxide precursors as mentioned elsewhere. XRD patterns of the synthesized powders and sintered compacts of HEB showed single hexagonal phase without any oxide impurities. Lattice parameters of the sintered HEB compact was calculated to be $a \approx b \approx 3.1076$ Å, $c \approx 3.3777$ Å, which are in good agreement with the literature. The effect of SiC type and volume fraction on densification, microstructure and mechanical properties of the composites were studied. The high temperature properties such as oxidation and ablation resistance of the composites were also investigated and reported in detail.

## Acknowledgements:

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# Oxidation performance of ZrB2-SiC composites tested above 2000°C and effect of Y-containing additives.

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## Abstract:

The oxidation performance of $ZrB_2$-SiC composites with addition of $YB_4$ or $Y_2O_3$ was studied in static oxidation conditions up to 1650°C as well as under dynamic conditions of oxyacetylene torch facility at temperatures above 2000°C. The testing under static and dynamic conditions revealed quite different behaviour of materials. Static oxidation conditions led to the formation of a typical layered structure of $ZrB_2$-SiC composite with protective silica layer on the surface. However, the analysis of studied composites oxidized using oxyacetylene torch showed, that silica is not anymore present on the surface and the protective function was taken over by outer zirconia layer. The addition of $YB_4$ and $Y_2O_3$ resulted in spallation and deeper degradation, especially at higher static oxidation temperatures. Although the $YB_4$ as well as $Y_2O_3$ did not improve the oxidation resistance during oxidation in static air, the performance during oxidation in dynamic conditions indicates different results. During ablation at 2000°C, a dense cubic solid solution of $Zr_xY_{1-x}O_{1.5+x/2}$ was formed as the main oxidation product. This compound is very promising to protect the material at even higher temperatures when zirconia already evaporates.

## Acknowledgements:

This work was performed during the implementation of the project Building-up Centre for advanced materials application of the Slovak Academy of Sciences, ITMS project code 313021T081 supported by the Integrated Infrastructure Operational Programme funded by the ERDF. This work was supported by the project No. APVV-17-0328.

# The reactive sintering composites of B4C with additives consolidated by hot-pressing and pressureless sintering

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## Abstract:

Structural composites form a numerous and diverse group of construction materials. One of them used to produce composite materials is boron carbide. When compared to other ceramic materials, $B_4C$ is a valuable construction material. Therefore, it is widely used in the field of armor, construction due to its excellent thermal, chemical, and mechanical properties. Boron carbide can be obtained via many methods. The most common method is the carbothermal and magnesia-thermal reduction with boron oxide carried out at high temperatures.

This study aimed to obtain boron carbide-based composites via the reactive sintering with the different additives. This study describes the free sintering and reactive sintering of hot-pressed composites based on commercial $B_4C$ with different additieves.

The compositions containing $B_4C$ in the amount of 2.5%, 5%, 10%, 15%, and 20% of additieves were synthesized by both methods. To determine the effect of additives on the sintering of $B_4C$ composites, the samples were made of commercial $B_4C$. The samples were first subjected to pressureless sintering in a dilatometer at 2250 °C with the registration of the dilatometric curve to test the changes and to record the starting temperature of the sintering process. The determination of the sintering temperature made it possible to select the optimal sintering conditions by the hot-pressing (HP) method and revealed the effect of additives on the reduction of the sintering temperature. The remaining samples were sintered by hot-pressing under similar conditions in an argon atmosphere. Hot-pressing of submicrometric powders with various additives was carried out at 1850 °C. The applied various additives and the sintering technique also improve the mechanical properties of the obtained composites.

# Multicomponent composites based on reactive magnesia: contribution of 1D and 2D carbon-based nanomaterials and their combinations

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## Abstract:

The development of novel construction materials with low impact on the environment is nowadays focused on the search for an alternative for the ordinarily used Portland cement (PC). One of the most promising alternatives is Sorel cement, a reactive magnesia-based non-hydraulic binder with high compressive and flexural strength. Its chemical base is in the system of magnesium oxychlorides (MOC), which form rapidly after mixing powdered magnesium oxide with the aqueous solution of magnesium chloride. It is considered eco-friendly, due to the lower calcination temperature of the raw materials and therefore lower energy consumption and $CO_2$ production compared to PC. In this contribution, the effect of 1D and 2D carbon-based nanomaterials, used as dopants in very low amounts, on the mechanical, physical, and chemical properties of the most common phase of MOC, $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, was studied. Among the used nanomaterials, graphene (G), graphene oxide (GO), multi-walled carbon nanotubes (MWCNT), their oxidized analogues (MWCNT-ox), and other derivatives of these additives were used not only individually, but also in combination in order to determine their combined effects on the MOC matrix. The raw materials and the prepared composites were analyzed with XRD in order to determine their phase composition. XRF and EDS were used to analyze the chemical composition. SEM and HR-TEM were used to obtain information about the morphology and microstructure. OM was used to study the fracture surface of the samples. After 28 days of curing, the samples also underwent a series of mechanical tests in order to determine the effect of the C-based nanoadditives and to compare the mechanical properties with reference samples, which did not contain any nanoadditives.

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# Modification of the microwave heating properties of alumina fibre preforms by microwave absorbing coatings

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## Abstract:

A novel microwave assisted chemical vapour infiltration (MW-CVI) method is being investigated with a view to producing alumina fibre / alumina matrix composites within a European Horizon 2020-funded programme known as CEM-WAVE. The characteristic volumetric heating of the fibre preform with an inverse temperature profile during MW-CVI should significantly reduce the cost of the manufacture of composites, however, it is also well known that alumina-based materials generally do not absorb microwave energy easily at low temperatures. Thus the approach being taken to achieve heating of the alumina fibre preform is via the use of different microwave absorbing coating materials through either dip-coating or a continuous roll-to-roll process. Meanwhile, a fully tunable solid-state microwave source, operated with a 'probe and pump' technique, is being used rather than the more usual fixed frequency, magnetron-based microwave source. This was selected in order to achieve more uniform sample heating. The dielectric properties of the coated fibre preforms were characterised as a function of the temperature and the microwave heating behaviour of the coated fibre preforms was investigated, both numerically, via multiphysics simulations of the reactor loaded with the sample, and experimentally. The results for the heating of the alumina fibre preform to the target temperature to allow for the deposition of alumina will be reported.

# Thermoelectric properties of conductive polymer/ceramic composites

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## Abstract:

In recent years the demand for wearable and maintenance-free power sources has increased. Thermoelectric generators which can convert body heat to useful electricity have drawn wide attention as energy-harvesting technology for self-powered electronics (smart clothing, healthcare monitoring). Polymer-based thermoelectric materials are particularly interesting to wearable devices due to their low density, good flexibility, easy processability, and low toxicity. Furthermore, the transport properties of the thermoelectric polymers can be effectively modified by mixing the polymer matrix with the inorganic components as ceramics. Such composites usually demonstrate even better thermoelectric performance compared to the initial components.

The work aims to investigate the structural and thermoelectric properties of the conductive polymers (e.g. PEDOT:PSS) composites with the addition of ceramics particles (e.g. carbides, sulfides). Ceramic additives used for composites were characterized in terms of particle size distribution. All samples were prepared as films on glass and silicon substrates, with different inorganic particles volume content (25%, 50% and 75%). The obtained samples were examined in terms of the highest PF (power factor) and ZT parameter by measured Seebeck coefficient, electrical and thermal conductivity. SEM and AFM were used to investigate the microstructure and estimate the films' thickness. It was found, that the tested properties changed with the weight fraction of inorganic particles and depended on the added inorganic phase. The performed tests confirmed that the examined composites are promising components to be used as elastic thermoelectric materials.

## Acknowledgements:

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# High Performance Steel Ceramic Composites for Refractory Applications in Molten Aluminum Alloys

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## Abstract:

The development and characterization of novel Steel Ceramic Composites for direct contact with liquid aluminum alloys in refractory applications has been presented. The Steel Ceramic Composite consisting of 60 vol% 316L stainless steel powder and 40 vol% of MgO powder addition were manufactured by means of powder metallurgy. Selected sintered specimen undergone the surface preparation by the oxidation at 850 and 1000 °C for 24h.

The corrosion resistance of composite against molten AlSi7Mg0.3 alloy was investigated using wettability test, finger immersion tests and crucible corrosion tests. Wettability tests were performed on the Hot Stage Microscope using adapted capillary purification technique. Finger immersion tests were carried out at 850 °C for 24 h, whereas crucible corrosion tests were carried out at 850 °C for 24 h and 168 h. Specimens after the corrosion tests were investigated using SEM/EDS and XRD, focusing on the phase formation at the composite/aluminum alloy interface. The corrosion phases formed in the aluminum alloy were investigated by the help of SEM/EDS/EBSD and PSEM ASPEX AFA. Mechanical properties of composites before and after the preoxidation were investigated using the three-point bending procedure at both ambient and elevated (850 °C) temperature with subsequent fracture analysis by means of Laser Scanning Microscope.

The results of corrosion tests shown excellent liquid aluminum corrosion resistance of developed composite. It was revealed that surface preoxidation caused the formation of new phases based on MgO-FeO solid solution, which are stable in contact with liquid AlSi7Mg0.3. Moreover, the composite exhibited favorable mechanical properties with increase ductility both at room and elevated temperature.

## Acknowledgements:

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# Investigation of ultra-high temperature transition metals carbo-nitrides

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## Abstract:

The development of next generation space vehicles, high temperature turbines and nuclear reactors will be enabled by materials that can withstand extreme conditions, such as very high temperatures, thermal shocks and corrosive environments. Such materials can maintain their structural stability at temperatures exceeding 3000 K. Carbides of some transition metals, especially tantalum carbide (TaC) and hafnium carbide (HfC), are of particular interest due to their high melting temperatures (>3500 K) which are for nearly a century the highest reported among all materials. Recently, a modelling work reported $HfC_{0.56}N_{0.38}$ as the compound with the highest melting temperature, well beyond 4000 K. The uncertain results on the melting points reported and the development of new models to explore the materials composition highlight that further experimental investigation is needed, covering a broader spectrum of possibly ultra-high temperature compounds and using novel experimental techniques. In this framework, we studied Hf-Ta based carbo-nitride systems from stoichiometric samples to non-stoichiometric samples in order to investigate experimentally compounds close to the composition $HfC_{0.56}N_{0.38}$. Spark plasma sintering (SPS) was used to prepare dense carbo-nitride samples. The whole synthesis procedure was carried out under argon atmosphere to reduce oxidation of the initial air-sensitive powders. The final composition, morphology and structure of carbo-nitride samples were analysed by various characterization techniques (XRD, SEM, C/N analysers…). Finally, a laser heating procedure was established to analyse the melting point and the emissivity of ultra-refractory carbo-nitrides.

## Acknowledgements:

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# Enhancement of reduced remanent and magnetic energy product through exchange spring phenomenon in BaFe12O19+CoFe2O4 composite

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## Abstract:

The exchange spring magnets containing hard (hexaferrite) and soft (spinel) ferrite composite are getting attention/ interest technically and scientifically due to great exchange coupling behavior among soft and hard magnetic phases. The enhanced magnetic parameters lead to producing a new composite with higher reduced remanent ($M_r/M_s$) and magnetic energy product $(BH)_{max}$. The exchange spring effect has a potential application on recording media, permanent magnets, and microwave absorption. The composite of (x)%$BaFe_{12}O_{19}$ (BHF)+(100-x)%$CoFe_2O_4$ (CFO) for x=0, 10, 30, 50, 70, 90, 100 were prepared. XRD patterns confirm the phase formation of both $BaFe_{12}O_{19}$ and $CoFe_2O_4$ phases in the composite. The Rietveld refinement of the XRD pattern was carried out to obtain the lattice parameters of both phases. The FESEM micrographs reveal the uniform distribution of nanoparticles. The optimum value of energy product $(BH)_{max}$ and reduced remanent were obtained for x=50, due to strong magnetic interaction at the interface of soft and hard phases. The value of saturation magnetization, coercive field, remanent magnetization, $(BH)_{max,}$ and reduced remanent increase with the increase in temperature. The maximum (BH)max and reduced remanent are found to be 0.8 MGOe and 0.53, respectively for (50)BHF+(50)CFO annealed at 800 $^{o}$C. The enhancement of magnetic parameters at a lower temperature is observed due to the reduction of the thermal energy of magnetic moments at the surface. The saturation magnetization increases with the increase in annealing temperature, due to minimization of the spin disorders at the surface with higher annealing temperatures. At higher annealing temperature, the enhanced reduced remanent and $(BH)_{max}$ is found, because of enhancement of magnetic interaction. The magnetic interaction between two magnetic phases is analyzed by Henkel plots.

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The author acknowledges the Indian Institute of Technology Patna for providing the facilities to carry out the experiment.

# Synthesis of fireproof gels based on organic polymers and soluble silicates

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## Abstract:

This work presents the results of research on the preparation of fireproof gels based on the sodium water glass (WG) with a silicate modulus M = 2.05 and aqueous solutions of sodium acrylate (ANa) with a concentration of 15 and 20 wt.% and various mass ratios of WG to ANa. Their physicochemical characteristic was examined in terms of rheological, thermal and fire properties, taking into account also such features as color and transparency. Based on the results of the gelation kinetics and viscoelasticity, it was found that the use of sodium acrylate with a concentration of 15 wt.% allows to delay the gelling process, while samples with higher polymer content obtained higher G′ values what means better elastic properties. Analyzing the results of the TG/DSC thermal tests, it was noticed that most of the samples showed a two-stage weight loss during the measurements, what was caused by physical changes of water and thermal degradation of the polymer. The fire insulation tests allowed for the assessment of compliance with the requirements specified in the test standards. Only samples with a weight ratio of WG to ANa 1:1 and the content of sodium acrylate at a concentration of 20 wt.% reached the point temperature of 180 °C after 15 minutes. In these samples, the gel filling swelled, what means an increase in the specific surface of the sample, and thus an increase of the heat exchange.

