

# BOOK OF ABSTRACTS



FunGlass School 2022/2 Congress Centre of SAS Smolenice September 26-28







FunGlass School 2022/2

**Book of Abstracts** 

Smolenice, Congress Centre of SAS, September 26-28, 2022

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## Obsah

Z. Neščáková / Laboratory of biological testing at FunGlass - needs vs. possibilities
E. Vidomanová / Biological methods for the study of biomaterials
Z. Vargas / 3D bioactive composite scaffolds with high drug loading capacity for bone tissue engineering
S, Chen / Preliminary Study on Bioactive Glass Scaffolds with Biomimetic Cortical Bone Hierarchical Porous Structure
F. Kurtuldu / Gallium-containing mesoporous glass nanoparticles for bone regeneration 8
K. Mosas/ Ceramic Coatings for High Temperature Environments
M. Parchovianský / Synthesis and characterization of La <sub>2</sub> Ce <sub>2</sub> O <sub>7</sub> powder, mechanical and thermal properties of La <sub>2</sub> Ce <sub>2</sub> O <sub>7</sub> -YSZ composites
I. Parchovianská / Hydrothermal Corrosion of Double-Layer Glass/Ceramic Coatings Applied to AISI441 Stainless Steel Substrates
O. Sharifahmadian / Role of Fluorine in hydrophobicity and nanomechanical properties of the Diamond-like carbon (DLC) film on glass substrate
Ashokraja C. / Controlling AZ31 Mg alloy degradation <i>via</i> PEO-58S sol gel duplex coatings
A. Dasan / Binder-Jetting 3D Printing: Opportunities and Challenges
A. Mehta / Waste-derived Glass as Precursor for Inorganic Polymers: from Binders to photocatalytic destructors for Dye Removal
A. Novokhatska / Design and Manufacturing of Self-supported Electrolytes for Solid Oxide Fuel Cells Application by Stereolithography 3D Printing
R. Dagupati / $Er^{3+}$ doped oxyfluoride Silicate Glass-ceramics: Analysis of spectral conversion and ratio metric optical thermometry for temperature sensor application 17
M. Blaško / Experimental and theoretical study of the $(Ce_{0.2}La_{0.2}Pr_{0.2}Sm_{0.2}Y_{0.2})O_{2-\delta}$ high entropy oxide with fluorite structure
N. Mutlu / Biodegradable chitosan-based foams containing borate bioactive glasses for wound healing applications
M. Vitázková / Fabrication of B and Co co-doped mesoporous bioactive glass for enhanced angiogenesis
A. Anand / Blending of Cu and Sr amount in MBGs to establish the synergic effects on in- vitro bioactivity, cytotoxicity, and antimicrobial activity
A. H. Haridasan / Effect of annealing temperature and surfactant addition on the photocatalytic activity of ZnO thin films
H. Kandi / Novel smart phosphors for NIR mechanoluminescence and biomechanical imaging
B. Wolfrum / Red emission enhancement of YAG:Eu <sup>3+</sup> , YAG:Mn <sup>4+</sup> nanocrystals in YAG aggregates
Mai-Phuong N. Truong / Er <sup>3+</sup> /Yb <sup>3+</sup> Co-doped Oxyfluoride Transparent Glass-Ceramics Toward Up-Conversion Optical Properties



				O nanodendrites plitting	0		-	
			0	corrosion-resistance	•	•	, ,	
A. Gamal / Combination of cold plasma spray and Ion-exchange treatment for improvement of borosilicate glass vials for pharmaceutical packaging								
<b>M</b> . 1	Mokhtar /	' Inn	ovative Dye	e Sorbent Based on A	Additive Manufac	turing	g Technique	31
	-			ure properties of ge			-	
G. 7	Fameni / J	Upcy	cling of wa	ste glasses in novel	sustainable const	ruction	n materials	33



### Laboratory of biological testing at FunGlass - needs vs. possibilities

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#### ABSTRACT

On the occasion of the completion of the reconstruction and the opening of the new premises of the Funglass Center intended for biological analysis of materials, it is necessary to present the needs and possibilities that these new premises can offer.

The evaluation of the biological safety of all biomaterials which is coming to contact with the human body and could potentially cause any kind of harm or damage is mandatory. Together with the extensive physicochemical characterization, biological evaluation is an important part of risk assessment. Biological evaluation includes several steps and one of them is the assessment of biocompatibility, it's mean the measurement of how compatible materials are with biological systems. Thus, biocompatibility testing is a set of interrelated *in vivo* and *in vitro* tests that is important to eliminate unnecessary testing on animal models. In our laboratories, we focus on assessing biocompatibility with biological test methods based on *in vitro* models. cytotoxicity, hemocompatibility and genotoxicity by several different methods depending on the studied materials can be evaluated. Moreover, based on the final application we can perform special experiments outside the tests included in the biocompatibility testing as an assessment of bioactivity and biodegradability. Besides that, we can study biological effects such as protein adsorption, pyrogen test, endotoxin test, oxidative response, and antimicrobial properties.

The construction of these laboratories of biological testing of biomaterials opens a new era at FunGlass and represent a space that enables basic but also less conventional tests needed to assess the suitability and safety of the studied materials.

Keywords: Laboratory of Biological testing, biocompatibility, cytotoxicity, hemocompatibility and genotoxicity

#### Acknowledgment:





### **Biological methods for the study of biomaterials**

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#### ABSTRACT

Over the last decades, biomaterials became a very promising, interesting, and rapidly proceeding field of research. Biomaterials have a great impact on medical treatment and contribute to therapeutic or diagnostic medical needs. In vitro cell cultivation represents a standard method for the study of different effects of stress or improvements in environmental conditions. In traditional 2D cell cultures, cells grow as a monolayer on the surface of cultivation dishes to mimic the human body. Cells spread in 2D conditions on flat and hard surfaces and proliferate unnaturally. Many scientific works described the difference in cellular morphology, phenotype and functions, as cytoskeletal rearrangements, and aberrant gene expression, compared to cells in the natural environment. In the effort to create models which are more closely able to mimic conditions in vivo, 3D culture systems have gained increased popularity. The development of novel 3D in vitro models contributes to improvement in the field of cancer research, stem cell research, as well as drug and toxicity screening. Research strategies nowadays are also focusing on extending study opportunities for biomaterials in biological fields. I would like to show the possibilities of cell signaling pathways study, in cell cultures affected by biomaterials, on the model of apoptotic programmed cell death. Identification of changes in cell signaling pathways can significantly contribute to understanding biomaterials' effects in the treatment of damaged or diseased tissues.

Keywords: biomaterials, 3D cell cultivation, cell pathways study, apoptosis

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## 3D bioactive composite scaffolds with high drug loading capacity for bone tissue engineering

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#### ABSTRACT

As the aging population increases, the demand for highly functionalized biomaterials also increases at a considerable rate, driving the design of more precise and sophisticated structures. Particularly for injured bone tissue, its regeneration and recovery of its natural biological functionality remain a challenge<sup>1</sup>. In this regard, the development of novel organic/inorganic hybrid biomaterials has become necessary since the mixture of components of different nature provides special properties to the final material. The objective of this work is to develop hybrid scaffolds intended to mimic the structure of natural trabecular/cancellous bone with a high loading capacity of molecules of biological interest<sup>2</sup>. To achieve this aim, natural polymers and mesoporous silica were chosen, which allowed producing by freeze-drying a bioactive matrix of polysaccharides where modified SBA-15 rods were embedded. As a result, highly porous structures with an interconnected hierarchy of pores were observed by scanning electron microscopy (SEM) analysis. After studying these systems by mercury intrusion porosimetry (MIP), and from the data obtained, it was possible to calculate and estimate different properties associated with their porous nature using Pore Xpert software. The proposed theorical structure helped to understand their high loading capacity. Behavior that was evaluated and confirmed after loading simvastatin, which was released in a sustained manner over a long period of time.

