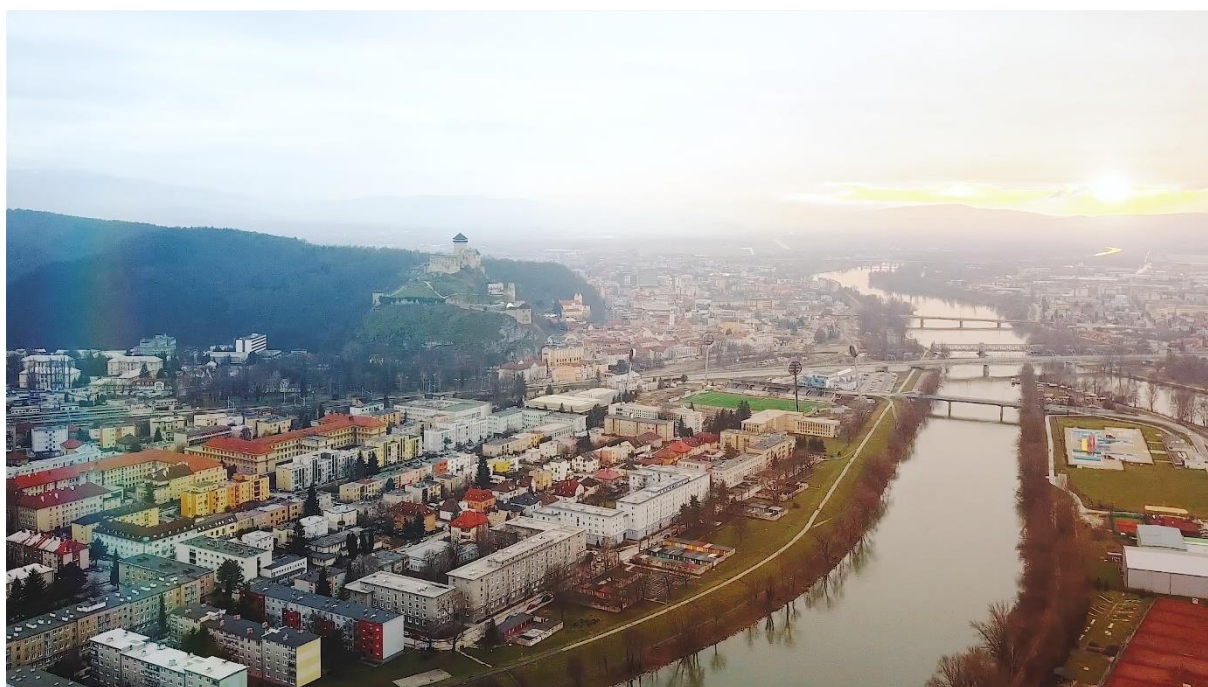




14 th INTERNATIONAL  
CONFERENCE  
ON SOLID STATE  
CHEMISTRY

14- 17  
JUNE  
2021  
TRENČÍN, SLOVAKIA

# Book of Abstracts



Centre for Functional and Surface  
Functionalized Glass



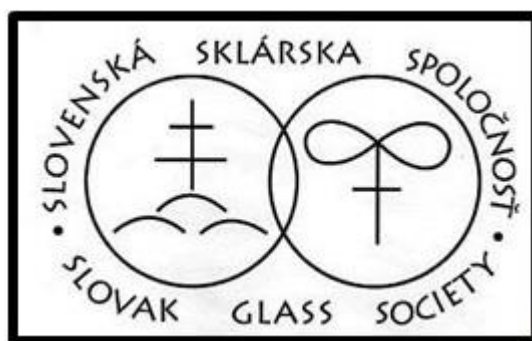
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## Welcome to SSC 2021

It is with pleasure that we can introduce to you the 14th International Conference on Solid State Chemistry (SSC) that follows those held in Karlovy Vary (1986), Pardubice (1989), Bratislava (1996), Prague (2000), Bratislava (2002), Prague (2004), Pardubice (2006), Bratislava (2008), Prague (2010), Pardubice (2012), Trenčianske Teplice (2014), Prague (2016) and Pardubice (2018). The conference series was founded by Prof. Frumar as a symposium for scientists working in the field of solid state chemistry, chemistry and physics of novel inorganic materials. New concepts, approaches, fundamental understanding, as well as the application aspects of inorganic materials have been discussed. The conference has become a truly international event with a worldwide geographical distribution of the participants.

The 14th International Conference on Solid State Chemistry will be another of a long row of international conferences founded originally by Prof. Frumar. For many years, these events have been organised jointly by institutions and universities from Czech Republic and Slovakia and become a well-established forum for scientists from all around the world working in the field of solid-state chemistry, chemistry, and physics of novel inorganic materials.

The conference will be for the first time organised by FunGlass Centre of the Alexander Dubček University of Trenčín.

Like many other conferences in the world, the organisation of the 14 th International Conference on Solid State Chemistry has been affected by the Covid 19 pandemia and, eventually, it had to be postponed to 2021. Due to unpredictable situation and difficulties in planning the conference will be for the first time organised in virtual mode. It will be a challenge and an interesting xperience, but with your support, we are confident to make it a memorable event.

We are really honoured by the trust of previous organisers and will do our best to make the conference again a great forum for meeting the scientist from all around the world. We cordially invite you to Trenčín, the Slovak capital of glass research.