## Acknowledgements:

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# Oxidation of Fe-16Cr ferritic steel modified with gadolinium oxide nanoparticles in different atmospheres

Łukasz Mazur, Justyna Chłędowska, Jan Wyrwa, Dariusz Zientara, Tomasz Brylewski

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## Abstract:

Solid oxide electrolyzer cells (SOECs) convert surplus electricity into fuel such as hydrogen via electrolysis. In order to increase power output, single cells can be connected to form a stack using so-called interconnects. The main issue with the use of metallic interconnects based on ferritic steel is the increase in area-specific resistance (ASR). Although the majority of oxidation studies have been conducted under isothermal conditions in air, the atmospheres specific to the real-life operation of electrolytic cells are mixtures that contain hydrogen and water vapor. For the study, the Fe-16Cr ferritic stainless steel (brand name: Nirosta 4016/1.4016) was selected. In order to improve its resistance to high-temperature oxidation, it underwent surface modification via either dip-coating or the electrolytic deposition of gadolinium oxide nanoparticles layer. Oxidation studies were conducted in air, a mixture of air/$H_2O$, and an $H_2/H_2O$ atmosphere at 1073 K. The samples were then examined via scanning electron microscopy (SEM) and X-ray diffraction (XRD). A DC 2-probe 4-point method was used for ASR measurements. The oxidation studies showed that samples modified with gadolinium oxide nanoparticles exhibit better oxidation resistance than the unmodified sample in all oxidizing atmospheres. This can be attributed to the active element effect (REE), which reduces the thickness of the scale and improves its adhesion to the metallic core. Based on the obtained results, the Nirosta 4016/1.4016 ferritic steel modified with gadolinium oxide nanoparticles was found to be suitable for the production of metallic interconnects designed for SOEC applications.

## Acknowledgements:

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# Tribological characterization of UHTCMCs for brake applications

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## Abstract:

The main requirements for brake materials are a stable coefficient of friction, a low wear rate, a low life cycle cost and a low weight. A brake is usually made of different materials, such as steel, C/C or C/C-SiC. Steel possesses a relatively high and stable coefficient of friction (COF) and a low wear rate. However, powerful vehicles require more power for braking. For these applications, ceramic matrix composites, such as C/C and C/C-SiC composites, are preferred for their higher damage tolerance and high temperature resistance. However, C/C composites are damaged by oxidation above 400 °C, possess a high wear rate and a low COF at temperatures below 200°C. While C/C-SiC composites have high COF and thermal shock resistance, but higher wear rate, decreased fatigue resistance and unstable COF. Thanks to their properties, such as high oxidation resistance and good high temperature strength, fibre reinforced ultra-high temperature ceramic matrix composites (UHTCMCs) are a promising class of material for braking application. The aim of this work is to investigate the tribological behaviour of these novel materials. In this study, the UHTCMC materials constituting the braking pads were tested against three different discs materials (C/C, C/C-SiC and Steel). Two different brake pressures (1-3MPa) and two kinds of reinforcement were tested: a long fibre fabric and a chopped fibre reinforcement respectively. Also, recordings of COF and temperature trends were shown. SEM analysis was carried out in order to investigate the friction layer formation. Preliminary results showed a quite stable COF for the tests with the Steel and C/C-SiC disc with a value of 0,5-0,4 and a low COF for the C/C disc with a value of 0,3.

# Zirconia- Few-Layer Graphene multifunctional composites: a compromise between mechanical and electrical properties

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## Abstract:

Since the discovery of graphene and its extraordinary properties, many works have been done for integrating this material in a wide range of applications. Due to its outstanding mechanical behavior, researchers have tried to overcome the inherent brittleness of ceramics by introducing graphene-based nanomaterials (GBN) as a reinforcing phase. However, in the case of zirconia composites, the improvement obtained was not as high as expected. Today, the interest of these composites relies more on the functionalities this nanophase could bring to the final composite than on the reinforcing effect.

In order to develop electrically conductive ceramic composites, a given amount of GBN should be added to the composite so as to exceed the percolation threshold. This quantity strongly depends on the dispersion degree and crystallinity of the GBN. However, a high secondary phase addition also leads to worse mechanical performances. Thus, a good compromise between the electrical/mechanical properties must be found and adapted to the different applications.

In this work, we have prepared 3Y-TZP ceramics (3 mol.% yttria-stabilized tetragonal zirconia polycrystal) containing different proportions of Few-Layer Graphene (FLG). Fully dense materials were obtained by Spark Plasma Sintering of the optimally dispersed composite powders. The microstructure and the electrical conductivity of all the resulting composites were characterized. Besides other classical mechanical properties, the crack growth resistance (R-curve) of selected compositions was also evaluated. During this presentation, we will discuss the possibility of preparing electrically conductive and slightly tougher 3Y-TZP ceramics that could be used in self-monitoring applications and/or be electrical-discharge machined (EDM).

## Acknowledgements:

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# Sintering of ZrB2 based UHTC composites by SPS technique

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## Abstract:

Ultra-high temperature ceramics (UHTCs) include borides, carbides, and nitrides with melting temperatures above ~2700°C. The UHTCs have been investigated for high temperature applications including thermal protection systems for hypersonic aerospace vehicles.

Five types of zirconium boride based systems (monolithic $ZrB_2$, $ZrB_2$ with 2 and 10 wt% of SiC and 2 and 10 wt% of $B_4C$) were fabricated by a sintering technique Spark Plasma Sintering (SPS).

The aim of the present contribution was to investigate the influence of the SiC and $B_4C$ addition on the microstructure development, hardness, fracture toughness and fracture characteristics of $ZrB_2$ based ceramics prepared by SPS.

Spark Plasma Sintering was conducted using HPD5 type, FCT system equipment. Samples were sintered in argon, under 35 MPa. The heating and cooling rate was 200°/min and soaking time was 10 min. The sintering temperatures were varying between 1700°C and 2100°C for pure $ZrB_2$ and between 1800°C and 2000°C for samples with sintering aids. For samples with SiC and $B_4C$ additives higher temperatures were not applied because liquid phase appeared in 2000°C and further heating could have cause damage of die and equipment.

After sintering samples were prepared for further investigation by cutting, grinding and polishing.

The relative density of sintered materials ranged from 97÷99%. The best SPS sintered materials were characterized by Young's modulus above 450 GPa, hardness over 19 GPa (for sintered with 10% $B_4C$ addition) at 1900°C. The crack resistance value KIc (HV10) was in the range of 2.9 $MPa{\cdot}m^{1/2}$ ÷ 6.5 $MPa{\cdot}m^{1/2}$ for sintered containing 10 wt.% SiC. The fracture toughness increased with addition of SiC and $B_4C$.

# Resistance of Ultra-High Temperature Ceramic Borides to Calcia-Magnesia-Alumina-Silicate Attack Under Isothermal Conditions

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## Abstract:

There is an urgent need to evaluate new candidate materials for gas turbine engine applications that exhibit resistance to degradation from molten environmental particulates. The resistance of ultra-high temperature ceramic (UHTC) borides to calcia-magnesia-alumina-silicate (CMAS) attack is evaluated here for the first time. $ZrB_2$ and $HfB_2$ are reacted with 23 mol % of CMAS 1000 °C, 1300 °C and 1600 °C, respectively, for 1 h, 10 h and 100 h, respectively, in atmosphere. Interestingly, borides first oxidize before reacting with CMAS to form $ZrSiO_4$ and $HfSiO_4$, respectively, which peaks at 1300 °C. At 1600 °C, the reaction with CMAS to form $HfSiO_4$ is greatly suppressed; moreover, $ZrB_2$ exhibits only oxidation and no reaction with CMAS nor formation of $ZrSiO_4$ or any other CMAS induced reaction product. This unusual inertness at temperatures above 1600 °C could enable new approaches to addressing the CMAS problem in thermal and environmental barrier coatings.

# Development and Tribological Studies of an Aluminium-CMC Hybrid Brake Disc

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## Abstract:

Future mobility concepts like electric powered vehicles demand for new braking technologies and brake disc concepts. E. g. due to recuperative braking capabilities, the corrosion of the brake discs and brake pads are problems which have to be coped with. Thusly the use case or rather the (performance) requirements for brake discs for electric powered vehicles are very different compared to brake discs for cars with internal combustion engines.

A new concept in the form of a metal-ceramic hybrid brake disc is propagated for the use in electric powered vehicles. It consists of an aluminium carrier body which is lined with ceramic friction segments on the friction surface of both sides. For the friction segments a short fibre reinforced ceramic matrix composite (C/SiC) is used. An overview is given on the potential application areas and on the design, construction, manufacturing and testing of said hybrid brake disc.

A potential use case of a mid-class sedan with a mass of around 1.8 t and maximum travelling speeds of up to 200 km/h is taken as a basis for the design and construction of a metal-ceramic hybrid brake disc prototype. This prototype was tested against three different brake pads (LowMet, C/SiC and C/C) on the dynamometer test bench at the University of Bayreuth under emergency braking conditions. Different characteristic values like wear, coefficient of friction and different temperatures were measured. The resulting friction surfaces of the brake pads were investigated using SEM. Furthermore, the friction surface and wear mechanism of the friction segments of the hybrid brake disc were evaluated using SEM. Comparative tribological measurements of standard commercially available brake discs (e. g. cast iron and carbon ceramic brake discs) were conducted.

# SiC materials based on binder from MgO-SiO2-H2O phase system

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## Abstract:

The SiC is a high temperature compound with good corrosion resistant and high thermal conductivity. This combination of features makes the SiC great refractory material. Beyond the advantages SiC has also some drawbacks, one of them is its vulnerable to oxidation, another problem is that SiC materials do not bond well. This is due to covalent nature of Si-C bonding and low self-diffusion coefficient. For this reasons new binding phases, that can be used in this type of materials, are being tested. Among others widely used are bonding phases based on oxides, they are low costs and promote densification of the material. In this work the binding phase, based on the MgO, $SiO_2$ and water is analysis.

The aim of this work was to evaluate binding potential of the phases from the MgO-$SiO_2$-$H_2O$ phase system in SiC based materials.

Study included homogenization of the powders of the SiC, MgO and $SiO_2$ in water (in different proportions) and drying obtained mixtures. Afterwards the mixtures were formed in to the pellets and heat treatment at 1200°C for 3 h. After heat treatment obtained samples were tested using SEM-EDS, XRD and FT-MIR. The apparent density and open porosity of the samples were characterized based on the Archimedes principle.

It was found that during the heat treatment process forsterite is creates. Also crystalline phases of $SiO_2$ were detected, which can indicate on oxidation of the SiC. Increasing content of oxide component increase compactness of the sample, but still overall porosity remains high. Obtained results indicate on potential of the MgO-$SiO_2$-$H_2O$ binding system in binding SiC based materials, however further detailed research of this system are needed.

## Acknowledgements:

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# Analysis of the corrosion mechanism of spinel refractory materials with different stoichiometry in contact with steel slags

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## Abstract:

Magnesium aluminum spinels are increasingly used in refractory materials due to their special characteristics. The high corrosion resistance of spinel-containing refractory castables increases the service life of the equipment in which they are used. Spinel has a high melting point, but above all excellent corrosion resistance. The degree of spinel stoichiometry affects its corrosion resistance.

Spinel in contact with the slag changes. A feature of spinel materials is the tendency to substitution one or two spinel components with other cations. Both magnesium and aluminum cations can be replaced by others with similar size. To investigate the occurring changes, spinels with different stoichiometry were tested in contact with slags from the CaO-$Al_2O_3$-$SiO_2$-MgO-$Fe_2O_3$-MnO oxide system. A stoichiometric spinel with a 1:1 molar ratio of MgO:$Al_2O_3$ was used for the tests. Two types of non-stoichiometric spinels have also been investigated: MgO-rich spinel and $Al_2O_3$-rich spinel.

This work investigated the effect of the stoichiometry of the magnesium aluminum spinel on the corrosion resistance in contact with steel slag. To enable this, the method of obtaining of highly dense spinel ceramics with a density close to the theoretical density of the tested spinels was optimized. The static contact method was used to determine corrosion resistance. SEM-EDS analysis was also performed to determine the microstructure changes of the samples tested. Moreover, for the equilibrium mixtures of spinel and slag, the phase composition of the tested materials was analyzed using the XRD method. The FactSage program allowed for the analysis of phase compositions vs. temperature, and in addition, thermal analysis was performed using the heating microscopy thermal analysis (HMTA).

## Acknowledgements:

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# Pressureless and spark plasma sintering of composites in B4C-Ta-B system

Paweł Rutkowski[1], Natalia Cieśla[1], Piotr Klimczyk[2], Radosław Lach[1], Magdalena Ziąbka[1]

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## Abstract:

The goal of the work was to investigate tantalum and boron additives influence on pressureless and spark plasma sintering of boron carbide. As additive, tantalum metal powder and amorphous boron were used together in quantity from 5 – 15 wt. %. Such additives should lead to tantalum diboride formation during material heating, therefore to reactive sintering process. In the first step prepared green bodies were subjected to dilatometric measurements giving shrinkage curves showing an influence of mixture composition on boron carbide sintering. It was noticed that during the sintering process, except the reactive $TaB_2$ formation, mass transport was possible by liquid phase at higher temperatures. The heat treated samples at temperature from 1400 – 2200°C were taken into examinations of their densification, phase composition and microstructural observations. The XRD analysis confirmed formation of titanium diboride in quantity of up to 9 wt.%. The dilatometric examinations revealed that sintering process is too rapid to be controlled at temperature exceeding 2000°C and that too intensive reactive sintering can decrease densification. That is why selected compositions basing on tantalum additive were taken to spark plasma sintering process. The SPS composites were investigates by means of density, microstructure, hardness, fracture toughness and elastic properties.