**Keywords:** 3D scaffolds, high loading capacity, highly porous structures, modified SBA-15 rods, organic/inorganic hybrid biomaterials, polysaccharides.

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#### **References:**

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## Preliminary Study on Bioactive Glass Scaffolds with Biomimetic Cortical Bone Hierarchical Porous Structure

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#### ABSTRACT

Bone tissue is divided into cortical and cancellous bone, where cancellous bone exhibits a porous structure with fully interconnected pores of 300-1600  $\mu$ m in diameter [1], while cortical bone has a complex layered pore structure. Cortical bone contains a variety of fine structures, such as Haversian canals in the 30-100  $\mu$ m range, Volkmann canals and osteocyte lacunae in the 5-15  $\mu$ m range, and small vascular channels and canaliculi in the 1-5  $\mu$ m range [2, 3]. A great deal of research has been devoted to the fabrication of tissue engineering scaffolds that mimic the textural structure of cancellous bone, while less has been reported on tissue engineering scaffolds that mimic cortical bone due to its more complex hierarchical structure.

The combination of bioactive glass microsphere/nanoparticle hydrogel composites with freezedrying technology is promising for the construction of hierarchical porous scaffolds with nanopores, micropores (1-20  $\mu$ m) and oriented micropores (30-110  $\mu$ m). This approach allows the tailoring of micron pore characteristics of scaffolds by controlling the freeze drying process and the ratio of microspheres/nanoparticles. Oriented micron pores will be achieved by freeze-drying techniques [4]. Microspheres with micron-scale pores (pore sizes mainly between 1-20  $\mu$ m) are produced by flame synthesis. Dense nanoparticles are produced by the sol-gel method. Microspheres and nanoparticles are dispersed in a polymer solution to form a hydrogel and freeze-dried to obtain a three-dimensional scaffold, which is then sintered to obtain a hierarchical porous bioactive glass scaffold.

In this preliminary study, bioactive glass microspheres and nanoparticles were dispersed in a gelatin/tannic acid aqueous solution to form a hydrogel composite, which then directly sintered without freeze-drying process to obtain the hierarchical porous bioactive glass scaffolds. SEM, EDX and XRD were carried to evaluate the hierarchical porous structure and bioactivity of these scaffolds.

**Keywords:** microspheres, nanoparticles, freeze-drying, sintering, hierarchical porous structure, bioactivity

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### Gallium-containing mesoporous glass nanoparticles for bone regeneration

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#### ABSTRACT

Mesoporous silica nanoparticles in the systems  $SiO_2$ -Ga<sub>2</sub>O<sub>3</sub> and  $SiO_2$ -CaO-Ga<sub>2</sub>O<sub>3</sub> have been synthesized using a microemulsion assisted sol-gel method. SEM, XRD, FTIR, and the N<sub>2</sub> adsorption-desorption method were used to characterize the physicochemical properties of nanoparticles (NPs). According to the electron microscopy and N<sub>2</sub> adsorption-desorption analysis, the presence of calcium affected the morphology and textural features of NPs. The calcium addition was increased the average diameter of the NPs (80 nm to 150 nm), and decreased their specific surface area (972 m2/g to 486 m2/g). Moreover, the morphology of all the samples was spheroidal, with a disordered mesoporous structure. An ion release study showed a sustained release of gallium in cell culture medium. In direct contact with NPs at concentrations of up to 100 µg/mL, Ga-containing NPs were non-cytotoxic to pre-osteoblast MC3T3-E1 cells. Moreover, in-vitro cell culture tests showed that Ga addition to NPs enhanced the alkaline phosphatase (ALP) activity and mineralization while disturbing osteoclast differentiation of RAW 264.7 cells. Physicochemical properties and biological characteristics of gallium containing nanoparticles make them a promising candidate for multifunctional applications, including drug delivery carriers or bioactive fillers for bone tissue engineering.

Keywords: bioactive glass, gallium, mesoporous, nanoparticle

#### Acknowledgment:





### **Ceramic Coatings for High Temperature Environments**

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#### ABSTRACT

High temperature corrosion on alloys and metals is one of the major issues for the selection and service life prediction of metallic components, which are operated at high temperatures. Metals and alloys must be protected against corrosion because their mechanical and tribological properties deteriorate at high working temperatures. Inward diffusion of oxygen, carbon, or sulfur may lead to the precipitation of by-products such as oxides, nitrides, sulfides, carbides, and/or their mixtures, resulting in a loss of material stability and a shortened lifespan for the components Coatings are layers of a material deposited onto the surface of a material as a protective layer to enhance the surface properties and create a corrosion-resistant barrier. The choice of coating materials may be desirable to protect the underlying substrate materials either as diffusion barrier layers, sacrificial layers, or electrochemical modifiers.

Thermal barrier coatings (TBCs) are ceramic coatings with very low thermal conductivity that reduce the alloy surface temperature by insulating it from the hot gas, and their development has been the primary focus in the high temperature materials industry for the past three decades. Plasma spraying (PS) and electron beam physical vapor deposition (EB-PVD) have recently been used in industrial production to manufacture TBCs. The high capital investment required, as well as the feasibility of coating complex and large components, limits the use of PS and EB-PVD processes.

Inorganic silicate coatings are very promising material for such protective coatings on different surfaces, including metal, due to their superior mechanical, chemical, and thermal resistance properties and are included in the category of high-performance coatings. Silicate-based binders can chemically react with the steel substrate, resulting in excellent adhesion of the coating and abrasion resistance of the dried/ cured film. Even though these coatings show reduced water stability, their adhesion to metal substrates and thermal resistance are excellent, and their properties can be tailored by varying the elemental composition. The coating formulations can be applied to various substrate components by well-established techniques such as spraying, dipping, dip-spin and brush techniques.

We aim to develop low cost, durable room temperature curable TBC formulations based on inorganic silicate binder, and to assess their microstructure, high temperature performance, repeatability, and reproducibility of the coatings.