Prof. Dušan Galusek

Conference chairman

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## Advances in solid state materials synthesis, new solids and compounds

# Hierarchical Zeolites as Superior Cracking Catalysts

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**Keywords:** hierarchical zeolites, mesoporosity, surfactant

## Introduction

Zeolites are one of the most useful and versatile class of catalysts, and therefore, widely used in a myriad of applications. Nevertheless, their micropores impose limitations on the mass transport of bulky feed and/or product molecules. [1] Recently, a new technique combining the use of cationic surfactants and mild basic solutions was introduced to synthesis mesostructured zeolites. [2-6] These materials sustain the unique characteristics of zeolites (i.e., strong acidity, crystallinity, microporosity, and hydrothermal stability), while including intracrystalline and tunable mesopores both in terms of size and amount of mesoporosity.

The role of intracrystalline mesoporosity on the catalytic performance of hierarchical zeolites has been tested using probe molecules and vacuum gasoil both in a ACE unit (Figure 1) and in several refineries. Commercial trial was carried out at Alon's Big Spring, TX refinery, in which 318 tons of the equilibrium FCC catalyst comprising mesostructured USY zeolite produced by Grace using Rive Technology surfactant-templating technology. Throughout the trial the combination of improved coke selectivity while increasing feed rate allowed to achieve a significant increase in both LCO and gasoline production. At the end of the commercial trial, the additional value that was delivered to the refinery by replacing the incumbent catalyst with the mesostructured USY containing FCC catalyst was estimated to be over US\$2.50/bbl of the FCC feed.[3]

## Materials and Methods

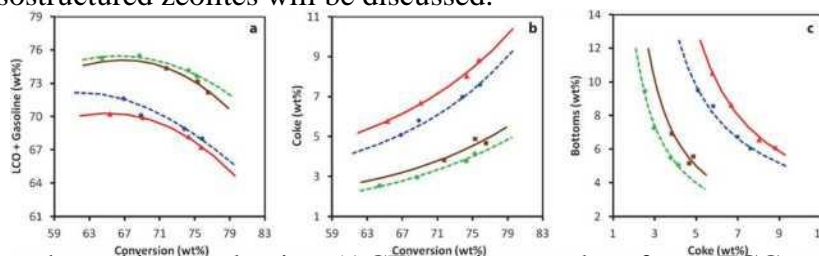
The materials and methods for the development of mesoporous zeolites by this process can be found in references [2-6]. In a typical synthesis, cetyltrimethylammonium bromide (0.7 g) was dissolved in 63.6 mL of a 0.36 M aqueous  $\text{NH}_4\text{OH}$  solution. To this solution, 1 g of USY zeolite (CBV 720, Si/Al = 15) was added. The mixture was subsequently stirred at room temperature for 20 min, and transferred to a Teflon-lined stainless steel autoclave. The hydrothermal treatment was carried out at 150 °C under static conditions for 6 h. Autoclaves were cooled-down to room temperature, solid products were filtered off, washed thoroughly with distilled water, and dried overnight at 70 °C. The calcination of the samples was carried out at 550 °C for 5 h ( $1.5^\circ\text{C min}^{-1}$ ); being the recovery yield close to 100%

## Results and Discussion

The catalytic performance of the FCC catalyst containing mesostructured zeolite Y was compared to a system prepared in an identical manner but comprising the original Y zeolite. The FCC tests were carried out in an advanced cracking evaluation (ACE) unit using both light and heavy VGO as feedstock. In both cases, higher yields in gasoline and LCO were observed whilst, at the same time, significantly less coke and bottoms (unconverted feed) were produced when using the mesoporous zeolite containing FCC catalyst (Figure 1). The improvement in selectivity was even better when employing heavy VGO.

These results highlight the role of intracrystalline mesoporosity in zeolites in increasing the accessibility of the feedstock molecules to the active sites and in facilitating the ready exit of the intermediates that leads to a significant decrease in the production of coke and an increase of gasoline and LCO. The increased selectivity towards intermediates (gasoline and LCO) of these materials shown both in the lab and the refinery commercial are clear evidence of the role of shorter diffusion path length in reducing overcracking reactions.

The mesostructured zeolites are now commercially available through Rive Technology, and show superior performance in VGO cracking.[4-6] During the presentation an overview of recent explorations in the introduction of mesoporosity into zeolites using surfactant-templating techniques will be provided. Various porous materials, preparation methods, physical and catalytic properties of mesostructured zeolites will be discussed.



**Figure 1.** Advanced cracking evaluation (ACE) testing results of two FCC catalysts containing mesostructured USY zeolite to two state-of-the-art catalysts with conventional USY using two different North American refinery feeds. Light VGO feed: FCC catalyst containing mesostructured

USY zeolite (green) and Conventional FCC catalyst (brown). Heavy VGO feed: FCC catalyst containing mesostructured USY zeolite (blue) and Conventional FCC catalyst (red). LCO + Gasoline yields vs. Conversion (A). Coke yields vs. Conversion (B). Bottoms yields vs. coke yields (C).

### Significance

The successful commercialization of surfactant-templated zeolites in FCC is expected to foster the development of new hierarchical zeolites and their use both in existing processes and new and exciting opportunities.

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## Pd-Cu Bimetallic Based Catalysts for Nitrate Reduction in Water

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**Keywords:** Carbon Nanotubes, Heterogeneous Catalyst, Nitrate Reduction, Titanium Oxide, Activated Carbon, Catalyst Characterization.