## Acknowledgements:

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# Spark plasma sintering of B4C- boride ceramics

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## Abstract:

The goal of the research was to obtain two types of composites in ternary phase system with boron carbide matrix. The studies are the first attempt to approach this type of materials. Both of materials contained 10 vol. % of introduced boride phases. The $B_4C$ – 5 vol.% CrB – 5 vol.% $TiB_2$ and $B_4C$– 5 vol.% CrB – 5 vol.% $HfB_2$ mixtures were spark plasma sintered using optimised process conditions set for reference boron carbide material. The densification on of reference sample and composites was determined. The manufactured materials were qualitatively and quantitatively phase composition characterized (XRD/Rietveld) and subjected to SEM observations with EDS analysis. The analysed composite polycrystals were taken into hardness, fracture toughness and thermal diffusivity/conductivity measurements (LFA).

## Acknowledgements:

This research was supported by the NCN statutory, project no. 16.16.160.557 of AGH University of Science and Technology in Krakow.

# Explanation of MgO-C lined steel ladles lifetime differences with use of computational techniques

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## Abstract:

Steel ladle is one of heat unit allocated for secondary metallurgy processes. As a refractory lining of ladles MgO-C materials are used. Wear rate of refractories limits the ladle lifetime. Different metallurgical parameters including thermochemical and thermomechanical factors have a direct impact on wear rate of refractories. Due to process parameters analysis and relations between them it is possible to explain differences in ladles lifetime.

In this work metallurgical parameters of three ladles which differs in lifetime were analysed. Key metallurgical factors were selected for analysis to asses its influence on wear rate. To asses relation between factors and its impact on wear rate of MgO-C type refractories different techniques were used including: PCA (Principal Component Analysis), k-means algorithm, PAM algorithm (Partitioning Around Medoids) and others. Additionally, traditional attempt for data grouping was presented.

# SiC/SiC ceramic fibre composites for turbine applications

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## Abstract:

SiC/SiC ceramic fibre composites offer a unique combination of properties not found elsewhere. They have the typical characteristics of ceramic materials, their high hardness, low density and creep resistance, combined with the tolerant fracture behaviour of a fibre composite. These properties together with a high oxidation resistance, high temperature stability and significant weight reduction compared to metals make them suitable materials in turbines for aerospace application.

From a variation of different SiC/SiC materials the processing route leaving a dense matrix via silicon infiltration gives the best opportunities to reach the necessary properties for turbine applications while offering an economical industrial production. The three major parts in making a SiC/SiC composite in this route as well as their interaction will be described in detail: CVI-fibre coating, matrix slurry infiltration and capillary silicon infiltration.To reach high mechanical values and a good oxidation resistance the proper interaction between the processing steps are highly necessary and require rigorous control. The effect of different fibre coatings and different infiltration slurries together with the final siliconization process will be discussed in detail and shown via microstructures, mechanical evaluation and oxidation tests.

# Self-protection capability of ultra-high temperature ceramic matrix composites manufactured by Water-based Powder Slurry Infiltration and Polymer Infiltration and Pyrolysis

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## Abstract:

There is an increasing demand for advanced materials able to withstand severe environments. Ultra-high temperature ceramic matrix composites (UHTCMCs) are novel materials which can overcome the main limitations of currently used CMCs (C/C and C/SiC), showing higher temperature capability and ablation resistance. Their specific application is in hypersonic and propulsion, typical components may be thermal protection systems tiles, leading edges or nosecone, rocket nozzle, divergent parts of engine and chamber inserts.

The oxidation behaviour and self-protection capability in air of $C_f/ZrB_2$-SiC, manufactured by slurry impregnation followed by polymer infiltration and mild pyrolysis, was investigated. Short term oxidation tests in air were performed for 1 and 5 min at 1500 and 1650 °C in a bottom loading furnace. Microstructure and oxidation behaviour were compared with other ceramic matrix composites. Particular emphasis has been given on the synergic effect of the amorphous state of polymer derived SiC(O) and boron oxide to prevent fibre vaporization in temperature range in which SiC matrix has a failure.

# Thermal Properties of (Ti,Cr)B2 Ceramics

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## Abstract:

Previous research showed that Cr content changes the densification behavior, grain size, Vickers hardness, and flexural strength of $(Ti,Cr)B_2$ ceramics. Hardness and strength of the $(Ti,Cr)B_2$ ceramics were highest for a Cr content of 10 at%. The goals of the present study are to determine if the effect of Cr solid solution extends to the thermal properties of $(Ti,Cr)B_2$ ceramics and whether Cr content affects the anisotropy in the coefficient of thermal expansion (CTE). $(Ti,Cr)B_2$ ceramics containing varying amounts of Cr solid solution will be synthesized by boro/carbothermal reduction. Powders will be consolidated by spark plasma sintering. The CTE will be determined for the principle crystallographic directions by variable temperature X-ray diffraction. Thermal diffusivity of sintered samples will be measured by the laser flash method and will be used to calculate thermal conductivity. Specific heat capacity will be measured by differential scanning calorimetry. The discussion will focus on identifying any systematic changes in properties that occur as the Cr content of the $(Ti,Cr)B_2$ ceramics changes.

# Development of a shear thinning gel for the purpose of composite production

Becky Steadman

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## Abstract:

Ceramic matrix composites (CMC's) can be produced in a variety of different ways. This work focuses on the production of a novel phosphate based CMC and the development of a shear-thinning gel to infiltrate alumina fibres. Different gels will be characterised and compared using FTIR, Rheology, TGA/DSC and the final composites will undergo mechanical testing. Future work based around composite production will also be discussed as well as potential uses for this gel system.

## Acknowledgements:

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# Influence of Thermal Pre-Treatment on the Efficiency of Iron Leaching in Non-Refractory Grade Raw Bauxite

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## Abstract:

Among other raw materials, bauxite is an important resource for the production of refractories. In 2020 the European Commission added bauxite to the list of critical raw materials. This illustrates that availability of sufficient raw material qualities will become increasingly difficult, not only for the aluminum producing industry. In the refractory industry, particularly iron contents > 2 % in calcined raw material cause problems. For some years, therefore, various studies have already been carried out on the reprocessing of these high iron non-refractory grade bauxites.

In this study, the use of an acid leaching process with HCl to decrease the iron content in raw bauxites, even with different grain sizes, is specifically investigated on a laboratory scale. It is shown that, in addition to the leaching parameters used and the chemical composition, mineralogy of the raw material also plays an important role. $Al_2O_3$ and $Fe_2O_3$ contents obtained after leaching of bauxite previously thermally treated at T = 300 °C, T = 500 °C and T = 1000 °C and as well as untreated bauxite are compared. Together with the investigation of the mineralogical composition by means of powder X-ray diffraction (PXRD), conclusions could thus be drawn about the leachability of the bauxite and the containing iron phases. In addition to the optimization of the leaching parameters used, this would provide a further opportunity to improve process efficiency or selection of suitable raw material sources.

## Acknowledgements:

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# Metal-ceramic beads containing Nb and alumina produced by alginate gelation

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## Abstract:

Full metal-ceramic composite beads containing different amounts of niobium/tantalum and alumina, particularly 100 vol% alumina, 100 vol% niobium, and 95/5 vol% niobium/alumina, were produced by the alginate gelation process. The suspension for bead fabrication contained sodium alginate as gelling agent and was poured dropwise through nozzles with different diamters into a calcium chloride solution to trigger the consolidation process. After debinding in air, sintering of the composite beads was performed under inert atmosphere. Full beads with good spherical shape and average final diameters in the range 1.75-2.9 mm were obtained. Investigations by mercury intrusion porosimetry revealed that pure alumina beads featured smaller pores compared to composite beads, although the open porosities were comparable. The fracture strength was evaluated on single beads. Contrary to the pure alumina, the composite beads showed a clear plastic deformation. Pure niobium beads showed a ductile behavior with very large deformations. XRD analyses revealed the presence of calcium hexaluminate and beta-alumina as minor phases in the alumina beads, while the composite ones contained about 25 wt% of impurities. The impurities comprised NbO arising from the oxidation, and beta-$Nb_2C$, from the reaction with the residual sodium alginate. This study demonstrated that the gel casting process allows to reliably produce spherical grains with defined properties, which can be used as aggregate fraction in new coarse-grained refractory castables, among others.

## Acknowledgements:

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# The importance of the ceramic strut morphology: mechanical and physical characterization of Al2O3-C foam filters produced by distinct processing routes

Bruno Luchini[1], Enrico Storti[2], Tony Wetzig[2], Jana Hubálková[2], Martin Abendroth[2], Victor Pandolfelli[3], Christos Aneziris[2]

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## Abstract:

In this work the influence of the production route and filter dimensions on the mechanical properties of carbon-bonded alumina foam filters was investigated. Features like cold crushing strength and fracture behavior were analyzed and used to compare them. Microfocus computed tomography µCT was applied to characterize the geometry of the filters, providing a deep correlation with their fracture behavior. Furthermore, computer-generated filter geometries were used as reference. The results indicated that the centrifugation process is better suited for the production of carbon-bonded alumina filters, and is even more effective when the foam dimensions are increased in the range of those analyzed in this research. Finite element simulations showed the influence of the relative density and strut tapering on the cold crushing strength of filters, providing a correlation between filter structure and its failure mechanism. The attained results provided further insights towards the production of inclusions-free metal parts.

## Acknowledgements:

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# The RF-CVI Optimization on Cf/ZrB2 Composites Production

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## Abstract:

CMC are increasingly used as structural materials for their thermostability, damage tolerance and lightweight. Meanwhile, UHTCs offer the ability to cope with extreme temperatures but struggle with thermal shock environments. It is hoped that their combination, UHTCMCs, are suitable for a wide range of civilian and military applications at above 2500°C, heat fluxes above 10 MW/m$^2$ and temperature changes can be extremely rapid, all in corrosive and oxidative atmospheres. Therefore, there is considerable world-wide research into the composition, structure and manufacturing methods. RF-CVI provides an efficient procedure for introducing a matrix into a carbon preform; infiltration times can be 1/40th of the time required for conventional CVI. Similarly, carbon fibre preform-reinforced $ZrB_2$ composites are a good balance of the cost and performance. For example, $ZrB_2$ is roughly 1/10th the cost of $HfB_2$ and half the density, yet it can offer thermoablative resistance to 2500°C, which is 3000°C for $HfB_2$.

In the current work, the RF-CVI mechanisms are being investigated with respect to the deposition of carbon and $ZrB_{2,}$ in 2.5D $C_f$ preforms. Experimental attention is focused on the manipulation of parameters such as temperature, pressure, and precursor ratio; chemical kinetics theory suggests their influences on activation energies and deposition rates. Taking advantage of modeling using COMSOL, the chemical vapour's flow path is being analysed and the resulting internal morphology is being captured by micro-CT. In parallel, electron microscopy is being used to characterise the microstructures to understand how and why they develop. The goal is to be able to enhance future RF-CVI production, particularly with multiple ceramic matrix phases, e.g., combinations of $ZrB_2$ and $HfB_2$.

# Ceramic Matrix Composites (CMCs) for Ultra High Temperature Applications

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## Abstract:

Ultra High Temperature Ceramics (UHTCs) are potentially appropriate materials for use in different application areas, for example aerospace sector (gas turbines, structural re-entry thermal protection), military (missile nozzles) and energy sector (heat exchangers, fusion reactor walls). $ZrB_2$ and $HfB_2$ based ceramics are some of the most promising materials in the UHTCs family, thanks to their high melting point, low density, high strength, high hardness and good electrical and thermal conductivity.

It is known that the carbon fibres ($C_f$s), $ZrB_2$ and $HfB_2$ all begin to oxidise by ~500°C but only the surface 200-500 µm of UHTCs oxidise and the $C_f$ below ~200 µm survives; yet the $C_f$- reinforced $ZrB_2$ and $HfB_2$ ultra high temperature ceramic matrix composites (UHT-CMCs) can survive high heat fluxed, high gas velocities at temperatures >2000°C in the air for many minutes. In the current study, various mixtures of $ZrB_2$/$HfB_2$ based UHT-CMCs were produced using radio frequency (RF) chemical vapour infiltration (CVI), which is a much faster CVI process since the use of RF allows the deposition process to be achieved in about 25 h rather than the more normal 1000 h. The focus of this work is then to understand how the presence of the boride protects the carbon fibres. Results to date will be presented.

# Improvement of the mechanical properties of TiB2 for armour applications using different additives and sintering techniques.

Simone Taraborelli, Simone Failla, Diletta Sciti

*ISTEC CNR, Faenza, Italy*

## Abstract:

$TiB_2$ is a promising material in several fields including impact resistant armor, seals, cutting tools, crucibles and wear resistant coatings given its physical, mechanical and chemical properties, in particular thanks to the combination of high hardness and exceptional wear resistance. It is however very difficult to sinter below 2000°C, also under mechanical pressure, and is limited by its low fracture toughness. By using sintering additives, it is possible to improve the sintering process and increase the mechanical properties since the additives react with oxidized layers to form secondary phases.

In this study, we explored different preparation methods, various combinations of additives ($B_4C$, $Si_3N_4$ and $MoSi_2$), and sintering techniques (hot pressing and pressureless sintering). Thanks to the synergy between optimized process and tailored composition, an almost fully dense material was obtained at 1700°C with hardness of 24.4 ± 0.2 GPa and fracture toughness of 5.4 ± 0.2 MPa $m^{0.5}$. However, the highest hardness value (30 ± 1 GPa) was obtained for samples sintered by pressureless sintering, featuring a core-shell grain structure.