**Keywords:** Alkali metal silicate, Geopolymer, High temperature oxidation, Hot corrosion, Thermal barrier coatings.

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## Synthesis and characterization of La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> powder, mechanical and thermal properties of La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub>-YSZ composites

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#### ABSTRACT

In this work, La<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub> (LC)powder was synthesized by solid-state reaction and investigated as a material for TBCs application. Moreover, LC-yttria-stabilized zirconia (LC-YSZ) composites with different content of YSZ (40 - 70 wt. %) were prepared by conventional mixing of LC and YSZ powders, followed by sintering of the powders by hot pressing at 1400 °C for 1 h. Scanning electron microscopy (SEM) of the prepared LC powder revealed agglomerated structure consisting of finely and uniformly distributed grains with a 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 behaviour of the LC powder was analyzed by differential scanning calorimetry (DSC) in the temperature range of 25 °C - 1350 °C. Neither endothermic nor exothermic peaks were observed from the DSC curve at the tested temperature range, indicating the high phase stability of the LC powder and its suitability for TBC applications. LC-YSZ composites with varying wt. fractions of YSZ (40-70 wt. %) were made by hot pressing and examined as a material for thermal barrier-coating (TBC) applications. For this reason, the impact of YSZ addition on phase composition, microstructure, mechanical performance, and thermal behaviour was investigated. XRD examination revealed that the LC-YSZ composites were mostly formed of a cubic ZrO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>-ZrO<sub>2</sub> solid solution with a pyrochlore structure, indicating that the reaction between LC and YSZ occurred during hot pressing. SEM demonstrated that the produced composites had great microstructural stability, as pore development was significantly controlled and a high relative density (>97%) was attained. The microstructure of LC-YSZ bulk samples was fine-grained, with an average grain size of less than or close to 1 m. The Vickers hardness (HV) of the LC-YSZ composites was increased by YSZ doping; the composite containing 70 wt. % of YSZ had the maximum HV, with a value of  $12 \pm 0.62$ GPa. LC-YSZ composites have fracture toughness values ranging from 2.13 to 2.5 MPa.m<sup>1/2</sup>. There was no statistically significant variation in heat capacity or thermal conductivity between the composites with varying YSZ contents. According to the findings, LC-YSZ composites exhibit relatively low thermal conductivities between ambient temperature  $(1.5-1.8 \text{ W.m}^{-1}\text{.K}^{-1})$  and 1000  $^{\circ}$ C (2.5–3 W.m<sup>-1</sup>.K<sup>-1</sup>). The LC-YSZ composite materials that have been developed are thus suggested to be promising candidates for TBC applications.

Keywords: solid-state reaction, LC-YSZ composites, mechanical and thermal properties

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### Hydrothermal Corrosion of Double-Layer Glass/Ceramic Coatings Applied to AISI441 Stainless Steel Substrates

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#### ABSTRACT

The objective of the present study is to demonstrate the possibility of fabrication of environmental barrier coatings on metallic substrate (stainless steel AISI441) as well as to asses and discuss their corrosion behavior under hydrothermal conditions. For that purpose, a double layer coating consisting of a polymer derived ceramic (PDC) bond-coat and a PDC top-coat that contains ceramic passive and glass fillers were developed. To investigate the environmental protection ability of the coatings, quasi-dynamic corrosion tests under hydrothermal conditions were conducted at 200 °C for 48 – 192 h. The extent of corrosion in the coated and uncoated samples was monitored by the weight change of the corroded samples, followed by detailed study of the microstructure, phase and chemical composition before and after corrosion tests, and the formation of corrosion products.

Two types of corrosion product morphologies were found on the exposed uncoated steel surface. Most of the surface was covered by a thin layer of rod-shaped crystallites identified by Raman spectroscopy as a mix of Fe<sub>2</sub>O<sub>3</sub> and (Mn, Cr, Fe)<sub>3</sub>O<sub>4</sub> spinels. Occasionally, Fe- and Cr-enriched globular crystallites were found on the corroded steel surface after the corrosion tests. In the case of the coated samples, scanning electron microscopy (SEM) of the corroded surfaces revealed randomly distributed globular crystallites approximately 3.5 µm in diameter. Energy dispersive X-Ray spectroscopy (EDXS) of the precipitates showed the presence of Ba, Al, Si, and O. Analysis of corrosion solutions by inductively coupled plasma optical emission spectrometry (ICP-OES) confirmed the presence of Ba, Al, Si, Y, Zr, and Cr, the main component of the steel substrate, in the corrosion medium. The results of weight gain measurements together with SEM and ICP-OES indicate that a state of saturation was achieved in the early stage of the dissolution reactions. These reactions were followed by the precipitation of spherical-shaped BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> crystals. The predominant phases detected after corrosion tests by X-ray powder diffraction analysis (XRD) were monoclinic and cubic ZrO<sub>2</sub>, originating from the used passive fillers. In addition, the crystalline phase of BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> was also identified, which is in accordance with the results of EDXS analysis of the precipitates formed on the coating surface.

Keywords: coatings, corrosion, fillers, PDC, stainless steel

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## Role of Fluorine in hydrophobicity and nanomechanical properties of the Diamond-like carbon (DLC) film on glass substrate

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#### ABSTRACT

Recently, growing needs of having hydrophobic surfaces with low friction coeficient has been great interest in various applications such as self-cleaning windows, glass windshields, and photovoltaic cells. To improve both hydrophobicity and tribological properties of the glass, the plasma enhanced chemical vapor deposition (PECVD) technic with mixtures of CH<sub>4</sub> and CHF<sub>3</sub> were used to fabricate the fluorine-doped diamond-like carbon (F-DLC) film. The X-ray photoelectron spectroscopy results showed that by incorporating the fluorine into the DLC film, some fluorocarbon compounds such as CF, CF<sub>2</sub> and CF<sub>3</sub> were formed. The  $sp^3/sp^2$  ratio of the carbon atoms reduced as fluorine atomic concentration increased in the films confirmed by the Raman spectroscopy. Presence of fluorocarbon compounds on the surface improved the hydrophobicity of the F- DLC films compared to the fluorine-free DLC film. A strong correlation between the fluorine content and the nanomechanical properties of the DLC film reduced by adding fluorine into the DLC film. The fluorine into the DLC film reduced by adding fluorine into the DLC film. The fluorine doped DLC film with moderate concentration of fluorine (19.2 at. %) will enable the development of the robust interfaces with excellent hydrophobicity for self-cleaning application.

Keywords: DLC, Fluorine, Hydrophobicity, Self-cleaning, Plasma

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## Controlling AZ31 Mg alloy degradation *via* PEO-58S sol gel duplex coatings

#### Ashokraja C.<sup>1</sup>, E Merino<sup>2</sup>, A.H. Pakseresht<sup>1</sup>, D. Galusek<sup>1</sup>, A. Duran<sup>2</sup>, Y. Castro<sup>2</sup>

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#### ABSTRACT

Magnesium (Mg)-based materials, a new generation of orthopaedic implant materials, are projected to replace permanent implants due to their similar mechanical qualities to bone and the fact that they totally disintegrate under physiological conditions. Despite their biocompatibility, the quick degradation of Mg-based materials under physiological conditions prevents their clinical application. To circumvent this constraint, a variety of techniques, including alloying elements, surface treatment, and surface modification/coating, have been employed to manage the Mg degradation rate.

In the current study, oxide layers were developed by plasma electrolytic oxidation (PEO), and then 58S bioactive glass was deposited on AZ31 Mg-alloys through dip coating. Glycerol (GLY), ethylene glycol (EG), and polyethylene glycol 200 (PEG), which also act as bonding agents for the coatings at annealing temperatures, were used to stabilise the 58S sol. According to the polyols used, the effect of the polyols on coating morphology and thickness resulted in thicknesses ranging from 1.5 to 1.76  $\mu$ m. As a result, different contact angles based on the polyols were established. The most hydrophilic thin films were PEG (17.5° contact angle), then polyol-free thin films (28°), and the least hydrophilic thin films were GLY (37°) and EG (39°). Systematically, all of the films were investigated by XRD, RAMAN, and FESEM. To determine the biodegradability profile under physiological settings, the electrochemical impedance as well as pH variations and hydrogen release were measured.