In recent years, with the development of industries, particularly the large-scale use of nitrogen fertilizers in agriculture, the nitrate content of water has gradually increased. The removal of nitrates from water will be necessary to protect the environment and human health.

Catalytic reduction of nitrates is a promising method; it involves the use of hydrogen as a reducing agent in the presence of a heterogeneous supported catalyst to selectively reduce nitrate and nitrite to nitrogen. The nature of the support affects the catalytic activity and selectivity of the reaction; this is partly due to the surface finish of the support. Among the supports reported in the literature are Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, SnO<sub>2</sub> and activated carbon.

In this work, the reduction of nitrates under hydrogen on a Pd-Cu supported catalyst was studied. Several supports (MWCNT multi-walled carbon nanotubes, activated carbon, and titanium oxide) were evaluated. The catalyst is deposited on the support by co-impregnation in a metal salt solution (Cu(NO<sub>3</sub>)<sub>2</sub>, PdCl<sub>2</sub>) and then reduced with a reducing agent (NaBH<sub>4</sub>). The carbon nanotubes were previously purified and functionalized in nitric acid. The prepared catalysts were characterized by FTIR, DRX, SEM, BET and EDX.

The main objective of this work is to study the effect of the support surface on the performance of the prepared catalyst in order to select the most promising catalyst system for nitrate reduction.

The results obtained show that even though activated carbon has the largest specific surface area, among the different supports used, MWCNT have the highest catalytic activity. It has been observed that the support plays an important role in catalytic performance, and in some cases it could participate in the reaction mechanism.

# Synthesis, Structural and Optical Properties of Zinc Titanite for Selective Sensing of Heavy Metal Ions

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**Keywords:** Zn<sub>2</sub>TiO<sub>4</sub>; Raman spectroscopy; scanning electron microscopy; FT-IR; bandgap

Zinc orthotitanate, Zn<sub>2</sub>TiO<sub>4</sub> is a promising ceramic material that has been used in various applications, such as microwave dielectrics, pigments, sensors and catalysts. In recent years, Zn<sub>2</sub>TiO<sub>4</sub> has been extensively investigated as a potential alternative to TiO<sub>2</sub> for photocatalytic reactions due to its excellent electrical, optical, and physico-chemical properties. However, pure Zn<sub>2</sub>TiO<sub>4</sub> is not easily obtained because generally it contains rutile (TiO<sub>2</sub>) as an additional phase. In the present work, phase pure Zn<sub>2</sub>TiO<sub>4</sub> has been synthesized by solid state method using low-cost raw materials, metatitanic acid (TiO(OH)<sub>2</sub>), which is obtained as an intermediate product during the manufacture of TiO<sub>2</sub> and ZnO of 1:2 molar ratio. The reaction mixture was calcined at different temperature ranges 550°C to 950°C. The phase evolution was identified by Raman spectroscopy, Fourier-transform infrared spectroscopy and X-ray diffraction methods. Scanning electron microscopy (SEM) was used to study the morphology of the material, which showed irregular micron-sized and aggregated particles. Upon calcination at 950°C, rutile-free, phase pure cubic Zn<sub>2</sub>TiO<sub>4</sub> was obtained as evidenced by the aforementioned spectral analysis. Raman spectrum of the calcined product at 950°C, showed the peaks at 722, 478, 359, 306 and 246 cm<sup>-1</sup> could be attributed to the cubic structure Zn<sub>2</sub>TiO<sub>4</sub>, corresponding to the normal modes of representations A<sub>1g</sub>, F<sub>2g</sub>, F<sub>2g</sub>, E<sub>g</sub> and F<sub>2g</sub> respectively. FT-IR showed Zn-O-Ti group bond vibrations in the range of 550 cm<sup>-1</sup> to 650 cm<sup>-1</sup>. The optical bandgap of the calcined products was calculated using UV-Visible diffuse reflectance spectra, which were found to be in the range of 3.55 to 3.85 eV. The fluorescent emission characteristics of the Zn<sub>2</sub>TiO<sub>4</sub>, their quenching effects by adding various metal ions, owing to the formation of complexes between the metal ions and surface of the Zn<sub>2</sub>TiO<sub>4</sub>, were investigated. The sensing properties were also evaluated using the standard Stern–Volmer quenching model. The results showed that Zn<sub>2</sub>TiO<sub>4</sub> possesses high sensitivity and selectivity for iron (Fe) ions.

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## Elimination of carbon from sol-gel prepared YAG precursor

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**Keywords:** YAG, flame synthesis, glass microspheres

Modified sol-gel Pechini method was used to prepare yttrium aluminium garnet (YAG) precursor powder. The method leads to the contamination of YAG powder by residual carbon from the used reagents, especially citric acid and ethylene glycol. Carbon contamination in turn negatively affects density of the glass microspheres of YAG composition prepared from the precursor powder by flame synthesis, yielding hollow particles. Residual carbon reacts with oxygen during the flame synthesis, yielding CO<sub>2</sub> which blows the microspheres. Such hollow glass microspheres are not suitable as a raw material for preparation of transparent or translucent YAG, impairing their optical properties. This study is therefore focused on developing a reliable and reproducible method for the elimination of residual carbon from the YAG precursor powder. Carbon burn-out from the precursor was carried out at temperatures between 600 – 1200°C with 2 h dwell time. After carbon burn-out the treated powder was used for flame synthesis. The density of glass microspheres was evaluated by helium pycnometry. The presence of hollow glass microspheres was confirmed by the scanning electron microscopy (SEM). The TG/DTA analysis revealed that the weight loss takes place mainly from 815°C to 910 °C, but additional, minor weight loss (0.25 %) was observed also in the temperature interval 1170-1350 °C. The fraction of hollow glass microspheres was correlated to the residual carbon content in precursor powder.