# Effect of the electric field on the in-situ formation of graphene nanoplatelets during reactive sintering of B4C-TiB2 composites

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## Abstract:

The aim of the work was to prepare boron carbide composites with the addition of 10 vol.% $TiB_2$ by reactive field assisted sintering technology, in which the final materials were obtained by the in-situ reactions between $B_4C$, $TiO_2$, and carbon black. The combined effects of electric current and in-situ reactions (accompanying by the formation of a significant amount of CO gas) resulted in the formation of electrical arcing. At the same time, a significantly different electrical resistivity of $TiB_2$ than that of $B_4C$ caused a significant local overheating at the $TiB_2/B_4C$ interfaces, which led to a partial decomposition of $B_4C$ grains to form graphene nanoplatelets. When one of the two factors was absent during the preparation process, e.g. during hot pressing without electric field, or non-reactive field assisted sintering of $B_4C$ and $TiB_2$ powders, no formation of graphene nanoplatelets was observed. The work also proposed an innovative approach to prevent the decomposition of $B_4C$ grains from happening, by the use of so-called isolated reactive field assisted sintering. A short dwell time (30 s after a degassing step of 6 min) and the uniform distribution of fine $TiB_2$ grains were the main advantages of isolated SPS over the reactive hot press and SPS processes, respectively.

## Acknowledgements:

This work was supported by the Slovak Research and Development Agency under the contract no. APVV-17-0328 and the projects VEGA 2/0007/21 and VEGA 2/0116/22. The support of MVTS project of SAS "BioFun" within the scheme of JRP SAV – TUBITAK (No. 546676) and the Joint Mobility Project under the CAS-SAS agreement (SAV-21-04) is also acknowledged.

# Phosphate-bonded refractory materials with controlled setting and adhesive properties

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## Abstract:

The aim of this work was to optimize and partly predict workability time, setting time and adhesive properties of phosphate bonded unshaped refractory materials. Two mixtures were chosen for testing. The first mixture was composed of calcium aluminate cement, calcium nitrate tetrahydrate and phosphoric acid. The second mixture was composed of reactive aluminium oxide, dead burned magnesium oxide and phosphoric acid. Influence of composition on properties of fresh mixtures during setting was studied by cyclic tear off test and by rotational rheometer. Influence of reaction conditions especially the influence of temperature on setting progression was studied too. Combination of both mentioned mixtures with aluminosilicate aggregates resulted into refractory material that was optimized for the purpose of repair mixtures. Based on composition changes, it was partly possible to predict a change of adhesive properties and setting time.

# Effect of Sintering Temperature on Fracture parameters for an alumina-mullite-zirconia refractory via Wedge Splitting Tests at 600°C

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## Abstract:

Representative parameters are necessary for design and sizing of refractories. In this context, it becomes important that laboratory testing conditions are as close as possible to in-service conditions. However, high-temperature mechanical tests are complex and their post-processing is usually delicate. This work aims to discuss so-called Wedge Splitting Tests (WSTs), which are known to ensure stable crack propagation even for quasi-brittle materials. The studied castable refractory consisted of an alumina matrix with mullite-zirconia aggregates. The experiments were performed at room-temperature and at 600°C, and were assisted by Digital Image Correlation (DIC). Two sets of specimens were analyzed, namely, sintered at 1400°C and 1450°C. Moreover, fracture simulations were carried out using cohesive elements.

Cohesive zone model parameters were obtained using a weighted finite element model updating technique by minimizing the error between simulations and experimental data, namely, the Notch Opening Displacements (NODs), obtained via DIC, and the loading force. NODs were used to extrapolate crack mouth opening displacements (i.e., the displacements where the force was applied to the specimen).

It is shown that the cohesive strength was more influenced by the testing temperature, but did not change much between both studied heat treatments. Conversely, the fracture energy increased 20% with a 50°C increase in firing temperature. These parameters also allowed for the calculation of the Hillerborg length, which is directly related to the fracture process zone length. The latter increased with the testing and sintering temperatures.

## Acknowledgements:

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# Synthesis and mechanical characterization of YB2C2-based ceramics

Antonio Vinci, Luca Zoli, Laura Silvestroni, Nicola Gilli, Diletta Sciti

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## Abstract:

There is a growing interest for materials able to withstand increasingly more challenging conditions, such as temperatures above 2000°C, corrosive atmospheres, and combinations of mechanical stresses that are beyond the capabilities of current materials based on C/C or C/SiC composites. To tackle this challenge, a new class of materials based on ultra-high temperature ceramics reinforced with carbon fibres has been developed, tested and validated for use in extreme environments, demonstrating the capability of this fibre/UHTC coupling to provide both oxidation and mechanical resistance at high temperatures. However, due to the high temperatures required for the consolidation of these composites, fibres partially undergo reaction at the interface with the matrix, strongly limiting pull-out. The use of a coating has been shown to partially address this issue, but the high costs and long processing times associated to the coating deposition render the process unappealing. From our previous studies, following the introduction of $Y_2O_3$ in $ZrB_2$-based UHTCMCs, the formation of a ternary boro-carbide of formula $YB_2C_2$, belonging to a new class of layered compounds akin to MAX phases, was observed at the fibre/matrix interface, and this was associated to significantly increased mechanical properties. These layered phases possess high melting points and could be responsible for the toughening of UHTCMCs, but their properties and role were never fully investigated. In this study, we explored the potential routes for the synthesis of $YB_2C_2$ phases, starting from four different boron sources (B, $B_4C$, $B_2O_3$, BN) and analysed their microstructure by SEM, XRD and TEM. With the most suitable powder mixture, $YB_2C_2$ ceramic composites were sintered and mechanically characterized.

# Influence of matrix densification on the properties of weak matrix ox-ide fibre composites

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## Abstract:

Like other ceramic matrix composites (CMC), oxide fibre composites (OFC) are offering a quasi-ductile fracture behaviour due to embedded ceramic fibres in a ceramic matrix. Oxide fibres in an oxide matrix offer high strength for application temperatures up to 1100 °C depending on the used fibres. If the fracture behaviour of the OFC is derived by the weak matrix concept, the porosity has a great influence on their mechanical properties. A certain amount of porosity is needed to enable the damage-tolerant behaviour. The influence of a decreasing porosity on the mechanical properties of a Nextel™ 610/$Al_2O_3$-$ZrO_2$ composite was investigated. The standard material was reinfiltrated with zirconium-n-butoxide up to seven times thereby decreasing the open bulk porosity. Matrix porosities in the range of 34 - 47% were investigated. The microstructure of the samples was investigated in regard to possible porosity gradients due to reinfiltration and the effects of matrix densification. The three-point flexural strength and interlaminar shear strength (ILSS) were used to determine the influence of the porosity on the fibre- and matrix-dominated mechanical properties, respectively. With decreasing porosity, the bending strength decreased with every infiltration step. The damage-tolerant behaviour was lost at a matrix-porosity of 34 % and lower. The interlaminar shear strength increased first but reached its maximum at a matrix porosity of 35 %. At higher densities, fibres were acting as flaws and cause a renewed decrease in interlaminar shear strength.

# Effect of stoichiometry of magnesium-aluminum spinel on mechanical and thermomechanical properties of no-cement and ultra-low cement refractory castables

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## Abstract:

As well known, the thermal shock resistance, refractoriness, refractoriness under load and hot modulus of rupture of refractories are a major issue and important index for high temperature applications. Since, mentioned properties play a relevant role in view of potential application, the current research on property of $Al_2O_3$-$MgAl_2O_4$ castables are focused on both modelling of phase composition and selection of appropriate firing conditions (temperature and time).

The modelling of phase composition of the refractory castables may be related to both application of different amounts of magnesium-aluminum spinel with different stoichiometry and other compounds with different thermal expansion coefficients. A lot of scientific works focus on the relationship between the properties and both quantity and grain size distribution of the spinel phase. However, there are no studies in the literature on the influence of stoichiometry of magnesium aluminum spinel on the selected properties of refractory corundum-spinel castables. Castables may contain two kind of spinel: pre-formed and situ forming. The in-situ spinel formation process is associated with volume increase what lead to the formation of microcracks in the microstructure. The formation of microcracks may be associated with deterioration of the thermomechanical and mechanical properties of castables.

This work investigates the effect of stoichiometry of magnesium-aluminum spinel on mechanical and thermomechanical properties of spinel containing and spinel forming refractory castables. The characterization of the castables include both room temperature mechanical properties and hot property testing like: thermal shock resistance, hot modulus of rupture and refractoriness under load.

## Acknowledgements:

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# Reactivity, pyrolysis, mass-loss kinetics and carbon residue of phenol-formaldehyde resins with different hexa-contents

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## Abstract:

Phenolic resins are important thermoset materials in numerous applications such as MDF boards, brake pads, heat ablation materials for reentry vehicles, refractories and as C-precursors for producing ceramic matrix composites.

The cross-linking and pyrolysis mechanisms of phenolic resins are complex and part of current investigations. Cross-linking of novolak-type phenolic resins requires a well-defined amount of additional hardener and controlled cross-linking conditions to achieve materials with the required properties. The most commonly used hardener for novolak is hexamethylenetetramine ("hexa").

This work investigated the influence of the hexa-content on the reactivity, pyrolysis reactions, mass-loss kinetics and residual carbon amount for two phenolic resins, each with different novolak-hexa mixtures (0 to 15 wt.-%).

The reactivity and viscosity of resins was studied in a rheometer. Pyrolysis reactions, mass loss kinetics and residual carbon content were investigated by using TG-DSC-FTIR-GC/MS.

The obtained results show, that the reactivity, viscosity and the residual carbon amount increase with increasing hexa-content. A model to predict the viscosity and residual carbon depending on the hexa-content was developed. If the amount of hexa was varied, the pyrolysis reactions change significantly. The dependence of the mass loss rates of resins during pyrolysis on the hexa-content was determined and a model for this process introduced.

The presented models are promising tools to find the suitable resin-hardener mixture for the desired application, a more efficient processing technology and a deeper understanding of the pyrolysis of phenolic resins. This may lead to distinct time- and cost-savings for future applications of phenolic resins in several industrial sectors.

# The Influence of High Temperature on the SiC/SiC Composites

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## Abstract:

Ceramic Matrix Composites with SiC fibers and SiC-based matrix are very promising candidates for high-temperature lightweight design of future aero engines due to their high temperature resistance, low density and relatively high strength. Degradation behavior and oxidation resistant plays a crucial role for such a composites. In this study, the influence of elevated temperature on SiC/SiC composites with BN fiber coating was investigated. Oxidation tests were performed at 980°C, 1100°C and 1300°C. The oxidation tests were accompanied by XRD measurements to characterize the phase composition before and after oxidation. Moreover DTA/TG analysis was performed to better understand the mechanisms of oxidation. Additionally, microstructure investigations were done using SEM and optical microscopy

# Polymer Derived Ceramics For High Temperature Applications

Muhammed Younas

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## Abstract:

Advanced technical ceramics offer a range of solutions for the design of materials for use in extremely challenging environments. However, to overcome the inherently low toughness of ceramics, it is often necessary to fabricate ceramic matrix composites (CMCs) that are based on ceramic fibre-reinforcement. Unfortunately, these can be difficult to make at cost with the required performance by traditional powder/slurry-based infiltration techniques followed by sintering. To address these challenges, an alternative route is via the pyrolysis of polymeric precursors. Ceramics obtained by this technique are typically referred to as polymer derived ceramics (PDCs) and have become the subject of a great deal of both academic and commercial interest. This particular research project focuses on the modification of silicon carbonitride based resins with aluminium yielding Si(Al)CN, which has been shown to dramatically improve the hydrothermal stability, making it an excellent ceramic material for use in high temperature oxidative and corrosive environments. The application of the Si(Al)CN ceramic system has not yet been explored for use as a matrix in CMCs, which could potentially provide a novel approach to design CMCs with the desired high temperature and corrosion resistant properties at low cost. The project seeks to explore the properties and performance of Si(Al)CN CMCs reinforced with SiC fibres. The results of this project will give good insight into the long-term service capability of this material, which could potentially offer a novel approach to the design and manufacture of high temperature capable CMCs.

## Acknowledgements:

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# Polymer-derived Ultra-High Temperature Ceramic Matrix Composites

Elia Zancan

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## Abstract:

The interest in polymer-derived ceramics (PDCs) for the fabrication of ceramics has constantly increased ever since the invention of the Yajima process in the 1970s thanks to their high flexibility and degree of customization. This approach is now being considered to use PDCs to make specialist ceramics for (ultra-)high temperatures (UHT) applications. SiC and SiCN precursors have both been used in the fabrication of UHT ceramics since $SiO_2$ provides a well-known self-healing effect by spreading on the surface when melted, sealing cracks and pores and preventing further oxygen diffusion towards the sample's inner part. The protection can be enhanced with the addition of boron, as the resulting borosilicate glass flows even better due to its lower viscosity. The evaporation of this protective layer occurs, however, very easily, even at moderate temperatures (>1000°C) and it is blown away in extremely short times under ablative conditions.

In this work, the possibility of decelerating the borosilicate glassy layer evaporation by dissolution of a transition metal oxide is being investigated. The modification of polymeric precursors with a secondary metal also provides an increased network strength, resulting in an improved ceramic yield upon conversion and delayed onset of matrix degradation at high temperature. $C_f/ZrB_2$-Si(Hf)CN ceramic-matrix composites (CMC) are being manufactured by dip coating 2D carbon fibre plies with a ceramic slurry and densified via polymer infiltration and pyrolysis with a modified polysilazane commercial precursor. Their oxidation behaviour will be tested at 1600°C in flowing dry air for 5, 10 and 20 h, and characterised in terms of microstructural modifications and specific mass change by comparing the basic and Hf-containing SiCN matrices.