Keywords: Bioactivity; Bioglass; Dip coating; Control degradation; Plasma electrolytic Oxidation

#### Acknowledgment:





### **Binder-Jetting 3D Printing: Opportunities and Challenges**

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#### ABSTRACT

Technology advancements in 3D printing or Additive Manufacturing (AM) have allowed printed parts to meet product performance requirements and be cost-effective at low production volumes without expensive tooling. Binder Jetting (BJ) is an AM process based on conglomerating powderbased materials employing a liquid binding agent. The advantage of BJ technology is not only great design freedom but also that no support structures are needed, and warping is not an issue. Moreover, the range of printing materials (including metals, polymers, sands, and ceramics) is relatively wide. BJ is attractive for several industrial sectors, such as aerospace, medical, and automotive. However, developing novel materials with suitable binders and subsequent postprocessing methods that maximize part performance is still a challenge.

This presentation demonstrates the BJ 3D printing (Voxeljet, VX200, Germany) of sand-based materials (SiO2, quartz) with complex architectures. Challenges associated with the printing process include 3D modeling, additive direction, and the effect of the binder (furfuryl-based) and activator (mixture of xylene and toluenesulphonic acid) will be discussed. Finally, opportunities for future development toward industrial application will also be addressed.

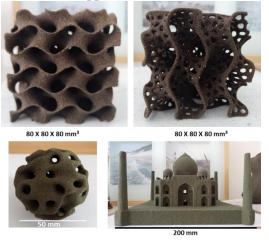


Fig.1 Demonstration models printed by binder-jetting

Keywords: Binder-Jetting, Additive Manufacturing, Powder bed, Ceramics, Glasses

#### Acknowledgment:





## Waste-derived Glass as Precursor for Inorganic Polymers: from Binders to photocatalytic destructors for Dye Removal

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#### ABSTRACT

Binders for the building industry (e.g., portland cement) generally having a significant environmental impact. The interesting replacement is offered by inorganic polymers (IPs), i.e., gels typically achieved by low temperature with the dissolution of alumino-silicate raw materials, in alkaline environment, followed by condensation reactions. Synthetic alumino-silicate glasses may yield inorganic polymers, through activation with alkali hydroxide solutions. In this framework, we formulated a glass prepared by the melting of red mud from bauxite refinement, combined with coal combustion fly ash, discarded pharmaceutical glass and a minor addition of sodium carbonate. The activation with 6 M NaOH aqueous solution allowed for the manufacturing of highly porous foams, by gas generation at the early stages of gelation. These foams featured an extensive formation of zeolite at cell walls which, combined with the presence of magnetite formed upon cooling of the melt, favoured the application of the foams as sorbents for dye removal from contaminated water. The powders prepared by crushing the highly porous foams showed an excellent water purification ability documented by efficient removal of methylene blue used as a model contaminant. The specific iron oxide polymorph facilitated both magnetic recovery of dispersed powders and photocatalytic destruction of the dye under UV irradiation.

Keywords: Alkali activation; gelation; sorbents; zeolites; dye removal.

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## **Design and Manufacturing of Self-supported Electrolytes for Solid Oxide** Fuel Cells Application by Stereolithography 3D Printing

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#### ABSTRACT

Solid oxide fuel cell (SOFC) is a promising electrochemical energy conversion device operating at temperatures 800–1000°C, which has attracted much attention for its high conversion efficiency, environmental friendliness, and high fuel flexibility [1]. A SOFC stack fabricated by conventional manufacturing processes such as tape casting, punching, screen-printing, laminating, and stacking commonly requires lots of steps that are not only time-consuming and not reproducible, but the cost is extremely high [2]. Moreover, these techniques allow manufacturing of only planar or tubular SOFCs that affect stack geometries and their power output.

The three-dimensional (3D) printing technology is rapidly evolving owing to its advantages of material saving, high production efficiency, and low cost. 3D printing methods have widened the scope for designing more performing microstructures for SOFCs [3]. Topological modifications of electrolytes facilitate ion transport and increase the electrochemical performance of the cell. The project aims to study all aspects of 3D printing, debinding, and sintering electrolyte ceramic materials to optimize its parameters for the preparation of high-quality self-supported SOFCs. In this work, new approaches of 3D printing were explored with the aim of thickness reduction and increasing the surface area of yttria-stabilized zirconia self-supported electrolytes.

The slurries with different solid loading ratios (30, 50 and 70 % wt.) using photo-curable resin (Flexible UV sensitive resin for 3D printing, Prusa Research a.s., Prague, Czech Republic) and yttria-stabilized zirconia powder (8 mol.% yttria, TZ-8Y, Tosoh Corp., Japan) were prepared. Planar electrolytes with different thicknesses (150, 250 and 500 µm printed in 3, 5 and 10 layers, respectively) were manufactured with the use of a stereolithography (SLA) 3D printer (Original Prusa SL-1, Prusa Research a.s., Prague, Czech Republic) operating in the visible light range (405 nm) and sintered at up to 1500 °C in air. The shrinkage and density of printed objects were investigated. The results show that after sintering at 1400 °C the shrinkage is 33 % for all specimens, plate thicknesses decreased by 10 times compared to green bodies and reached the 15 µm for samples printed in 3 layers. The maximum value of ceramic density is 5.54 g/cm<sup>3</sup> for samples printed in 5 layers that is approximately 93 % of theoretical density  $(5.96 \text{ g/cm}^3)$ . It was found that an increase in the sintering temperature up to 1500 °C did not affect the increase in the density and shrinkage of printed samples. The ceramics microstructure, phase stability, and mechanical properties of printed electrolytes will be examined.

Keywords: SOFCs, SLA-3D printing, yttria-stabilized zirconia, self-supported electrolyte.

#### **Acknowledgment:**



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Infrastructure and funded from the European Regional Development Fund.

## Er<sup>3+</sup> doped oxyfluoride Silicate Glass-ceramics: Analysis of spectral conversion and ratio metric optical thermometry for temperature sensor application

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#### ABSTRACT

In many scientific and technical domains, temperature (T) is a vital parameter that has to be monitored with accuracy [1]. Traditional temperature measurement tools, including contact temperature sensors based on electrical changes in materials, have limitations in a range of circumstances, including nano- and micro-scale regimes, quickly moving objects, corrosive environments, within cells, and so on [2, 3]. Therefore, the creation of affordable, transportable, trustworthy, and secure temperature sensors is crucial for a variety of applications. Because of its quick response, electromagnetic passivity, self-reference, and high sensitivity, optical thermometry based on fluorescence intensity ratio (FIR) has drawn a lot of attention in recent years among the various temperature measurement techniques.

In this context, the transparent oxyfluoride glass-ceramics (GCs) with embedded  $Na_{1.5}Y_{1.5}F_6$  crystals doped with  $Er^{3+}$  ions were made utilizing a melt-quenching process and subsequent heat treatment. The precipitation of crystals and partition of the  $Er^{3+}$  dopant into the crystals were confirmed using structural characterizations and spectroscopic methods. Glass-ceramics that were doped with  $Er^{3+}$  (Er-GC) exhibit an up-conversion (UC) emission that was bright green. The temperature range of 298 K to 823 K was used to examine the temperature-dependent visible UC behavior based on thermally coupled energy levels (TCLs) and non-thermally coupled energy levels (NTCLs), with a maximum relative sensitivity ( $S_r$ ) of 1.1% K<sup>-1</sup> for TCLs in Er-G and Er-GC samples at 298 K.