## Materials and processes of data storage



## Phase Change Memory Materials by Design

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It has been a long-time dream of mankind to design materials with tailored properties. In recent years, the focus of our work has been the design of phase change materials for applications in data storage and advanced photonic applications. In this application, the remarkable property portfolio of phase change materials (PCMs) is employed, which includes the ability to rapidly switch between the amorphous and crystalline state. Surprisingly, in PCMs both states differ significantly in their properties. This material combination makes them very attractive for data storage applications in rewriteable optical data storage and active photonics, where the pronounced difference of optical properties between the amorphous and crystalline state is employed. This unconventional class of materials is also the basis of a storage concept to replace flash memory. Today's talk will discuss the unique material properties, which characterize phase change materials. In particular, it will be shown that only a well-defined group of materials utilizes a unique bonding mechanism (metavalent bonding), which can explain many of the characteristic features of crystalline phase change materials. Different pieces of evidence for the existence of this novel bonding mechanism, which we have coined metavalent bonding, will be presented. In particular, we will present a novel map, which separates the known strong bonding mechanisms of metallic, ionic and covalent bonding, which provides further evidence that metavalent bonding is a novel and fundamental bonding mechanism. This insight is subsequently employed to design phase change materials for photonic applications. We will demonstrate how the optical contrast can be tuned in different regions of the spectral range, including the realization of plasmonic phase change materials.

# Switching dynamics of phase change memory devices — from materials physics on the nanoscale to beyond-von-Neumann computing

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**Keywords:** phase change materials, crystallization kinetics, threshold switching, memory devices, neuro-inspired computing

The switching dynamics of phase change materials has been studied over many decades. Based on those investigations it was possible to successfully realize a variety of applications, mainly in the field of information processing and storage. Yet, some fundamental scientific questions are still not answered in an unequivocal way. For instance, the mechanism behind the abrupt breakdown of the amorphous state's electrical resistivity at a critical bias, commonly referred to as 'threshold-switching', remains controversially debated.

In addition, current trends in the development of modern computing hardware put an emphasis on how nano-confinement affects the dynamic properties of phase change materials. Neuro-inspired circuits, for example, require control of the drift of electronic properties over time. Accomplishing it would clear a major obstacle for multi-level programming of synaptic weights in individual phase change devices as part of novel in-memory computing schemes.

Remarkably, it is increasing demands from the most advanced applications that let arise the proposal of the most drastic simplification of a phase change material's composition, i.e. the choice of a pure chemical element (Salinga et al., 2018). Implications for both fundamental research and applications will be discussed in this presentation.

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## Phase change memory materials: Why do Ge/Sb/Te alloys dominate

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**Keywords:** Phase change materials, Ge/Sb/Te (GST) alloys

Phase change materials (PCM) have dominated the world of optical storage media, particularly rewritable media like DVD-REW and Blu-ray Disc RE, for at least 30 years. Nanosized bits in a thin polycrystalline layer are switched reversibly and extremely rapidly (on a timescale of nanoseconds) between amorphous (a-) and crystalline (c-) states, which can be identified by measuring the resistivity or optical reflectivity. The elements involved are almost always from groups 13-16: Te (group 16) is almost always present, followed by Ge (14) and Sb (15). Ge/Sb/Te alloys in the composition range  $(\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x$  ( $0 < x < 1$ ) have been the materials of choice in commercial devices: all have metastable rock salt structures that change little over decades at archival temperatures, and all contain vacancies (cavities). The prototype  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (GST) is the most widely studied member of this family.

The rock salt structure of GST comprises a perfect sublattice of Te atoms and a disordered sublattice comprising Ge, Sb, and vacancies. This unusual structure can be understood using a model [1] with simple ingredients:

(1) the particular status of Ge, Sb, and Te among elements of groups 13-16 arises from the pronounced similarity between their valence (outermost s- and p-orbitals) atomic orbitals, in spite of the range of atomic numbers (32-52). This is a consequence of “secondary periodicity” among elements [2].

(2) The average number of valence electrons per site, including vacant sites, is close to 5, and we may adopt the arguments of H. Jones [3], who explained the structure and semimetallic properties of Bi as arising from a (“Peierls”) distortion of a simple cubic structure.

(3) The preference for an average occupancy of five valence electrons leads locally to vacancies close to Te atoms and to the perfect Te sublattice. Both features are experimentally established [4].

These observations allow us to rationalize the structures of Ge/Sb/Te alloys and to discuss alternative compositions of phase change materials. An alternative approach involving a change in bonding between crystalline and amorphous states will be mentioned.

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## Advanced glasses, ceramics and polymeric materials and nano materials

## Structural heterogeneity of glassy materials

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**Keywords:** structural heterogeneity, silicate glass

Structural heterogeneity is a universal feature of glassy materials, however, its classification has been elusive. Here, we will discuss practical approaches which enable quantification of structural heterogeneity by means of heterogeneous elasticity, variations in the timescale of structural relaxation, or density fluctuations. By way of example, we will consider a range of silicate glasses for quantitatively studying the effect of material densification on non-Debye scaling of the vibrational density of states, and on elastic heterogeneity.