## Acknowledgements:

The author thanks QinetiQ for the support and feedback. This project is funded by the Defense Science and Technology Laboratory (DSTL).

# Theoretical predictions and synthesis of high-entropy diboride systems with different molar ratios of transition metals

Inga Zhukova[1], Vasanthakumar Kombamuthu[2], Naser Hosseini[1], Hakan Ünsal[1], Monika Tatarková[1], Alexandra Kovalčíková[3], Ivo Dlouhý[4], Ján Dusza[3], Peter Tatarko[1]

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## Abstract:

High-entropy borides (HEB) have recently received wide attention due to their excellent physical and chemical properties, including high hardness, chemical intertness and superior electrochemical properties. Until now, most of the research interest has been focused on the HEB materials with equimolar composition of transition metals. Among all of the HEB materials, $(TiZrHfNbTa)B_2$ is one of the most investigated compositions. The present work was aimed at studying the effect of various 5-metal ratios on the properties of highly disordered $(TiZrHfNbTa)B_2$ structure by the first-principles calculations using Density Functional Theory (DFT). The goal is to understand the effect of individual metal element and different atomic positions and concentrations on the formation of diboride structure. The results were then compared to the properties of equimolar $(TiZrHfNbTa)B_2$ composition. It is known that cohesion energy makes a significant contribution to the structure and it is a prediction that can help to select structures with the highest cohesion energy index. Therefore, the cohesive energies were calculated for both the stoichiometric and non-stoichiometric diboride compositions. The results of theoretical predictions were verified by the experimental work. The individual HEB compositions were synthesized using boro/carbothermal reduction of oxide precursors, followed by Spark Plasma Sintering at temperatures in the range of 1800 – 2200°C. The lattice parameters of the synthesized materials were calculated using Rietveld refinement of XRD patterns, and the results were compared to the theoretical results. The effect of various molar ratios on the mechanical properties, such as hardness, fracture toughness and strength was investigated.

## Acknowledgements:

This work was also supported by the Slovak Research and Development Agency under the contract no. APVV-17-0328. The support of VEGA 2/0161/22 project and the Joint Mobility Project under the CAS-SAS agreement (SAV-21-04) is also acknowledged.

# Thermal stability of polymer derived ultra-high temperature ceramic matrix composites

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## Abstract:

There is an increasing demand for improving durability of ceramic matrix composites (CMCs) at temperature exceeding 2000 °C [1]. Ultra-high temperature ceramic matrix composites (UHTCMCs) are novel materials which can overcome the limits associated with currently used CMCs. UHTCMCs are potential materials for manufacturing of leading edges and Thermal Protection System (TPS) in hypersonic vehicles or rocket nozzles and turbine blades for propulsion [2]. We explore the thermal stability of a $ZrB_2/SiC/C_f$ material manufactured via powder slurry infiltration (SI) followed by six cycles of Polymer Infiltration and Pyrolysis (PIP) technique with allylhydrido polycarbosilane.

The material was investigated, firstly, after a consolidation under the mild conditions of 1000 °C, after which the polymer derived SiC is still amorphous [3], secondly, after post-consolidation thermal treatments from 1100 °C to 1900 °C to evaluate microstructural evolution of the matrix: crystallization and increase of porosity. Finally, elevated temperature mechanical properties were studied through bending tests up to 1500 °C.

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## Acknowledgements:

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# Ablation behavior of rare-earth modified ZrB2–SiC composites prepared by reaction sintering of ZrSi2, B4C and C

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## Abstract:

$ZrB_2$-SiC composites were fabricated using Field Assisted Sintering Technology (FAST). The composites containing 25 vol% SiC particles were prepared by in situ reaction of $ZrSi_2$, $B_4C$ and carbon black powders, which is a method to densify $ZrB_2$-based composites at low temperatures. Furthermore, rare-earth (RE) based additives were used to improve the ablation resistance of $ZrB_2$-SiC composites. The microstructures of the $ZrB_2$ based composites were characterized by X-Ray Diffraction and Scanning Electron Microscopy. Both the room temperature (hardness, strength, fracture toughness) and high temperature (ablation resistance using an oxy-acetylene flame with a temperature up to 2700 °C) properties were investigated. The results showed that homogeneous microstructure and nearly fully dense $ZrB_2$-25vol.%SiC composites with a relative density above 99% were obtained after sintering at the temperature of 1600°C under the pressure of 70 MPa for 10 min. During sintering, the additives were completely transformed into $ZrB_2$ and SiC particles, which were homogeneously distributed in the $ZrB_2$ matrix. The RE-based additives were also uniformly distributed at the grain boundaries of $ZrB_2$. The mechanical properties of $ZrB_2$-SiC composite, such as hardness, strength and fracture toughness, were slightly improved by the addition of RE additives. The ablated zone of $ZrB_2$-SiC consisted of three distinct ablation layers. Most importantly, the ablation resistance of $ZrB_2$-based materials was significantly improved by the addition of RE, and further improved with their increasing amounts.

## Acknowledgements:

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# Influence of Si and Al metallic additives on the mechanical properties and microstructure of the qAl2O3-C refractory material.

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## Abstract:

Depending on the metal additive used and the heat treatment temperature, a carbide bond may be formed in the material, determining its mechanical parameters and microstructure.

The paper presents the results of structural tests and mechanical properties of $Al_2O_3$-C refractory materials with the addition of metallic Si or Al in the amount of 1%, 3% and 5%, after heat treatment at temperatures of 800°C, 1000°C, 1200°C and 1400°C. The samples were heat treated in the carbon bed to limit the access of oxygen. The experimental work was preceded by the development of diagrams with the areas of durability for the Si-C-N-O and Al-C-N-O systems.

The results of the XRD test show that aluminum carbide, $Al_4C_3$, is formed in the material after heat treatment as low as 800°C, while silicon carbide, SiC, is formed as a result of heat treatment above 1000 C. The increased amount of added Si causes an increase in the open porosity and a decrease in the apparent density of the material samples after heat treatment. A significant increase in mechanical strength occurs in the case of the addition of 3% of Si and heat treatment at 1200°C, and in the case of the addition of 1%, 3% and 5% of Si after heat treatment at 1400°C. In the case of Al, it content at the level of 5% translates into the lowest open porosity, where the highest apparent density was obtained for 3% of Al - this material is also characterized by the highest compressive strength (samples after heat treatment at 800°C, 1000°C and 1400°C).

Studies shows that depending on the metal additive used, in order to obtain a material with the desired properties and microstructure, the amount of this additive and the heat treatment temperature should be adjusted.

# Symposium J: Silicate / Traditional Ceramics, Arts + Design

Invited presentation:

# Porcelain versus porcelain stoneware: so close, so different. Sintering kinetics, phase evolution, and vitrification pathways

Chiara Zanelli[1], Sonia Conte[1], Chiara Molinari[1], Matteo Ardit[2], Giuseppe Cruciani[2], Michele Dondi[1]

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## Abstract:

This contribution was aimed at comparing the sintering kinetics, the evolution of the phase composition and the properties of the melt during the vitrification process of four representative industrial ceramics (soft porcelain, vitreous china; three different batches of porcelain stoneware, of which one containing a soda-lime glass). These bodies were prepared on a laboratory scale, simulating industrial processing. Every batch was designed with the same ingredients (kaolin, ball clay, feldspar, quartz) but in different ratios. To shed light on the reasons behind the different sintering behavior, densification kinetics (isothermal and non-isothermal optical dilatometry), phase evolution during firing (XRD-Rietveld) and microstructure (SEM) were determined. The melt properties were estimated by predictive models based on the chemical composition of the liquid phase. An increasingly faster sintering kinetics was observed in the order: soft porcelain < vitreous china < porcelain stoneware, as confirmed by a decreasing apparent energy of activation of the viscous flow. Densification rates are related to the rheological properties and amount of the liquid phase (porcelain stoneware has a melt viscosity lower than porcelain). This reflects different vitrification pathways depending on the kinetics of feldspar and quartz dissolution and mullite formation (with notable differences when primary or secondary mullite occurred). These phenomena have determined a distinct evolution of chemical features and pseudo-structural parameters of the melt. As a result, soft porcelain and vitreous china kept an almost constant bulk viscosity above 1250°C, significantly higher than porcelain stoneware at 1200°C, and consequently a less firing deformation.

Invited presentation:

# Method for Viscosity Measurement of Silicate Melts by Hot Stage Microscopy

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[2] *Dipartimento di Scienze della Terra, Università degli Studi di Torino, Torino, Italy*

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## Abstract:

The viscosity of silicate melts represents a key parameter to control the manufacturing processes in the ceramic and glass industries and to understand nature phenomena (e.g., volcanic eruptions). The techniques generally used are time wasting, requiring equilibrium conditions, and limited to small viscosity ranges. The reduction of testing time represents a challenge for both academic and industrial aims. For this purpose, hot stage microscope (HSM) technique was selected as alternative for a rapid viscosity determination and an experimental methodology was set up. Specimens (pressed powders) were heated at 10°C/min till melting. Characteristic shapes (Start sintering, End sintering, Softening, Sphere, Hemisphere and Melting) were found at characteristic temperatures (CT). Seven natural glasses, with a measured viscosity-temperature dependence (Vogel-Fulcher-Tammann, VFT) were selected. Each CT viscosity was calculated based on the experimental VFT parameters. The observed shape is given by a cumulative viscosity-surface tension effect. This circumstance let the viscosity values at each CT linearly scale with the surface tension. The viscosity was calibrated introducing correction factors based on glass chemistry. By this way, two independent data sets can be obtained – CT (by HSM) and the corresponding characteristic viscosity (from the glass composition) – to be used to calculate the VFT parameters. The comparison between the calculated and the experimental viscosity shows a good correspondence, significantly improved with respect to previous attempts in the literature using HSM data only. These results also disclose a promising prospect of this noncontact technique in evaluating the effects of crystalline particles and porosity on silicate rheological properties.

Invited presentation:

# Characterization of raw strontium glazes with changing the molar ratio of Na2O/K2O

Katarzyna Pasiut, Janusz Partyka

*AGH UST, Kraków, Poland*

**Abstract:**

The paper presents the results of the research on glazes from the $SiO_2$-$Al_2O_3$-CaO-MgO-$Na_2O$-$K_2O$ multicomponent system with a high potassium oxide content. Glazes with three different additions of strontium oxide were tested. During the tests, the characteristic temperatures were determined and the surface parameters (color, gloss, roughness, and chemical resistance) were characterized. Analysis of the internal construction was also done using spectroscopic methods (in the mid-infrared and Raman spectroscopy) as well as in the field of phase composition and observation of the microstructure. The results presented show the relationship between the parameters internal structure and the obtained parameters of the fired glaze surface.

# Gibbsite-based ceramics for humidity control tiles

Javier Castellano[1], Vicente Sanz[1], Eugeni Cañas[1], Ilaria Pin[2], Enrique Sánchez[1]

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## Abstract:

The humidity control or regulation from ceramic materials is a topic of current interest for the comfort of interior spaces in buildings due to the significant energy savings that are obtained with the use of these passive solutions. Humidity regulation is achieved through the adsorption and desorption phenomena of water vapour by means of porous structures with a considerable presence of mesopores, small pores between 2 and 50 nm in size that facilitate a capillary condensation.

Although allophane-based materials and volcanic soils were the first to be used for this purpose, gibbsite-based materials are more interesting due to the preservation of the porous structure at high temperatures. Indeed, during the sintering process of gibbsite-based ceramics, transition alumina occurs which leads to a mesoporous structure preserved up to temperatures of around 1200 °C when alpha alumina crystallisation takes place. This quality of gibbsite-based ceramics is particularly appealing for the formulation of coatings to apply on tiles and provide humidity regulating functionality.

Under these premises, an analysis of the effect of the composition of different gibbsite-based materials, mixed with other raw materials such as clay and quartz, on the moisture adsorption and desorption of laboratory specimens was addressed. Also, relating humidity control to porosity and pore size was carried out. From these results, optimal formulation and processing conditions for the development of ceramic tile coatings possessing humidity regulating ability were established.

## Acknowledgements:

Acknowledging Ministerio de Ciencia e Innovación of Spanish Government and European Regional Development Fund (ERDF) of European Union for the funding received in the framework of RTC-2017-5904-5 CONFORTMA project. Authors are also grateful for the collaboration of the company Vicar in the supply of compositions.

# Mobility of hazardous elements in ceramic bodies

Sonia Conte[1], Chiara Molinari[1], Chiara Zanelli[1], Matteo Ardit[2], Mantovani Luciana[3], Giuseppe Cruciani[2], Mario Tribaudino[4], Michele Dondi[1]

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## Abstract:

Waste recycling can potentially become a common practice for improving the environmental sustainability of the ceramic manufacturing process. However, the introduction of waste can considerably expand the compositional spectrum of raw materials with possible inclusion of hazardous components. Therefore, prior to the resorting of any secondary raw material, it is fundamental to assess the degree of inertization of hazardous elements (HEs) through the ceramization process. The aim of the present work is to quantitatively assess the mobility of various HEs (Ba, Co, Cr, Cu, Mo, Pb, Sb, Sn, Sr, V, Zn) introduced in silicate ceramics. For this purpose, four batches were formulated following the typical recipes to obtain: three largely vitrified ceramic products (i.e., two different porcelain stoneware bodies and a red stoneware) and a largely unreacted body (low fired brick). An artificial waste, with an aluminosilicate matrix containing all the HEs cited above, was added to all the batches in the amount of 10%wt. The eight batches were experimented at the laboratory scale, simulating the industrial tile-making process. After the characterization of the main technological properties of the fired products (water absorption and bulk density), they were subjected to leaching test (EN 12457-2:2002, to evaluate the HEs mobility), XRPD-Rietveld analyses for the quantitative phase composition, and SEM-EDS observation to determine the microstructure and the HEs diffusion. Obtained data indicated a different mobilization mechanism depending on both specific hazardous element and ceramic typology, with significant criticisms related to Mo, Cr and Sr, mostly in the largely unreacted body.