**Keywords:** Oxyfluoride silicate glass-ceramic; Photoluminescence; Optical thermometry; Up-Conversion; Relative sensitivity.

#### Acknowledgment:



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#### ABSTRACT

A new class of ceramics, called Entropy Stabilized Oxides (ESO) or High Entropy Oxides (HEO), has gained significant interest over the years due to their unique structural characteristics and correlated possibilities for tailoring of functional properties. Manipulation of configurational entropy is the main key for extraordinary behaviours, leading to unprecedented material design and innovations. Substantial research has been conducted on HEO bulk systems [1,2]. The diversity of materials design, provided by the entropy-mediated phase-stabilization concept, allows engineering of new oxide candidates for practical applications such as energy storage, water splitting, catalysis, thermoelectricity generation, and others. It has been shown that oxide ceramics containing rareearth elements (REE) in equimolar ratios have a strong tendency to crystallize in single-phase structures, stabilized by the high configurational entropy[3]. In this study, multicomponent rare-earth oxide were synthesized by solid state sintering with using combinations of Ce, La, Pr, Sm, and Y oxides in equimolar proportions. A combination of Ce and Pr in the ME-REO (multicomponent equiatomic rare earth oxide) systems helps to achieve both phase purity and lower band gap, which are largely independent of the other RE cations present. Prepared samples annealed in the air and cooled slowly led to a phase conversion from single fluorite to single bixbyite structure [4,5]. These results suggested that the structure stabilization depends not only on the entropy effect, but also on the type of cations, the synthesis method, heating and cooling rates and crystallite size. The effects of composition, sintering atmosphere, and cooling rate on phase formation were investigated. The system shows single cubic or monoclinic structures obtained through a slow cooling, confirming that the rare-earth oxides follow a different structure stabilization process than transition metal high-entropy oxides. The microstructure of the material was studied using SEM, EDS and XRD methods. The theoretical approach such as molecular dynamics, density functional theory will be focused on finding stable structures for particular composition and optical, mechanical, and thermal properties will be calculated. Also, it will be used to find stable structures for different compositions with variable molar ratios of REE. Understanding the electronic structure of atoms and solids, phase formation of multicomponent rare-earth oxide ceramics is essential for design new materials.

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Keywords: High-entropy ceramic, Functional ceramics, High-entropy ceramic, sintering, DFT.

#### Acknowledgment:



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### Biodegradable chitosan-based foams containing borate bioactive glasses for wound healing applications

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#### ABSTRACT

Wound healing is one of the complex physiological responses of a living system to an injury. It involves various cell types and their interactions to restore tissue integrity. To help the process, a scaffold can be applied, which has to fulfil several key requirements. It must be non-toxic, maintain a moist environment, have highly porous structure, and be permeable to water and gases. Wound dressings that can deliver various biologically active agents represent a new generation of materials for wound therapy. One of the most frequently used dressing materials is chitosan. It is non-toxic, biocompatible, and biodegradable with strong antibacterial and hemostatic activity. In this study, we produced chitosan-zinc complexes by an in-situ precipitation method and combined them with borate-based bioactive glasses. The foam-based platforms were produced for dual delivery of therapeutic ions via freeze drying technique. The resulting foams showed a highly porous structure. The biodegradation of the foams was investigated in lysozyme containing medium as a function of pH up to 7 days incubation: significantly increased zinc release was detected at low pH (4.5). The cytotoxic response and cellular attachment were assessed with stromal cells and mouse fibroblasts respectively. A positive effect of the foams on cell viability and migration was observed. The novel biocomposites show promising properties for their use in wound treatment.

Keywords: borate bioactive glass, chitosan, chelation, zinc, wound healing

#### Acknowledgment:





## Fabrication of B and Co co-doped mesoporous bioactive glass for enhanced angiogenesis

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#### ABSTRACT

Mesoporous bioactive glass nanoparticles (MBGNPs) doped with Boron and Cobalt in the binary system of SiO<sub>2</sub>-CaO were synthesized using the microemulsion-assisted sol-gel method. This modified Stöber method ensures the synthesis of nanoparticles without agglomeration and allows to control over properties of nanoparticles such as pore volume, pore size and particle size. Both boron and cobalt, have known to show an angiogenic effect [1], [2] as they affect two important angiogenic paths upregulating hypoxia-inducible factor  $1\alpha$  (HIF-1a) and intensification of TNF- $\alpha$  in fibroblasts [2], [3]. To achieve these effects, it is necessary to adjust the chemical concentration and degradation rate of glasses for optimum therapeutic effect without causing cytotoxicity. Therefore, it's necessary to study the doping of therapeutic ions effect on the morphology, textural and chemical properties of MBGNPs. For this reason, MBGNPs were doped individually with boron and cobalt and then codopped with both of these ions to achieve the synergic effect on angiogenesis. Scanning electron microscopy analysis revealed spheroidal particle shape and their average size in between 100 to 230 nm. XRD diffraction patterns showed that all samples were amorphous. Furthermore, the chemical compositions were determined by the acid digestion method using the inductively coupled plasma-optical emission spectrometer (ICP-OES). The bioactivity and ion release behaviour of MBGNPs was studied in simulated body fluid (SBF) for up to 7 days of incubation. Ion release study showed burst release of therapeutic ions after 1 day of incubation, followed by a steady release of ions up to 7 days. These preliminary results of cobalt and/or boron-doped MBGNPs shows potential for enhancing the angiogenesis activity of biomaterials.

Keywords: MBGNPs, therapeutic ions, angiogenesis

#### Acknowledgment:



This item 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 739566.

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## Blending of Cu and Sr amount in MBGs to establish the synergic effects on in-vitro bioactivity, cytotoxicity, and antimicrobial activity

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#### ABSTRACT

Mesoporous bioactive glass (MBG) is a suitable material for therapeutics ion delivery in bone-tissue regeneration approaches. Two MBG glass powders, one doped with 4 mol.% of copper (Cu) second with 4 mol.% of strontium (Sr) were blended together in the weight ratios of (Cu:Sr; 70:30, 50:50, 30:70 to reduce the cytotoxicity of Cu and enhance the antimicrobial and angiogenesis activity of Sr. The synergic effects of Cu and Sr ions on bioactivity, cytotoxicity, and antimicrobial activity were studied in detail. The TEM examination of Cu-MBG and Sr-MBG initially characterized by transmission electron microscopy showed fringes related to the formation of ordered mesoporous structures. The specific surface areas of the Cu-MBG and Sr-MBG was 286 and 348 m<sup>2</sup>/g, respectively.