## Low-frequency light scattering and intermediate range order structures in borate glasses

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**Keywords:** Raman scattering, Boson peak, borate glasses, dynamic correlation length, intermediate order range structure, superstructural groupings

Investigation of the low-frequency light scattering plays an important role in glass science. Although the origin of the Boson peak (BP) in the Raman spectra of glasses is still a matter of debate, the idea of localizing acoustic phonons (most likely transverse phonons) on the nanometer-sized clusters has become widespread [1]. In the framework of this idea, the dynamic correlation length, which is a characteristic of medium-range order in glasses, can be determined through Boson peak position ( $L_c = \frac{v_t}{c\omega_{BP}}$ ).

On the other hand, it is acknowledged, that borate glasses have unique structural features known as superstructural groupings or intermediate-range order (IRO) structures. These superstructural units consist of well-defined arrangements of basic structural units with no internal degrees of freedom in form of variable bond and/or torsion angles [2, 3]. Several publications [4-6] have reported that the origin of the BP and its characteristics are related to the presence of superstructural groupings in the borate glasses. Therefore, a correlation between  $L_c$  and a certain linear size characterizing the superstructural groupings can be expected if the BP is indeed related to the IRO structures. In this work, these questions are explored based on the Raman spectra of  $\text{Li}_2\text{O-B}_2\text{O}_3$  and  $\text{Na}_2\text{O-B}_2\text{O}_3$  glasses and thermodynamic models developed by Shakhmatkin and Vedishcheva for these systems [7].

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## Polarization-dependent birefringence in sodium borate glasses induced by femtosecond laser pulses

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**Keywords:** femtosecond laser, laser-induced modification, form birefringence, nanogratings, borate glass

The need for development of novel components for microoptics and integrated optical circuits is promoting the research in the field of direct laser nano- and microstructuring of transparent dielectrics. Femtosecond laser-induced nanoperiodical structures in glasses and crystals known as nanogratings attract strong interest in this context because they possess form birefringence whose characteristics such as retardance and orientation of the slow axis can be tuned by variation of laser beam parameters. This feature opens a new way to the development of ultrastable glass-based optical memory [1], optically active phase elements [2], etc., whereas the reduced chemical durability of nanogratings can be applied for fabrication of complex microfluidic devices [3]. Most of the theoretical and experimental studies concerning direct laser writing of nanogratings were performed on silica glass. At the same time, studies on the laser inscription of nanogratings in multicomponent glasses which is also of practical interest [4] and can help to go deeper in understanding the mechanism of laser-matter interactions have drawn less attention. In the present study, we show the possibility of the femtosecond-laser inscription of polarization-dependent birefringence in sodium borate glasses tentatively assigned to the nanorating formation depending on chemical composition of glass. A set of binary  $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$  glasses with sodium oxide content varying from 10 to 33 mol.% was fabricated. Laser exposure conditions giving rise to the form birefringence with slow axis perpendicular to the polarization plane of the writing laser pulses were determined. The dependence of optical retardance of the laser-written birefringent structures on the alkali content was revealed. The role of the glass-forming oxide and the modifier in laser writing of polarization-sensitive structures in borate glasses is analyzed and discussed.

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## Femtosecond laser patterning of crystalline tracks in lithium niobium germanate glasses

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**Keywords:** lithium niobium germanate glass, lithium niobate, laser-induced crystallization, form birefringence, femtosecond laser

Advances in technology and engineering are promoting the continuous development of materials science. Among the novel methods of the synthesis of polycrystalline and single-crystal materials, femtosecond (fs) laser-induced crystallization of glasses can be distinguished as a unique tool for microfabrication of crystalline architectures inside transparent dielectrics. Due to the multiphoton absorption of focused ultrashort laser pulses in strongly confined microdomains, it is possible to selectively heat and crystallize glass with high spatial resolution while the parameters of laser exposure significantly influence on the morphology of precipitated crystalline dots or tracks. In many glasses, highly oriented crystalline architectures with c-axis oriented along the direction of the laser writing can be grown [1]. However, the development of functional components such as active waveguides, electro-optical modulators, etc. through the implementation of unique properties of non-centrosymmetric crystal-in-glass architectures requires a variation of the crystal structure orientation. In this regard, a novel type of fs laser-induced crystallization recently reported and thoroughly studied for lithium niobium silicate glass [2] is of great interest as it demonstrates space-selective precipitation of self-organized  $\text{LiNbO}_3$  nanocrystals and the control of their c-axis orientation by the laser beam polarization.

In this work, we studied fs laser-induced orientable crystallization of  $\text{Li}_2\text{O-Nb}_2\text{O}_5\text{-GeO}_2$  glasses. A set of glasses with a molar composition of  $25\text{Li}_2\text{O} \cdot 30\text{Nb}_2\text{O}_5 \cdot 45\text{GeO}_2$  and  $30\text{Li}_2\text{O} \cdot 25\text{Nb}_2\text{O}_5 \cdot 45\text{GeO}_2$  were synthesized by melt-quenching technique and their crystallization properties were investigated. Glass crystallization was performed using fs laser operating at 1030 nm and emitting 180 fs pulses with energy up to 5  $\mu\text{J}$  at a pulse repetition rate of 200 kHz. The laser beam was focused inside glass bulk by microscope objective lens ( $\text{N.A.}=0.65$ ). The sample was translated relative to the beam by the motorized 3D stage. The precipitation of the  $\text{LiNbO}_3$  crystalline phase in laser-written tracks was confirmed by  $\mu$ -Raman spectroscopy. The orientation of the slow axis of birefringence in crystallized tracks depended on the polarization of the writing beam, which suggests that they can possess nanoperiodic structure similar to that reported for the fs laser-crystallized areas in lithium niobium silicate glasses [3]. The correlation between their morphology and laser exposure parameters was established. The obtained results contribute to the further development of concepts of controlled laser patterning of functional crystalline architectures in oxide glasses.