# Nanomechanical properties of glass-ceramic materials from the SiO2-Al2O3-Na2O-K2O-MgO system with an addition of CaO

Karolina Kaczmarczyk, Janusz Partyka

*AGH University of Science and Technology, Krakow, Poland*

## Abstract:

Glass-ceramic materials consist of finely dispersed crystalline phases embedded in a glassy matrix. The strength depends then not only on the properties of the individual crystalline phases but also on their interactions and of the matrix. Differences in mechanical properties for materials with similar chemical compositions are most likely related to diverging microstructures. Crystal orientation, grain-size distribution and shape, the ratio of the glass matrix to the crystalline phase, and homogeneity control the flexural strength of glass-ceramic materials. This work presents the relations between microstructure, chemical composition, and mechanical properties, which were established for glass-ceramic materials from the $SiO_2$-$Al_2O_3$-$Na_2O$-$K_2O$-MgO-CaO system. The aim of the present research is the examination of changes in the chemical composition of glass-ceramic materials, by the nature of the crystallized phases like their morphology and microstructure in relation to the nanomechanical parameters.

## Acknowledgements:

KK has been partly supported by the EU Project POWR.03.02.00-00-I038/16-00

# Determination of the subcritical crack growth parameters in C130 electroporcelain

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[2] AGH University of Science and Technology, Kraków, Poland

## Abstract:

Electrical porcelain, like any ceramic material, has a tendency to subcritical cracking under long-acting stresses. The slow growth of defects present in the material can cause a significant reduction in the service life of porcelain insulators. The study was conducted using the Constant Stress Rate test method. It allows determining the crack propagation speed using biaxial bending tests. The tests were performed for four groups of specimens, made of electroporcelain type C130. The groups differed in sintering conditions, and in addition, glazed and unglazed samples were compared in each group.

# Preparation and properties of new thermal-insulating building materials with high content of coffee grounds

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## Abstract:

Over the past 10 years, the average increase in world coffee consumption has been 1.9% per year. Last year's coffee production amounted to 10 million tons. All of this mass, increased by the content of unfiltered water (about 50%), became waste. Due to its properties (in particular, the constant grain composition and organic nature), this waste can be an ecological raw material for the production of ceramic materials with improved thermal insulation properties, as well as a burnout component, thanks to which it is possible to reduce energy / fuel consumption during firing. This synergistic ecological effect is in line with the global climate policy, in particular with the short-term goals of reducing $CO_2$ emissions included in the "Fit for 55" adopted by the European Parliament, as well as with the long-term assumptions of the "Green Deal".

The research is aimed at the development of high-porosity, thermal-insulating building materials with satisfactory compressive strength. It presents the properties of waste coffee grounds and the properties of the clay raw material used to make the ceramic materials, the properties of the ceramic masses, method of producing materials and their properties. The most important research presented in this work: is the study of the heat of combustion and calorific value of coffee grounds in order to determine the value of energy gain from the combustion of coffee waste in the ceramic mass, the thermal conductivity coefficients of final materials to characterize their thermal insulation and the value of compressive strength to characterize their applicability.

## Acknowledgements:

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# Influence of the freeze tape casting process on the properties of use of kaolinite and halloysite-based ceramics

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## Abstract:

In the present study, kaolinite- and halloysite-rich clays were used to manufacture silicate ceramics shaped by tape casting. A commercial kaolin (KCR) (provided by Imerys) and a halloysite-rich clay from Cameroun were used as starting clays. Conventional tape casting (noted TC) was used to promote the platelets alignment of kaolinite particles in order to highlight the effect of platelet against tubular shape on the properties of use. Freeze tape casting (noted FTC) was used in order to include a multiscale ordering thanks to ice templating effect within kaolinite or halloysite-based samples. The as-obtained freeze tape casting samples were freeze-dried prior to their sintering at 1200 and 1300°C. The porosity and biaxial flexural strength were determined. The final properties of use will depend on the relative amount of mullite phase, consolidation degree and remaining porosity (size distribution, texture…). SEM observation and XRD analyses were performed on the dried and sintered samples shaped by TC and FTC.

The porosity of dried KCR samples was 30% higher than the porosity of dried HCR samples when using TC. However, with FTC process, the obtained KCR and HCR samples exhibited the same porosity content. In general, the porosity obtained with FTC was at least twice the porosity of the same formulation shaped by TC. The sintering of all samples at 1200°C lead to an increase in porosity values due to the consecutive decompositions of organics and clays. The thermal conductivities values were in agreement with a greater amount of 3:2 mullite within KCR samples sintered at 1200°C. Despite the great porosity of sintered FTC samples(70%), their mechanical resistance was less affected. Sintering at 1300°C allowed improving some properties of the HCR samples.

# Processing and properties of use of porous silicate ceramics using kaolinitic and illitic clay with peanut shells addition

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## Abstract:

Clays are widely included in the formulation of such ceramics, thanks to their availability and low cost. Currently, the development of porous ceramics is gaining interest for various applications in the field of energy production, water treatment and purification [1,2]. To achieve the production of porous silicate ceramics, porogenic phases can be included in order to have a better control of pores content and size, distribution… [3,4]. In the present study, we aim at processing porous silicate ceramics using a raw clay from Burkina Faso and a local readily available waste as porogenic agent. Therefore, a kaolino-illitic clay from Ouagadougou (Burkina Faso) and a commercial clay provided by IMERYS (France) were used as starting materials and labeled as KORS and KCR respectively. The commercial kaolin KCR serves as a reference kaolinite-rich clay compared to KORS. Peanuts shells (noted PCA) from Burkina Faso were collected, dried, ground and sieved down to 500 um in order to serve as porogenic additive. Indeed mixture of KORS or KCR with 0 - 40 mass% of PCA were prepared and shaped by compaction. The obtainend materials were characterized before and after firing. It appears that KORS samples exhibit higher porosity and mechanical resistance content after firing at 900 °C and 1100 °C compared to KCR samples In all cases, the porosity content tend to increase while the PCA content increases. Conversely, the mechanical resistance tends to decrease with increasing PCA content. the presence of fluxing oxides in KORS together with the addition of 30 mass% of PCA allow obtaining the optimal pore content and stress to rupture values after sintering at 900 °C. These results are promising for developing alternative solutions for water microfiltration easy to use and recycle.

## Acknowledgements:

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# Physical, chemical and thermal properties of fly ashes with various grain sizes

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## Abstract:

Fly ash is a fine grained fraction of coal combustion residues that is carried along with a stream of gases coming out of the combustion chamber and captured on electro-filters. Due to the coal combustion temperature in the pulverized coal boilers and due to the high degree of coal fragmentation, the grains of ash produced are fine-grained and mostly vitrified. The mentioned features and chemical composition similar to clay minerals influence the interesting for traditional ceramics thermal properties of ashes. The fine-grained nature and the large amount of vitreous phase contained in fly ash contribute very high surface energy of this material what results in its high tendency to sinter in relatively low temperatures. The increased amount of alkali oxides in the ash promotes the formation of the liquid phase during sintering, which further intensifies sintering phenomena. This work presents the possibilities of obtaining of fly ashes characterized by fine graining, high content of glass and alkaline oxides and determination of their thermal characteristics. From the results of the research, it can be concluded that fine fractions of fly ash indicate their potential use as an additive intensifying the sintering process of traditional ceramic materials.

## Acknowledgements:

The research was financed from the statutory funds of the Faculty of Materials Science and Ceramics AGH contract number 16.16.160.557.

# Insights into the firing technology of the Cucuteni pottery

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## Abstract:

The Cucuteni-Trypillia civilization is considered one of the most intriguing subjects when analyzing South-Eastern European prehistory (5th -4th millennia BC). The ceramic repertoire consists of anthropomorphic and zoomorphic figurines and sophisticated polychrome pottery which have significantly improved our knowledge of daily life and manufacturing skill of Old European civilizations.

This study aims to examine the degree of standardization registered in various sequences of the ceramic chaîne opératoire. To identify the technological characteristics of ceramic production, we have applied a multi-analytical methodological approach to the analysis of thirty-nine pottery samples selected from the eponymous site of the Cucuteni civilization and of ceramic replicates prepared in the laboratory. The compositional and microstructural features of the ceramic paste were determined by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy analysis (EDX), while the firing parameters were identified by X-ray diffraction (XRD) and magnetic and dielectric measurements.

The estimation of the firing parameters for the majority of the investigated pottery samples suggests the use of a controlled atmosphere and temperature throughout the firing process. This may be caused by a possible transformation in the social and economic strategy related to pottery manufacturing.

## Acknowledgements:

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# Scale and Agglomeration dust for preparing ceramic glaze

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## Abstract:

This study is focused on the evaluation of the possibilities to re-utilize inorganic waste containing metals, such as agglomeration dust and scale, to prepare glazes. Dust and scale are very promising types of industrial waste, due to their richness in iron (about = 72 % Fe). Iron pigments are among the most widely used dyes in industrial applications. Changes in certain parameters directly influence the modification of iron oxides, as well as the coloring of the final pigment. Agglomerating dust was used both thermally pre-calcined at 700 °C and 900 °C, and in its original state for preparing glazes. Engobes contained a ceramic clay base with 1, 5, 10 and 50 wt% of dust as pigment. Final engobes fired at 900 ° and 1060 °C were red and grey. Non-oiled scale was modified: a) as received b) thermally pre-treated at 700 and 900 °C, c) mechanically treated in planetary ball mill (60, 120 and 240 minutes) and vibratory disc mill (60 and 120 minutes). Dust and scale were used as a coloring component of a transparent glaze matrix with 1-50 wt%. Prepared glazes were applied (by spraying and dipping) on the surface of ceramic tiles and fired at 800 °C, 900 °C and 1060 °C. It is necessary to keep a defined temperature for the final glaze firing, in order to obtain the desired colour (red, brown, yellow) and quality. The pigments were characterized by XRF, PSD, TG and DTA, SEM. The color of the samples was described by CIE L*a*b* values. Changes of some parameters have a direct influence on the modification of iron oxides and colour of the final pigment. Careful control of the treatment process together with the temperature of final glaze firing is necessary to obtain the glaze of a desired color and quality.

## Acknowledgements:

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic under Project No. CZ.02.1 .01/0.0/0.0/17_049/0008426 and SP2022/13 - Low energy processes and materials in industry.

# The impact of the Na2O/K2O molar ratio on the properties of ceramic glazes

Janusz Partyka, Katarzyna Pasiut, Karolina Kaczmarczyk, Dawid Kozień

*AGH University of Science and technology, Faculty of Materials Science and Ceramics, Kraków, Poland*

## Abstract:

The alkali metal oxides $Na_2O$ and $K_2O$ are the basic fluxes used in ceramic glaze technology. Some technologists treat them as equal and, in belief, use them interchangeably. However, when the behavior of albite and orthoclase, which occur as components of sodium and potassium feldspar, especially with different characteristic temperatures, different high-temperature viscosities, and different melting methods, they point to something different. The presentation will show cases of glaze compositions in which there are significant differences in the properties of ceramic glazes caused only by the exchange of alkali metal oxides, sodium oxide, and potassium oxide.

## Acknowledgements:

The work was carried out thanks to support from statutory activity 11.11.160.617

# An impact of strontium oxide addition on the crystallization of zirconium glazes

Katarzyna Pasiut, Janusz Partyka, Dawid Kozień

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## Abstract:

The study investigated glazes with an increasing amount of zirconium silicate (1, 3, 6 and 12% wt.), to which the amount of strontium oxide (0, 1, 3, 6 and 12% wt.) was added. The prepared glazes were suspended in water and then dried. Raw glazes were used to measure the characteristic temperatures on the basis of which the firing process was carried out. In order to obtain similar firing conditions (viscosity, surface tension), the glazes were fired at the indicated temperature of the half-sphere. The finished glazes were subjected to qualitative and quantitative determinations of their phase composition, as well as observations of the size and habit of the crystals. The result of the experiment is the dependence of the amount of silicate crystalline phases in the function of added strontium oxide.

## Acknowledgements:

This work was partially supported by the Polish State Ministry for Education and Sciencewith subvention for AGH University of Science and Technology (project No. 16.16.160.557)

# Characteristics of ceramic masses as materials for the construction of a violin resonance body

Katarzyna Pasiut, Dorota Czopek, Janusz Partyka

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## Abstract:

The aim of the experiment was to determine the possibility of using ceramic masses as a material for the construction of a violin resonance body. Three materials were used for the tests: white stoneware, hard porcelain and C-130 porcelain fired at 1260, 1400 and 1310°C, respectively. Samples in the form of tiles with dimensions of 300 x 100 x 5 mm were subjected to acoustic tests to characterise the interaction of masses with sounds. A wooden fragment of the violin soundboard was used as a reference sample for comparison purposes. Phase composition studies were also performed, and then the determined acoustic parameters were related to the number of crystalline and amorphous phases. The analysis of the results obtained made it possible to select the mass from which the ceramic resonance body of the violin was made. Installing the elements necessary to play the horsetail made it possible to obtain a full-fledged instrument made of unusual material.

## Acknowledgements:

This work was partially supported by the "Rector's Grant" Competition, edition 2021.