X-ray diffraction (XRD) confirmed the formation of hydroxyapatite (HAp) layer when soaked in stimulated body fluid for all studied samples. The system with the Cu:Sr ratio of 30:70 showed diffraction pattern with a higher intensity of the diffraction maxima attributed to HAp, comparing to other blended samples. Due to similar ionic radii of  $(Ca^{2+} 1Å \text{ and } Sr^{2+} 1.16Å)$  a high amount of Sr can replace Ca in the crystal lattice of HAp. Cauliflower-like morphology characteristic for HAp crystals was observed for all blended powders by SEM. The blended powder showed higher cell viability (up to 90%) towards MC3T3-E1 preosteoblast cells at powders concentrations of 1 wt./vol.% or lower. The release of Cu ions from the powders generate hydroxyl radicals and enhances the pH which disturbed the cellular membrane of microbes and results in enhanced antimicrobial activity against gram negative *E.coli* and gram positive *S. aureus* bacteria.

The obtained result suggest that blending of Cu and Sr doped MBG combines an effect on bioactivity, and bone cells viability with antibacterial properties. It is proposed that the observed features of Cu and Sr 30:70 blended MBG system may offer multifunctional properties for bone tissue regeneration.

Keywords: bioactive glass, bioactivity, cytotoxicity, synergic effect

#### Acknowledgment:





## Effect of annealing temperature and surfactant addition on the photocatalytic activity of ZnO thin films

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#### ABSTRACT

The heterogeneous photocatalysis is one of the most effective methods for environmental remediation. During the last two decades,  $TiO_2$  has been considered a benchmark photocatalyst associated with its positive properties. However, ZnO has gained considerable importance during the last years due to its excellent properties, including favourable band-gap positions, low cost, high redox potential, nontoxicity, and environmentally friendly features [1]. Among the different synthesis techniques, sol-gel technique is one of the most attractive methods to prepare ZnO as a coating due to its low-cost and low-temperature process, fine control of the morphology, and high compositional homogeneity. Moreover, the development of ZnO photocatalyst as a film offers many advantages over the use of powder catalysts, such as easier fabrication and no need to remove the residual powders after the photocatalytic process [2]. Although ZnO photocatalysts have been the subject of numerous investigations, it is still a challenge to increase their photocatalytic activity. Recently, many works have focused their attention on the development of ZnO coatings with high specific surface area through the incorporation of surfactants to enhance the photocatalytic activity [3].

In this work, we have studied the importance of annealing temperature and the effect of addition of Triton x-100 on the photocatalytic activity of ZnO thin films prepared by sol-gel and deposited by dip-coating method. ZnO coatings have been prepared using a ZnO sol prepared in basic condition and deposited on glass-slide and annealing at different temperatures (300 - 550 °C / 1 h). Then, the coatings have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), ellipsometry, ultraviolet-visible spectrophotometry (UV–Vis) and X-ray photoelectron spectroscopy (XPS). The photocatalytic activity was studied considering the decomposition of methyl orange dye under solar light irradiation. XRD pattern and Raman spectra confirmed hexagonal wurtzite structure as the unique phase of ZnO thin films. The maximum degradation of methyl orange under a solar irradiation was obtained for ZnO thin films annealed at 400 °C / 1 h. The addition of Triton-100 to ZnO sols increases the photocatalytic activity of ZnO coatings.

**Keywords:** Methyl orange, Photocatalytic activity, Sol-gel method, ZnO thin films. **References:** 

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## Novel smart phosphors for NIR mechanoluminescence and biomechanical imaging

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#### ABSTRACT

A phosphor is a sort of luminescent substance that may emit light when exposed to a certain type of incident energy without being heated. Phosphors may be excited by a broad variety of energy sources; this allows for a rich taxonomy of luminescence phenomena, such as photoluminescence, cathodoluminescence, electroluminescence, chemiluminescence, and mechanoluminescence [1]. Mechanoluminescence (ML) refers to the luminescence that occurs when a material is subjected to any mechanical stress which has piqued the curiosity of experts in recent years. Deformation of solids by mechanical stimuli might be elastic, plastic, or fracture [2]. In the framework of mechanoluminescence, a number of different synthesis techniques, including solid-state reaction (SSR), sol-gel (SG), and others, have been created and analyzed [3].

Near-infrared emitting phosphors are in scarce supply despite their importance in medical imaging applications. On the other hand, more intelligent materials are required for the modern age. Smart materials (such as, piezoelectric, ferroelectric materials (FEMs), etc. (Figure 1)) are a kind of intelligent materials that can perceive, process, and react to one or more environmental stimuli in a reversible and controlled manner (such as, electric or magnetic field, mechanical stress, temperature, chemical or light signals) [4]. Among these materials, FEMs are still in their infancy as a research tool. As a result, finding brighter, more practical smart phosphors requires a trial-and-error approach.

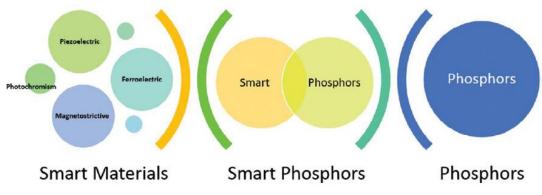


Fig. 1 The smart phosphors approach [4].

The preparation of smart materials (piezoelectric/ferroelectric) doped with RE ions (such as,  $Nd^{3+}$ ,  $Er^{3+}$ ) and as new type of the smart phosphors for mechanoluminescence and biomechanical imaging in the NIR spectral range is the focus of the PhD research. The structure and morphology of the prepared ML materials such as phase composition, particle size, sample morphology, and homogeneity of the dopant distribution in the prepared samples will be characterized. Extensive research and analysis into the influence of dopant concentration on the emission characteristics of ML materials, as well as an investigation of the luminescence properties of these materials both without and under mechanical stimuli, will be done.

**Keywords:** Bioimaging, Ferroelectric Materials (FEMs), Mechanoluminescence (ML), Near-infrared (NIR), Smart Phosphor, Solid-State Reaction (SSR), Sol-gel (SG).



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## Red emission enhancement of YAG:Eu<sup>3+</sup>, YAG:Mn<sup>4+</sup> nanocrystals in YAG aggregates

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#### ABSTRACT

The widespread substitution of fluorescent lighting by solid-state lighting in the last decade enabled important energy savings, going from 60 lm·W<sup>-1</sup> for a mercury vapour lamp to light-emitting diode (LED) lamps released last year achieving 210 lm·W<sup>-1</sup>[1]. These new light sources generally lack in the orange–red part of the spectrum. Red radiation in common light fixtures demands harsh conditions for the synthesis of the emitting species, generally doped fluorides or nitrides. In addition, to improve the colour uniformity cast by the lamps, visible–light diffusers are blended in the resin containing the phosphors. Herein is proposed a combination of safer to synthesise phosphors and inclusion of the diffusers in the phosphor matrix, as an attempt to improve the optical properties. A blend of SiO<sub>2</sub> nanospheres acting as light scatterers and  $Y_3Al_5O_{12}$  garnet (YAG) doped with Ce<sup>3+</sup> ions is compared to an inclusion of such scatterers in the same matrix. Then, YAG:Eu<sup>3+</sup> and YAG:Mn<sup>4+</sup> powders are synthesised to study their viability as red emitters.