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## The chemistry of melting oxynitride phosphate glasses

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**Keywords:** Glasses; Oxynitride Glasses; Structure; Ionic conductivity; Solid electrolytes

It will be soon 40 years since the first oxynitride phosphate glasses were obtained by R. Marchand at the University of Rennes [1], as a mere lab curiosity. However, it immediately proved to be worth of further investigations as a consequence of the relevant improvements of the properties on the original phosphate glasses. These are well known to be very soluble in water and reactive in humid environments though the substitution of some oxygen by nitrogen makes them to drastically reduce their dissolution rates [2]. The original research on nitrated phosphates was thus oriented to the development of low temperature sealing glasses but soon it was realized that lithium phosphate glasses experienced also an increase of their ionic conductivity making them potential candidates to be used as solid electrolytes in battery applications [3,4]. When nitrogen substitutes for oxygen, new phosphate tetrahedra appear that may have one or two nitrogen atoms,  $\text{PO}_3\text{N}$  and  $\text{PO}_2\text{N}_2$ , in which the nitrogen anions can be bonded to two or three neighboring phosphorus. This increases the bonding density and strength of the glass network, which is at the origin of the great improvement of their properties.

Unlike silicate oxynitride glasses which are prepared by melting with metallic nitride compounds, phosphates are rather synthesized through the ammonolysis of the melt at relatively low temperatures, usually below  $800^\circ\text{C}$ , where not only the viscosity of the liquid plays an important role but also the composition of the glass in terms of the modifier elements that it contains. Meanwhile the nitridation reaction mechanism has been well explained, several works have demonstrated the influence of the composition onto the final structure and nitrogen content of the oxynitride glasses [5,6]. Furthermore, several combinations with other anions, such as  $\text{F}^-$  and  $\text{S}^{2-}$ , have been successfully tested and expanded the range of applicability. This work will present the most important issues and intricacies of the nitridation of phosphate glasses and decipher the clues that should be considered in the design of novel compositions that can be of interest for their application [7].

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## Structure and magnetic properties of Bi-doped CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass microspheres

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**Keywords:** Gehlenite, Bi-doped glass microspheres, Crystallization, Magnetic properties

Bi-doped CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass microspheres with Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> (gehlenite) composition were prepared by combination of solid-state reaction and flame synthesis. The concentration of Bi was 0.5, 1 and 3 mol. %. The structural and magnetic properties of prepared glass microspheres and their polycrystalline analogues were studied by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and Quantum Design SQUID magnetometer. The closer inspection of glass microspheres surface by SEM confirmed smooth surface and revealed no features indicating presence of crystalline phases. All Bi-doped microspheres are X-ray amorphous, however in case of undoped microspheres XRD detected traces of crystalline gehlenite. XRD analysis of samples crystallized at 1000 °C for 10 h revealed the presence of gehlenite as the only crystalline phase. The finding was supported by SEM examination, which revealed morphological features characteristic for crystals. The presence of gehlenite in crystallized samples were also confirmed by Raman spectroscopy and FTIR. All samples (glass microspheres and their crystalline analogues) showed diamagnetic or weak ferromagnetic behavior at room temperature, whereas paramagnetic or weak ferromagnetic behavior was observed at 2 K.

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## HP, RHP and SPS of $\text{Al}_2\text{O}_3 - \text{Y}_2\text{O}_3$ glass microspheres: sintering conditions, grain size, and mechanical properties of sintered ceramics

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**Keywords:** yttrium-aluminate glasses, flame synthesis, thermal analysis, HT XRD, HP, RHP, SPS

Yttrium aluminate glass microspheres with eutectic composition (76.8 mol.%  $\text{Al}_2\text{O}_3$  and 23.2 mol.%  $\text{Y}_2\text{O}_3$ ) were prepared by combination of sol-gel Pechini method, freeze drying and flame synthesis, and studied by differential scanning calorimetry (DSC), X-ray powder diffraction (XRD), high temperature X-ray diffraction (HT XRD), scanning electron microscopy (SEM) and electron backscattering (SEM EBSD) analysis. Based on the results of DSC and HT XRD analysis of the microspheres the conditions of hot pressing (HP), rapid hot pressing (RHP) and spark plasma sintering (SPS) (the temperatures in the interval 1200-1600°C, and holding times between 0 and 30 min) were determined. Heating rate 20°C.min<sup>-1</sup> and pressure 40MPa was applied during HP. Heating rates 100°C.min<sup>-1</sup> (to prevent crystallisation during heating) and pressure 80 MPa were applied in RHP and SPS experiments. The preparation process including freeze-drying step resulted in glass microspheres with narrower size distribution and the lower mean diameter ( $\approx 10\mu\text{m}$ ). All applied pressure assisted sintering techniques resulted in dense bulk samples with fine grained microstructure consisting of irregular  $\alpha\text{-Al}_2\text{O}_3$  and  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (YAG) grains percolating at a submicron or micron level. Microstructure with fewer pore and defects was observed in samples sintered by conventional HP at temperatures 1400, 1500 and 1600°C, without holding time and with applied pressure 40 MPa. The highest value of Vickers hardness ( $\text{HV} = 16.5 \pm 0.3$ ) was obtained in the sample sintered at 1600°C.