# Development of an innovative, environment-friendly production technology of large-format, deeply structured ceramic tiles using a pioneering method of recycling green scraps generated at the product forming stage

Izabela Puchyrska, Robert Pacan, Dawid Cegłowski

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## Abstract:

The presented research results were co-financed by the European Union from the European Regional Development Fund: Intelligent Development Operational Program 2014 -2020 under the project "Development of an innovative, environment-friendly production technology of large-format, deeply structured ceramic tiles in stoneware technology using a pioneering method of recycling green scraps generated at the product forming stage", implemented under the competition held by the National Centre for Research and Development named "Fast track" contract No. POIR.01.01.01-00-0503/19-00".

Breakthrough process solutions have been developed (transition from the "wet" method to the "dry" method), enabling the return of all soft waste generated during the product formation stage, and then using this waste to produce full-value, high physical, chemical and strength parameters and the manufacture of a ceramic product in accordance with the industry standard EN 14411.

The research effort will also be devoted to creating new knowledge in the field of production technology, which will be verified by conducting test production on a pilot technological line. Its construction is necessary to confirm the achievement of the Project objectives - obtaining the assumed parameters of the new product.

The planned result will be obtained through industrial research and development works divided into three stages.

Stage 1 research work gave positive parameters for the final product. Changing the technological process will affect the quality and efficiency of production. Thanks to the introduced innovation, it is estimated that water consumption will be saved at the level of 750 m3 per month and gas savings at the level of 43,000 m3 per month. The use of the "dry" method of turning back soft defects also gives a very important pro-environmental aspect. The reduction of water consumption will contribute to the reduction of CO2 emissions produced during the drying of the wet body composition by traditional methods.

# Suitability research of waste material from hard coal beneficiation process in the production of traditional porous ceramics

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*AGH University of Science and Technology, Kraków, Poland*

## Abstract:

Traditional hard coal mining generates large amounts of wastes. Regulations related to environmental protection require the recovery or neutralization of the generated waste. Technological progress in the field of the so-called clean coal technologies make mining waste a raw material for other industries. The possibility of using waste depends on its chemical and mineral composition and on the properties of the final product. The properties of extractive waste depend on the coal enrichment process in which they are generated. Often, in addition to the minerals, these wastes contain a significant amount of carbon, which can be recovered in various ways. The subject of this study is waste from the coal recovery process with the consistency of a thick paste, which is stored in landfills, which is a nuisance for the environment. The aim of this study is to characterize the waste material and to assess the possibility of using it for the production of traditional porous ceramics. The phase composition was investigated by XRD and STA methods, and thermal properties were characterized by heating microscopy. The gaseous products released during the thermal treatment with the TG/MS method were analyzed. The particle size distribution and the specific surface area of the sludge sample were also measured. Initial analyzes of the possibility of using this waste as a raw material for the production of traditional fired porous ceramics were carried out.

## Acknowledgements:

The research was financed from the statutory funds of the Faculty of Materials Science and Ceramics AGH contract number 16.16.160.557.

# Effect of potassium and additives concentration on alkali-based geopolymers for high temperature applications

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## Abstract:

Thermal resistance is an essential property for different applications. Inorganic refractory materials are generally used. However, the preparation of these materials requires high-temperature solid state reactions. As an alternative, geopolymer materials, synthetized at low temperature (less than 100 °C), are known to have good thermal stability. This work aims to optimize geopolymer formulations and to highlight the impact of alkali earth cations and alkali concentration of potassium alkaline solutions on the thermal behavior of geopolymer materials. For this, different mixtures composed of kaolin, calcium carbonate, dolomite, sand and potassium feldspar and two potassium alkaline silicate solutions with different concentrations were used (5 and 6 mol.L$^{-1}$). At first, the effect of rotary calcination parameters at 750°C such as the dwell time was investigated. It was demonstrated that the kaolin dehydroxylation is quasi complete (> 90 %) and do not significantly depend on the dwell time. Whereas the carbonate decomposition degree increases with the increase of dwell time and the decrease of powder weight but still not complete (<80 %). These differences influence the feasibility of consolidated materials. Indeed, a flash setting occurs for samples based mixtures with high calcium carbonate decomposition degree (> 50 %) and low wettability values (500 μL/g) for the three used alkaline solutions. The thermal behavior at 1000 °C depends on the chemical composition of the aluminosilicate source and the concentration of alkaline solution. A conservation of the compressive strength at 43 MPa after thermal treatment at 1000 °C of geopolymers based on mixture with low potassium concentration solution (5 mol.L$^{-1}$) was evidenced.

# The impact of the addition of different grain size of limestone to cream-firing clays on the color properties of sintered ceramics

Kornelia Wiśniewska, Ewelina Kłosek-Wawrzyn, Waldemar Pichór

*AGH University of Science and Technology, Kraków, Poland*

## Abstract:

It is well known that grain size of used raw additives to ceramic masses has a significant impact on the properties of ceramic materials. The additive, such as limestone affects the final properties of ceramic products not only due to the reduction of porosity caused by the action of the flux, but also due to its chemical composition. This study deals with technological and color properties of ceramic materials based on Borkowice clay, as main raw material and limestone from Bukowa deposit, as color changing additive. The aim of the experiment was to compare the color (L*a*b* coordinates) of ceramic materials with an addition of limestone flour, characterized with different grain sizes. The test was carried out for materials fired at different temperatures: 1120, 1140, 1160 and 1180 °C. It was noticed that the presence of the limestone additive directly affects the phase composition and microstructure of the materials and indirectly their color. Moreover, the color of the material changes depending on the particle size distribution of the additive. The surface of the material is lighter than the surface of the reference material when using a fine-grained additive and darker when using a coarse-grained additive. The research presented in the experiment allows to understand the mechanism of color change of a ceramic material and to design a material with better color properties.

## Acknowledgements:

Kornelia Wiśniewska has been partly supported by the EU Project POWR.03.02.00-00-I038/16-00.This work was supported by the Polish Ministry of Science and Higher Education under the subsidy no. 16.16.160.557

# Ring shear based powder analyzer as a device for testing the rheological properties of granules for the production of ceramic tiles

Łukasz Wójcik[1], Marcin Gajek[1], Alicja Rapacz-Kmita[1], Joanna Mastalska-Popławska[1], Izabela Puchyrska[2], Robert Pacan[2], Dawid Cegłowski[2], Yurii Delikhovskyj[1], Piotr Izak[1]

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## Abstract:

The rheological properties of granulates for the production of ceramic tiles are particularly important due to the stages of the production process. After production, the granulate is transported to silos, where it is self-compacted, and then is subjected to a pressing process. All these stages affect its rheological properties, which ultimately translates into the degree of filling the mold and the final properties of the product. Research on the rheological properties of powders and granules can be carried out in several ways, starting from the simplest ones - measuring angle of fall through a Ford cup, ending with much more sophisticated ones, where rheometers operating at controlled shear rate are used. (CR) and powder analyzers based on the Shulz ring shear tester.

In this work, ceramic tiles granulates of various grain size compositions were examined using the Brookfield PFT device, determining the flow function, time related flow function and bulk density as a function of consolidation stress, and the classic tests of the angle of repose and the bulk density were carried out.

The obtained results showed that the classic tests, consisting in measuring the angle of fall, only to a small extent illustrate differences between granulates, and flow function measurements are a much better analysis tool to precisely illustrate the changes in the flow of granulates along with the change in their particle size distribution.

# Decreasing Usage of Zinc Oxide and Zircon in Sanitaryware Glazes

Ebru Çırakman

*ECZACIBAŞI BUILDING PRODUCTS INC. CO. - VitrA, Bilecik, Turkey*

**Abstract:**

In this project, the same surface quality with cost-effective alternative raw materials is achieved by reducing the proportions of zinc oxide and zircon, which are the most expensive raw materials according to the cost index. The project is customized by taking advantage of the principles known in the literature as "Zachariasen's Rules for Glass Formation".

# Elastic property evolution of silicate ceramics in the CaO–Al2O3–SiO2 system determined via temperature-dependent impulse excitation

Petra Šimonová, Eva Gregorová, Willi Pabst

*University of Chemistry and Technology, Prague, Prague, Czech Republic*

## Abstract:

Silicate ceramics from the CaO–$Al_2O_3$–$SiO_2$ system are important in wall tile production and in the context of ancient ceramics. The system is rather complex due to the occurrence of calcium-aluminum-silicate phases like gehlenite and anorthite. This work summarizes the reactions that may occur in this system and reports experimental results obtained for uniaxially pressed powder compacts based on kaolin-limestone mixtures fired at different temperatures (from 650 to 1300 °C). The crystalline phase content of the different samples was determined by XRD (Rietveld-based semi-quantitative phase analysis). The ceramics were characterized by the Archimedes technique (open porosity 33-37 % and bulk density 1.7-1.8 g/$cm^3$), and helium pycnometry was used to determine the true density of the samples (2.4-2.7 g/$cm^3$). The glass phase content, together with the total porosity, was determined from the deviation of the measured true density from the sample's theoretical density as calculated on the basis of the crystalline phases alone. Elastic properties were measured via the impulse excitation technique at room temperature (Young's modulus 26-36 GPa, shear modulus 11-14 GPa) and during heating up to 1200 °C. The measured temperature dependence of Young's modulus reveals the temperatures of the reactions that are taking place during firing, including decomposition reactions such as the dehydroxylation of kaolinite and the decarboxylation of calcite. Moreover, when the original firing temperature is exceeded, the elastic moduli exhibit a steep increase that indicates the continuation of sintering and densification. Thus, the impulse excitation technique can complement (and in some cases even replace) the characterization of similar samples by conventional thermal analysis techniques.

## Acknowledgements:

This work was part of the project GA22-25562S "Impulse excitation as an unconventional method for monitoring phase changes and microstructure evolution during thermal loading of materials", funded by the Czech Science Foundation (Grantová agentura České republiky / GAČR). This work was supported from the grant of Specific university research – grant No. A2_FCHT_2022_004. Additional support from the grants of Specific university research – grant No. A1_FCHT_2022_002 is gratefully acknowledged as well.

# Symposium K: ICC9 Industrial and Educational Session

# Ceramic Roadmap to 2050

Renaud Batier (Belgium)

*Cerame-Unie – The European Ceramic Industry Association, Brussels, Belgium*

„In light of the EU's objective to achieve climate neutrality by 2050, the European Ceramic Industry developed a new decarbonisation Roadmap. This document presents how the ceramic industry can achieve carbon neutrality by 2050, a number of policy recommendations designed to ensure that and how the sector can fully contribute throughout its very wide and numerous value chains to the well-being of a resilient climate neutral society in 2050.

The Ceramic Roadmap to 2050: Continuing our Path to Climate Neutrality showcases what climate neutrality means for Ceramics. This is shown through the presentation of a decarbonisation model and pathway, technologies and decarbonised energy required, CO2 abatement costs and policy requirements, necessary for the European ceramic industry to successfully engage on the path towards climate neutrality and achieve the goals and ambitions of the EU Green Deal.

Renaud Batier, Director-General of Cerame-Unie – The European Ceramic Industry Association, will present the ceramic industry's path to decarbonisation and discuss the availability of the resources to enable the green transition. In the Ceramic Roadmap to 2050 we indicate that such alternative energy sources will be needed as: decarbonised electricity, green hydrogen, or biogas by 2050. Their supply however does not depend on the industry itself but on many factors, such as infrastructure and the right legal and policy framework."

# The refractory industry in the EU - as it stands and in view of future expectations

Jerzy Czechowski

*Refractory Materials Producers Association, Kraków, Poland*

## Abstract:

The world production of refractory materials is 34-35 million tons and, according to the forecast of one of the analysts, it will remain at a similar level until 2030. The production of refractory materials in the EU in 2020 amounted to approx. 4.8 million tons, worth about EUR 3.8 billion. Poland, which produces approx. 320 thousand tons, ranks 5th in Europe.

The situation of manufacturers of refractory materials is influenced by a number of factors, the most important of which are:

1. the situation of industries using refractory materials,
2. access and prices of raw materials,
3. energy prices,
4. legal regulations related to climate change,
5. unpredictable events: pandemic, war in Ukraine.

Individual factors were discussed, emphasizing the importance of dynamic changes that took place in the recent period and their impact on demand, production costs and competitiveness. Problems on the raw material market were presented. It was pointed out that apart from the awareness of the scarcity of natural resources, environmental protection and the pursuit of a circular economy, the rising costs of raw materials significantly contribute to the increased interest in recycling.

Reference was made to the model of gradual emission reduction in the ceramics industry presented by UC in "Ceramic Roadmap to 2050". The possibilities and limitations related to the implementation of certain solutions in refractory material sector were discussed.

The impact of the pandemic and the war in Ukraine on the production of refractories in the EU has been assessed.

# Ceramic demolition waste in the circular economy

Thomas Kronberg, Jan-Erik Eriksson, Leena Hupa

*Åbo Akademi University, Turku, Finland*

## Abstract:

Ceramic waste recycling and reusing is a way forward into a circular economy. Today, the utilisation of ceramic demolition waste is low. One reason is that a systematic collection system is lacking. Usually, a large quantity of sanitaryware, tableware, and ceramic tiles is collected as mixed demolition waste with concrete and bricks. However, the traditional sanitaryware and ceramic tiles consist of compounds produced in high-temperature reactions. Therefore, their end-of-life fractions are energy-intensive, valuable secondary materials for new materials and applications. Our new project aims to find more efficient ways to sort, recycle and reuse ceramic demolition waste.