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## Er<sup>3+</sup>/Yb<sup>3+</sup> Co-doped Oxyfluoride Transparent Glass-Ceramics Toward Up-Conversion Optical Properties

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#### ABSTRACT

Transparent oxyfluoride glass-ceramics (TGCs) doped with rare earth ions (RE<sup>3+</sup>) are one of the most promising groups of materials for high efficiency photoluminescence (PL) up- and down-conversion. TGCs are well suited for using in optoelectronics because of their transparency, mechanical and chemical resistance, low phonon energies and low refractive index inherited from fluoride crystals. To achieve the transparency of GCs, crystal size, morphology, isotropic crystalline phases and their homogeneous distribution in glass matrix need to be strictly controlled [1]. Li<sup>+</sup> ions are regarded as an alternative to Na<sup>+</sup>/K<sup>+</sup> in the crystalline phases of scheelite-type tetragonal morphology [2]. In particular, LiYF<sub>4</sub> crystals are considered a suitable matrix for trivalent RE<sup>3+</sup> ions with high capacity for isomorphic replacement of Y<sup>3+</sup> ions by other RE<sup>3+</sup> ions due to their similar ionic radio without strong effect on the lattice structure. With the smaller cationic radius compared to Na<sup>+</sup>/K<sup>+</sup>, and higher cation polarization power, the substitution of Li<sup>+</sup> can cause crystal field distortion and increase the asymmetry environment around the trivalent lanthanide ions. Therefore, it significantly affecting the emission intensity as reported recently [2, 3].

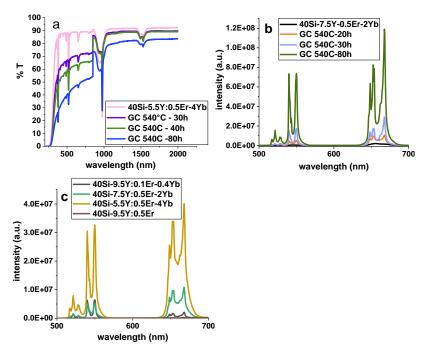


Fig 1. (a) Transmittance of the parent's glass 40Si-5.5Y:0.5Er-4Yb and its GCs treated at 540°C, for 30, 40 and 80h, (b) PL spectra of the GCs treated for 20, 30 and 80h at 540°C compared to their parent glass, and (c) PL spectra of various doped-GCs treated at 540°C for 20h.

In this study, the glasses with the composition of 40 SiO<sub>2</sub>-25 Al<sub>2</sub>O<sub>3</sub>-18 Li<sub>2</sub>O-7 LiF-(10-x-y) YF<sub>3</sub>-x ErF<sub>3</sub>y YbF<sub>3</sub> (x = 0, 0.1, 0.5; y = 0, 0.4, 2, 4) were prepared by melting and fast quenching processes, and subjected to thermal treatment at low temperatures, above glass transition temperature (T<sub>g</sub>+35°C), for



long dwell times (20, 40 and 80 h) to obtain GCs [4]. Under optimal temperatures and dwell times, ceramization process took place and nanocrystals of the fluorides were precipitated from the parent glass. The formation of GCs containing LiYF<sub>4</sub> nanocrystals was confirmed by XRD analysis. At fixed temperature 540°C, the increase in dwell times led to the increase in crystal formation and luminesce yield. Scherer's equation estimated the size of the LiYF<sub>4</sub> nanocrystals to be ~10 nm. The phases AlF<sub>3</sub> and LiSiAlO<sub>4</sub> are also present with crystal sizes ~20 nm after 80h of thermal treatment. Due to the nanosized crystals, which were significantly smaller than the wavelength of visible light, the GCs products were transparent in near-infrared and visible spectral region. However, the increase in thermal treatment dwell time led to the significantly decrease in transparency of the sample at visible window (Fig. 1a). In contrast, light emission increased with treatment times, around six times higher for 80 h of treatment compared to the 20 h one (Fig. 1b). There is energy transfer from Yb<sup>3+</sup> to Er<sup>3+</sup>, resulting in a higher UC luminescence yield compared to the solely Er<sup>3+</sup>-doped glass/GC systems (Fig. 1c).

**Keywords:** lithium fluoride, oxyfluoride, photoluminescence, rare earth ions, transparent glass-ceramics.

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## BiVO<sub>4</sub>/ZnO nanodendrites heterojunction as photoanode for photoelectrochemical water splitting

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#### ABSTRACT

A large electrochemical active surface area, broadband light harvesting and fast charge transport through 3D nanorods (NRs) assembly and photosensitization with narrow bandgap semiconductors offer an infusive way to advance the photoelectrochemical (PEC) performance. Here, BiVO<sub>4</sub>/ZnO nanodendrites (NDs) heterojunction was fabricated via a combination of the hydrothermal and electrodeposition processes. The primarily grown ZnO NRs on ITO glass substrates serve as the trunks for the branches of the NDs. Scanning electron microscopy and X-ray diffraction observations exhibits that well-aligned wurtzite ZnO NRs and monoclinic BiVO<sub>4</sub> were successfully formed in the heterojunction film. UV–vis spectroscopic measurements reveals that BiVO<sub>4</sub>/ZnO NDs possesses excellent light harvesting capability from the UV to visible light region, demonstrating the potential application as highly effective visible light photoanode. PL analysis displays significant inhibition of the recombination of photogenerated electrons and holes as a consequence of the formation of BiVO<sub>4</sub>/ZnO NDs heterojunction. Therefore, we believe that BiVO<sub>4</sub>/ZnO NDs may have a great potential as a photoanode in PEC cells in the light of the achieved morphological and optical characteristics.

Keywords: BiVO<sub>4</sub>, Photoanode, Photoelectrochemical water splitting, ZnO nanodendrites.

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## Integrated corrosion-resistance system for Al alloys (AA2024-T3) via Polyorganosilazane/GPTMS

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#### ABSTRACT

hybrid polyorganosilazane (OPSZ) 3-In the present study, а combined with glycidyloxypropyltrimethoxysilane (GPTMS) coatings were successfully synthesized for the first time to enhance the corrosion resistance of AA2024-T3 aluminum alloy. The polymers were cross-linked with the addition of tetra-n-butylammonium fluoride (TBAF), and the hybrid coatings were deposited on aluminum substrates by monolayer immersion and dried at 120°C for 2 h in the air. The obtained films were transparent, with a thickness of around 13  $\mu$ m. The kinetics of the degradation process of the prepared coatings was monitored using the potentiodynamic polarization technique (PDP) and electrochemical impedance spectroscopy (EIS) in 3.5 wt.% NaCl at room temperature. The electrochemical results confirmed that the synthesized hybrid coatings significantly improved the corrosion resistance of the aluminum substrate at 3.5 wt.% NaCl for a shorter exposure time. Field emission electron microscopy (FESEM) studies were performed to characterize the coating morphology and thickness. Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) and nuclear magnetic resonance (NMR) were used to keep track of chemical changes in the coatings. Contact angle measurements were performed to identify the wettability of coatings, which indicated that the hybrid coatings were hydrophobic and the contact angle was  $93 \pm 6^{\circ}$ .