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## Advanced Glass Up-Cycling by Alkali Activation

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**Keywords:** up-cycling, activator

Direct recycling of common soda-lime glass is known to be quite delicate, being possible only after an expensive sorting step. This situation is even worse when remelting is excluded a priori, for several reasons, e.g. in pharmaceutical, fibre and opal glasses. Sustainable options for up-cycling, i.e. transformation of waste glasses into new valuable articles, are offered by engineered alkali activation. Under basic attack, glass - especially in form of fine powders ( $<90\ \mu\text{m}$ ) - , undergoes dissolution, as a consequence of the dismantling of the siloxanic network; however, depending on the specific network modifiers, the glass surface may be coated by a 'passivating' gel layer, especially at low molarity of basic activator (NaOH or KOH  $<2.5\ \text{M}$ ). The formation of surface layers is useful in determining the progressive gelation of aqueous suspensions of glass powders, which can be easily foamed by intensive mechanical stirring, with the help of surfactants. 'Green' foams, from the drying of hardened suspensions, may be finally consolidated by low temperature viscous flow sintering, tuned only on the glass chemistry (and not on that of any foaming agent). The sintering treatment may be even excluded, replacing alkali hydroxides with sodium aluminate, as basic activator of aqueous suspensions (NaAlO<sub>2</sub>, 45wt%; glass/solution=50/50 wt%). The reaction between glass and activator leads to microporous semi-crystalline monoliths (porosity of  $\sim 40\%$ ), featuring hydroxy-sodalite as main crystalline phase, not degradable in boiling water. Operating with powders after a preliminary dealkalinization treatment generally determines changes in the crystalline phase, with promotion of zeolite A.

## Sol-gel synthesis and upconversion properties of nanocrystalline $\text{Er}^{3+}$ -doped $\text{Yb}_3\text{Ga}_5\text{O}_{12}$

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**Keywords:**  $\text{Yb}_3\text{Ga}_5\text{O}_{12}$ , garnet structure, sol-gel method, X-ray diffraction, optical properties, photon upconversion

Nanocrystalline oxide of composition  $\text{Yb}_3\text{Ga}_5\text{O}_{12}$  belongs to the family of materials with garnet-related structure. Variability of structural sites and cation sizes allows easy doping of materials with garnet structure with rare-earth and/or transition metal ions.  $\text{Yb}_3\text{Ga}_5\text{O}_{12}$  is a promising material with potential applications in the field of photonics when doped by lanthanides such as  $\text{Er}^{3+}$ . High ratio of  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$  content leads to dominant red upconversion emission at the expense of green emission.

One aim of this work is the synthesis of this material with various  $\text{Er}^{3+}$  concentration by sol-gel combustion route using citric acid as chelating agent. Phase composition and morphology of annealed products are examined by X-ray diffraction and by scanning electron microscopy.

The next aim is focused on optical properties of prepared nanocrystalline powders. Diffuse reflectance spectroscopy is used for determination of absorption bands associated with the presence of  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$ . Absorption bands of  $\text{Yb}^{3+}$  around 980 nm are then used for energy transfer to  $\text{Er}^{3+}$ . This leads to the visible upconversion emission provided by photoluminescence spectroscopy.

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## Effect of solvent and catalyst types on stability and properties of zinc phthalocyanine in the hybrid glass

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**Keywords:** ORMOSIL, metal-organic compound, dye, zinc phthalocyanine (ZnPc), optoelectronics, sol-gel, aprotic solvent, protic solvent

Hybrid materials (ORMOSIL) based on zinc phthalocyanine (ZnPc) and silica glass matrix were synthesized by the sol-gel method using protic solvents (methanol, ethanol, isopropanol, butanol) and aprotic solvent (N,N-dimethylformamide; DMF). The effect of alkaline environment with NaOH addition (a single stage process) and acid-alkaline environment with CH<sub>3</sub>COOH-NH<sub>4</sub>OH and HCl-NaOH (a two-stage process) was analyzed. UV-Vis spectroscopy was used to study stability of ZnPc in the sol. The highest stability of zinc phthalocyanine in the glass was obtained for synthesis with isopropanol in the presence of the alkaline catalyst. The lowest stability of ZnPc was observed when the aprotic solvent was used. The structure and optical properties of the gels were studied by SEM, FTIR and XRD techniques and optically stimulated luminescence (OSL) and thermoluminescence (TL), respectively. The thermal stability of the materials was analyzed by TG-DSC methods. The different ways of fabrication, i.e., kind of solvent and catalysts affect the optical properties of ZnPc in the glass matrix. OSL of samples obtained by a two-stage process characterizes the lowest luminescence intensity what is similar to TL results.

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## Influence of glassy powder compaction on the properties of sintered glass-ceramic materials

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**Keywords:** fly ash, glass cullet, sintering, devitrification, glass-ceramics.