The first project task was to map the quantity and quality of ceramic demolition waste generated in Finland. Then, the average composition of the sanitaryware and ceramic tiles in the demolition waste was analysed. The proportion of other materials (plastics, metal, mortar, etc.) remaining in the ceramic demolition waste was calculated based on the overall analyses. After mapping the potential utilisation of the waste fractions, the share and composition limits of these fractions to fit the properties and essential quality criteria of the most promising new applications were calculated. In this presentation, we report the first laboratory results of the influence of ceramic waste-based fractions for alkali-activated materials. The compressive strength development, durability, and morphology of mixtures consisting of the ceramics waste fractions and other inorganic large scale industrial side-streams together with different alkali activators will be discussed. Initial results will be presented on the impact of ceramic demolition waste as a substitute for natural minerals and/or cement in concrete.

# The waste glass as a base of the lining tiles. The results of the POIR project.

Zbigniew Woźniak

*Ceramika Paradyż, Opoczno, Poland*

## Abstract:

The presentation is a summary of the results obtained in the project POIR.01.02.00-00-0073/17, called as "Developing and confirming the final form of an innovative technology of manufacturing full-value cladding ceramic tiles from multi-grade waste glass - a breakthrough in the ceramic industry".

The strong ties of the business activity with the surrounding environment influences the undertaking by Ceramika Paradyż Sp. z o.o. pro-climatic activities. "Successful participation in the

competition for funding under sectoral programs allowed for the implementation of a project based on the concept of using glass waste while reducing CO2 emissions. This article presents a description of the work carried out and the results obtained during them. The ambitious design

assumptions concerned the use of glass waste at the level of 90% of the mass composition, while maintaining all standard quality requirements for ceramic lining products." [MCCM, Ceramic Materials, 73,1, 2021]

## Acknowledgements:

"Work financed under Measure 1.2: Sectoral R&D programs of the Smart Growth Operational Program with the support of co-financing granted by the National Center for Research and Development in the scope of funds from the EU European Funds Intelligent Development No. POIR.01.02.00-00-0073/17-00.I would like to thank the employees of the National Center for Research and Development of the Łukasiewicz Research Network, the Institute of Ceramics and Building Materials in Warsaw, and my colleagues from Ceramika Paradyż Sp. z o.o. who contributed to the implementation of the above project. Simple in assumption, it turned out to be demanding in implementation, discovering its complexity from the technical, process and economic point of view at subsequent stages.I would like to thank the editors of the "Materiały Ceramiczne /Ceramics Materials/" and "Glass and Ceramics" magazines for publishing the results of the project and contributing to their preparation for printing." [MCCM, Ceramic Materials, 73, 1, 2021]

# Symposium L: ECerS and JECS Trust Awards Ceremony

## Invited presentation:

# Large ceramic slabs: A tale of industrial research and innovation

Franco Stefani

*SYSTEM CERAMICS, Fiorano, Italy*

## Abstract:

A forward-looking approach and advanced technology reinvent the world of ceramics: with Lamina, System has transformed ceramics into an authentic surface. A state-of-the-art technology that has definitively revolutionized the use of this material, opening up new user and market sectors.

Explore, Dream, Discover. It was perhaps this that Franco Stefani, founder of the System Group, had in mind when in 2000 he presented Lamina technology for the first time at Ceramitec in Munich: a process that has revolutionized the traditional concept of ceramics, giving new life to this material. From the idea of a single tile came the development of an actual surface covering up to 1800x4800 mm with thickness ranging from 3 to 30 mm. It's a journey that has been transformed into an industrial adventure for its captain, founder in the 1970s of the System Group, which is today one of the most important enterprises in the world in the sector of industrial automation. The company has paved the way in ceramic innovation with brand new applications, entering sectors that until now simply could not be served. Its solutions are renowned for technology and architecture, where ideas are transformed into a unique and original work, in which the ceramic surface can be perceived as a canvas, a blank sheet ready to welcome the creativity of the artist, designer and architect. It's a technology that enchants and convinces by virtue of its versatility and its variable characteristics, able to produce the largest and thinnest ceramic slab in the world. This transformation, led by System, has meant that many areas hitherto unexplored have now become accessible, such as the furnishing and interior design sectors.

The invention of Lamina is an achievement that sees architecture and the art of living as an expression of human talent as, thanks to this process, unique surfaces can be obtained which, for example, are able to reproduce the finish of rusted metal, or the tactile sensation of wood and its natural veining, while maintaining the same qualities over time. Infinite applications are possible, where man with his imagination is free to retrace paths of antiquity, choosing perhaps marble, granite or the more precious stones in nature, or taking a more adventurous approach towards avant-garde architecture with cements, resins and metal effects in order to portray a futuristic vision of the world.

What lies behind the invention of Lamina is considerable research and development, market observation, process analyses and major challenges overcome over the years; when presented for the first time, sector professionals simply could not fully comprehend its potential and above all the standing it would have in later years, to the point of now being a leading reference technology worldwide. This industrial adventure started with Mr. Franco Stefani with his strong passion for science ever since he was a child, along with an innate curiosity regarding unexplored territories and that "artisan" spirit so dear to the Renaissance age.

# Bioceramics for Healthcare: Where the future lies?

Bikramjit Basu

*Indian Institute of Science, Bangalore, India*

## Abstract:

The next generation of engineering ceramics in healthcare is spearheaded by two core aspects, a) better (more holistic) understanding of their interactions with the components of the biological system at multiple length and time scales; b) probing the biocompatibility of lesser-explored ceramics for biomedical applications. The biocompatibility of materials is determined by their application-specific desired responses with proteins, cells, tissues, and blood. First, the Molecular Dynamics (MD) simulation results will be described to demonstrate the temporal kinetics of the fibronectin protein adsorption on doped hydroxyapatite (HA). In substantiating the second aspect, the cell and tissue compatibility of perovskites (BaTiO3, CaTiO3), either in particulate format or in bulk composite with HA, will be discussed. Some recent developments on blood compatible SiCxNyOz and BCxNyOz coatings will be presented next, in the context of their potential cardiovascular applications.

Towards the end of the presentation, a set of policy-related recommendations to take labscale research to large-volume manufacturing of implantable biomaterials will be discussed with a particular emphasis on the need for intense collaborative efforts among researchers from Academia, National laboratories, medical fraternity and industries. It has been envisioned that the Data Science (e.g. Artificial Intelligence/ Machine Learning algorithms) driven 'Biomaterialomics' approach will enable the integration of the computational tools, databases, experimental methods, machine learning, and advanced manufacturing (e.g., 3D printing) on a single platform. Such strategy will allow the accelerated development of the fourth-generation biomaterials and implants, whose clinical performance will be predicted using 'digital twins'. A few published studies from the speaker's research group serve as representative examples to illustrate the formulation and relevance of the 'Biomaterialomics' approaches for three emerging research themes, i.e. patient-specific implants, additive manufacturing, and bioelectronic medicine. Given the right support, the key recommendations of the speaker can be highly transformative to the field, while benefitting people's well-being and advancing economic development in many nations, in their energy and momentum.

# Zirconia for dental applications: what can we do with the 'ceramic steel'?

Jérôme Chevalier

*Université de Lyon, INSA-Lyon, UMR CNRS 5510 MATEIS, 20 Avenue Albert Einstein, 69621 Villeurbanne Cedex, France*

## Abstract:

40 years ago, Garvie and his Australian co-workers reported that the stress induced transformation of metastable tetragonal zirconia grains to the monoclinic symmetry could give rise to a powerful toughening mechanism. Their results even led them to consider zirconia systems as analogues of certain steels in terms of mechanical performances. This seminal paper generated extraordinary excitement in the ceramic community and led to a large variety of new applications, with a special interest in orthopedics first then in dentistry today. Zirconia in dentistry was first developed for dental restorations, for which translucency and optical properties must be associated to a high mechanical resistance and stability in vivo, and then for implantology where biological integration is emphasized.

Here we show that 'dental zirconia' is not one but a family of materials, with many different (mechanical/optical) properties. Playing with the microstructure (grain size), alloying (choice of dopant and content) and phase content through processing, it is possible to develop zirconia ceramics with a high degree of translucency and/or high strength and/or a certain transformation-induced plasticity before failure. Thus, 40 years after their inception for structural applications, zirconia ceramics can answer different needs as a function of the targeted application/product. We thus review the current choice of zirconia ceramics available for dental use and show current trends both for restoration and implantology, considering that there is always a trade-off between often mutually exclusive properties. New developments must be based on a solid knowledge on the strength of a given material (e.g. the ability to transform under stress), but also its weaknesses and points of vigilance (e.g. sensitivity to water-induced species). In this context, we present the research conducted at INSA-Lyon in collaboration with several (industrial and academic) groups these past 10 years on yttria-doped zirconia with an excellent balance between translucency-aging resistance-strength and on both ceria-doped and yttria-doped compositions that exhibit some transformation-induced plasticity before failure. These new developments may create new opportunities for clinicians in their practice. We also discuss about the added values and challenges of additive manufacturing in the framework of 'dental zirconia', as well as surface engineering that play a major role on biological integration of implants.

# Unique properties of layered inorganic materials

Ondrej Jankovsky

*UCT Prague*

## Abstract:

Layered inorganic materials possess many unique properties because of which they are widely used in energetics, catalysis, and electronics or as a part of complex composites. This contribution will focus mainly on misfit cobaltites, superconducting cuprates, and 2D carbon-based nanomaterials.

Misfit layered cobaltites belong to the group of high-temperature thermoelectrics with positive thermopower. To tune the material properties, it is necessary to understand the phase relations in these systems. Based on the experimentally obtained thermodynamic data and subsequent phase equilibria modeling, the Bi-Co-O, Sr-Co-O, Ca-Co-O, Bi-Sr-Co-O, and Bi-Ca-Co-O phase diagrams were constructed.

The research of the second group of high-temperature superconducting cuprates was focused mainly on the REBCO system, where RE = Y, Gd, Eu. Large-single domain REBCO bulks with sizes up to 150 mm can be prepared by the top-seeded melt growth technique. The growth experiments were underpinned by thermodynamic modeling of solid-liquid equilibria. Prepared bulks possess a unique ability to trap large homogenous magnetic fields, allowing the minimization and simplification of MRI machines. In addition, self-stabilizing magnetic levitation between REBCO bulks and permanent magnets allows for the construction of advanced contactless bearing and levitation conveyors. Thin-film REBCO tapes are an upcoming form of REBCO superconductors with many prospective applications.

At last but not least, is the area of 2D carbon-based nanomaterials. Notably, the optimization of graphite oxidation, the study of the mechanism of graphite oxides reduction, the synthesis of chemically modified graphenes, the synthesis of new carbon derivatives such as graphene acid, and the preparation of unique graphene oxide films were performed. With a wider variety of 2D carbon-based nanomaterials with faster and more reliable manufacturing, many prospective applications for 2D carbon nanomaterials are considered. Including but not being limited to heavy metals sorption from water, metal melt filtration in the steel industry, or enhancements of magnesium oxychloride cement for the construction industry.

# From Pottery to Battery - Advanced Ceramic Energy Storage Materials

Ralf Riedel

*Technische Universität Darmstadt, Institut für Materialwissenschaft, Otto-Berndt-Str. 3, D-64287 Darmstadt, Germany*

## Abstract:

The increase in energy density and power density requirements for lithium-ion batteries leads to continuous research for new electrode materials. Various insertion materials have been proposed as negative electrodes for rechargeable batteries. The highest theoretical capacity can be obtained when using metallic lithium (3862 mAh/g) or elemental silicon forming lithium-rich alloys (3578 mAh/g), however these materials are not commercialized due to safety reasons and rapid capacity fading, respectively. At present, mostly graphitic materials are used due to low price and high reversibility despite relatively low capacity (372 mAh/g), instability during long-time cycling and inadequacy high power applications. Therefore, new materials, which are economically interesting but demonstrate higher capacity, longer lifetime and better high rate capability, are urgently required to meet the technological demands of our future electro mobility and energy storage applications. In this context, novel anode materials based on ceramic nanocomposites comprised of derivatives of ternary SiCN and SiOC systems are discussed and evaluated in terms of their electrochemical performance.

## Reference:

Dragoljub Vrankovic, Magdalena Graczyk-Zajac, Constanze Kalcher, Jochen Rohrer, Malin Becker, Christina Stabler, Grzegorz Trykowski, Karsten Albe, and Ralf Riedel, Highly Porous Silicon Embedded in a Ceramic Matrix: A Stable High-Capacity Electrode for Li-Ion Batteries, ACS Nano 2017, 11, 11409-11416

# The Ball-on-Three-Balls-Test: Comparison with the Ring-on-Ring-Test for Ceramics

Maximilian Staudacher, Tanja Lube, Peter Supancic

*Department of Materials Science, Montanuniversität Leoben, Leoben, Austria*

## Abstract:

The strength of ceramic products that are available as (thin) discs or plates can be measured using biaxial strength tests. In the standardized Ring-on-Ring test, specimens with a diameter to thickness ratio $D/t \geq 10$ are supported by a ring and loaded coaxially with a smaller ring. Using compliant interlayers, an even load distribution under the loading ring is ensured and the influence of friction is minimized. The maximum tensile stress at failure is determined from the load at failure and the test geometry using analytically derived relations. For the Ball-on-Three-Balls test, specimens with $4 \leq D/t \leq 20$ are positioned on three balls which are free to roll and loaded by a fourth ball. Fitted analytical expressions of Finite-Element Analysis (FEA) results are utilized to evaluate the maximum tensile stress of the specimen and are available for many specimen size variations.

For this work, these tests were conducted and modified on alumina discs. The modifications involve the use of varying intermediate layers and multiple specimen geometries. Their results are compared based on Weibull theory. It is shown how the utilized interlayers or their absence influence the measured strength values. The obtained results are extensively rationalized with FEA to evaluate the effects of deviations from ideal loading conditions. More specifically, the influence of friction between sample and fixture and the effects of an inhomogeneous load distribution on the maximum stress were investigated. To support these findings, fractography was conducted.

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