Keywords: Corrosion, Polysilazane, GPTMS, Synthesis, Coatings, Electrochemistry, Al alloys

#### Acknowledgment:





## Combination of cold plasma spray and Ion-exchange treatment for improvement of borosilicate glass vials for pharmaceutical packaging

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#### ABSTRACT

The characterization, modification, and improvement of the surface of glasses for packaging of pharmaceutical drugs like vials, ampoules, prefilled syringes, and cartridges are a topic of primary importance especially when it aims at a substantial improvement of the final patient safety. Recently developed drugs are substances of increased complexity that can in some cases interact with the glass surfaces causing inactivation or dangerous adverse reactions like delamination. The aim of this work is to treat and improve the surface of the basic borosilicate glass vials by using a combination of two types of treatments. So at the first, the borosilicate type I glass vials received from Nuova OMPI company will be treated by cold plasma spray treatment by using different types of plasma burning (Air & Argon), and the adjustment of time from (5-10 seconds) is enough to fully coated of the inner surface of glass vials, then directly the ion-exchange process by using KNO3 at different conditions will be applied to the plasma treated vials at different temperatures (400, 450 & 500°C) for (2, 12 and 24 hrs.) to develop innovative/modified surface of glass vials. Furthermore, there is a need of new analytical methods aimed at characterizing these interactions occurring, and analyzing the surface chemical composition, mechanical and corrosion resistance properties of the treated glass vials. The morphology and basic chemical composition of vials will be investigated by Scanning Electron Microscopy (SEM with EDS detector) and X-ray photoelectron spectroscopy (XPS). The hydrophobicity/hydrophilicity of the inner surface will be assessed by dye tests with measuring of contact angle.

Keywords: Borosilicate Glass vials, Plasma treatment, Ion-exchange Process and Delamination

#### Acknowledgment:





## Innovative Dye Sorbent Based on Additive Manufacturing Technique

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#### ABSTRACT

Additive manufacturing (3D Printing) technologies enable the fabrication of objects with complex geometries in much simpler ways than conventional shaping methods. In the current study, we have applied stereolithography (SLA), which belongs to a family of additive manufacturing known as vat-polymerizations. all these machines are built around the same principle, using a light source, a laser or a projector to solidify a photosensitive resin into a hardened material. Pharmaceutical glass waste was milled and sieved below 40  $\mu$ m. Fine glass waste was suspended in the photocurable resin with a solid loading weight of 55 wt%. Gyroid structures were printed with a layer thickness of 50  $\mu$ m. After debinding, and sintering, the printed gyroids were immersed in 2.5 molars of sodium hydroxide for initiating alkali activation for 1 hour. The printed activated and non-activated gyroids were examined to adsorb methylene blue dye, and the adsorption efficiency of the printed glass gyroids was compared to other recent printed materials including titania, carbon, and ceramic filters.

**Keywords:** alkali activation; additive manufacturing; dye sorbents; glass waste; stereolithography.

#### Acknowledgment:





## High-temperature properties of geopolymers prepared from waste glass and AZS refractory

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#### ABSTRACT

Geopolymer materials, synthesized from silica and alumina-rich precursors, have excellent fire and heat resistance properties compared to conventional materials like Ordinary portland cement. However, the study of geopolymer materials properties when exposed to high temperature still requires a detailed study, especially when it comes to waste glass powder-based geopolymers. In this preliminary study, the effect of the addition of used AZS refractory powder and alkali concentration on the thermal properties of the geopolymer material is discussed. Geopolymer samples were prepared by mixing different weight ratios of glass fiber waste with AZS refractory powder and mixed with 3-8M of alkali solution (NaOH or KOH). Samples were cured at 60°C for 24hrs. Physical and chemical tests like FTIR, XRD, density, and strength tests were used to characterize the geopolymer samples after 28 days of curing. The samples were exposed to high temperatures of 800°C-1000°C for 1hr. Weight loss and XRD measurements were conducted to understand the post-exposure characteristics.

Keywords: AZS Refractory, glassfiber waste, geopolymer, thermal resistance.

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#### Upcycling of waste glasses in novel sustainable construction materials

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#### ABSTRACT

In the field of sustainability, recycling of glass is complex process. Not all type of glasses are easly recyclable and the exclusion may be due to the strict chemical composition and/or optical quality demands on final products, or to possible noxious emissions during re-melting [1]. COVID-19 emergency has increase the production of boro-alumino-silicate pharmaceutical glass that is not recyclable in a 'closed-loop'. One way could be 'open-loop' recycling, when glass could be reused for a new generation of marketable products, in a different context. The difference between economic value of the new products and manufacturing costs represents an undoubtedly challenging factor: only if high, open-loop recycling can be properly seen as 'upcycling' [2]. This work is focused on alkali activation of glass waste to obtain innovative and sustainable construction materials. The activation process is performed suspending fine milled waste ( $\emptyset < 75 \ \mu m$ ) in weakly alkaline solution (2.5 – 5 M) of NaOH and/or KOH. The solid loading is 60 wt%. During the mechanical stirring (500 rpm, 3 h) the alkaline solution partially dissolves the waste. The suspension is dried at 40°C for 7-14 days to obtain the final building material: new bonds between particles are created during this last phase of the process.

Pharmaceutical boro-alumino-silicate glass (referred as BASG; chemical composition:  $SiO_2 = 72$  wt %,  $B_2O_3 = 12$  wt %,  $Al_2O_3 = 7$  wt %,  $Na_2O = 6$  wt %,  $K_2O = 2$  wt %, CaO = 1 wt %, BaO < 0.1 wt %) with different grades of impurities has been tested in order to evaluate the efficacy of recycling processes; at the same time sodalime glass (referred as SLG; chemical composition:  $SiO_2 = 71$  wt %,  $Al_2O_3 = 1.2$  wt %, Na<sub>2</sub>O - K<sub>2</sub>O = 14.5 wt %, CaO = 7.5 wt %, MgO = 4 wt %) has been tested with addition of volcanic ash to improve mechanical properties. Preliminary comparative studies between BASG and SLG matrices allow to say that the first is better in harsh performances. Concerning BASG, best results have been obtained increasing stirring temperature (40°C) or molarity (5 M). Thanks to its properties, BASG has been used also as a matrix to embed other waste materials after mechanical stirring such as Plasmastone, foundry sands and bricks powder. Speaking about sodalime glass, it's possible to observed best results thanks to the addition of volcanic ash. It's possible to notice a significant increase in compressive strength, thanks to the replacement of glass with volcanic ash up to 50 wt%. In addition to compact products, to obtain materials with thermal and acoustic insulation properties, it has been also explored the possibility to foam, at room temperature, the activated mixture using sodium perborate monohydrate as foaming agent and sodium dodecyl sulphate (SDS) as stabilizing agent. First studies show that it's possible to tune pores dimension and mechanical resistance changing stabilizing agent and volcanic ash quantities, respectively. Samples have been characterized from different point of view. Boiling tests have been pursued to evaluate the stability of the gel formed during the drying phase. From the physical and chemical side, it has been used FTIR spectroscopy and XRD. Density and porosity analyses has been performed because of the interest to evaluate close and open porosity. To evaluate the mechanical properties the samples have been subjected to compressive strength. Finally, selected samples have been analysed using SEM-EDX for microstructural characterization.

Thanks to these preliminary studies it is possible to conclude that building materials could be obtained using glasses for which the conventional recycling methos are not allowed, such as the pharmaceutical BASG. The addition of foaming agent and stabilizing agent allows to obtain materials for thermal and acoustic insulation applications. Moreover, inert materials could be added to the glass matrix to obtain products comparable with the ones on the market and eventually that the use of other industrial waste



materials like wastewater or glass allow to obtain building materials, therefore a high degree of purity of the starting materials is not required.

Keywords: Alkali activation, Construction materials, Foam, Pharmaceutical glass, Waste valorizatio

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