Many industries generate wastes that are partially or fully vitrified. These include fly ashes from coal combustion in conventional pulverized coal boilers or glass cullet. Due to the glassy nature of this waste, they are used as raw materials and additives in the cement industry, glass industry and the production of sintered ceramics. In the latter application, the vitreous waste usually functions as fluxes due to the high content of alkali oxides. During high-temperature treatment, glass-crystalline materials are produced by parallel sintering and devitrification processes of powdered vitreous waste.

The dynamics of powder sintering, including reactive sintering, largely depends on the original grain contact surface, i.e. the original number of grain contacts. The contact area depends mainly on the graining of the powder. As demonstrated in this study, a significant method of forming the semi-finished product was adopted, as it directly affects the degree of packing of the powder grains. In the case of glassy waste sintering, it is important because physical sintering drives reaction sintering, including the process of glass devitrification. Hence, ground glass powders are devitrified at a lower temperature compared to unground glass.

One of the goals of the experiment was to partially try to separate the two processes. In order to investigate the effect of compaction, an experiment was carried out, consisting in sintering of powder mixtures of container glass cullet and conventional fly ash, formed and compacted in various ways. Semi-dry pressing (under different forming pressure) and mechanical granulation (with various addition of water) were used as forming methods. Glassy waste was subjected to granulometric analysis, determination of specific surface area, analysis of phase composition by XRD method and determination of characteristic temperatures in a high-temperature microscope. The sinters were tested for volumetric density, water absorption and the phase composition analysis using the XRD method.

## Functional materials

## Linear and nonlinear optical properties in glasses managed at the micrometer scale by an imprinting thermo-electrical process

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Combining glass chemistry and thermo-electrical processes allow to obtain new glassy structure, to access new properties and potentially to design multifunctional glasses. It also allows the fabrication of micro-structure by developing an imprinting thermo-electrical process. Such approach has been tested to control at the micrometer scale various properties: (i) surface reactivity, (ii) surface electrical potential, (iii) gradient of refractive index and (iv) second order (SO) optical properties. In the present study, we focus our attention on the control of optical properties at micrometer scale. We have demonstrated the formation of gradient of refractive index (GRIN) with large variations (up to  $5 \cdot 10^{-2}$ ) which have been optimized on both oxide and chalcogenide glasses. The effectiveness of this imprinting process of GRIN has been demonstrated by forming matrices of micro-lenses (sizes from 5 to 100  $\mu\text{m}$ ) on large area (several tens of centimeters square). Using the same process, SO optical properties have been patterned at the micrometer scale in glassy materials. A geometry control of the electro-optical anisotropy induced has been demonstrated and used to fabricate periodic structure such as SHG gratings. By adapting this approach to amorphous niobate thin films, we have induced for the first time in an amorphous material a magnitude of SO optical response comparable to that of a  $\text{LiNbO}_3$  single crystal ( $\chi^{(2)} = 29 \text{ pm/V}$  at 1.06  $\mu\text{m}$ ). This last result paves the way for the future design of integrated nonlinear photonic circuits based on amorphous materials enabled by spatially-selective and highly efficient SO optical response.

## Surface Mobility in Amorphous Selenium and its Similarities to Organic Molecular Glasses

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**Keywords:** amorphous selenium, surface diffusion, viscosity, surface crystal growth, glasses

Surface diffusion is important for a broad range of chemical and physical processes that take place at the surfaces of solids, including surface crystallization. Comparison of surface crystal growth with surface diffusion has a significant impact on the understanding of the crystal growth process, which is important for the preparation, processing, and utilization of amorphous materials. In the standard crystal growth models [1], the mobility of the reorganizing structural units is described by a diffusion coefficient which is usually substituted by bulk viscosity.

In this contribution, the surface mobility in amorphous selenium is studied by following the temporal evolution of periodic structures embossed into the surface of a-Se. The measurements provide information about the near-surface viscosity, as well as, the surface diffusion coefficients.

In molecular glasses [2], the surface diffusion coefficient ( $D_s$ ) has been shown to scale with surface crystal growth rate ( $u_s$ ) according to the power relation  $u_s \approx D_s^{0.87}$ . A comparison of surface crystal growth and found diffusion coefficient in a-Se revealed similar behavior to the organic molecular glasses [3]. In other words, the same power-law was found to apply to surface crystallization of a-Se, a representative inorganic polymer glass. This study shows that the surface diffusion coefficient can be used to quantitatively predict surface crystallization rates in a chemically diverse range of materials, and vice versa to assess the surface diffusion coefficients from surface crystal growth rates.

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## Sodium ion-doped chalcogenide glasses in the thioarsenate $\text{Na}_2\text{S}-\text{As}_2\text{S}_3$ system

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**Keywords:** Chalcogenide glasses, macroscopic properties, Conductivity,  $^{22}\text{Na}$  Tracer diffusion, Raman, Neutron diffusion

Sodium glassy/glassy ceramic chalcogenide systems exhibit high ionic conductivity values making particularly promising for application as inorganic solid electrolytes in all solid state sodium ion batteries. However, in contrast to their silver counterparts, the ion transport and structural information related to sodium systems is scarce. To this end, glass sample compositions in the quasi-binary  $\text{Na}_2\text{S}-\text{As}_2\text{S}_3$  chalcogenide system and over a large concentration range (up to 4 orders of magnitude in the sodium content) are synthesized and characterized for the first time.

The glass-forming region, determined by X-ray diffraction, for the  $(\text{Na}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$  extends up to  $x = 0.35$ . Macroscopic properties such as density, mean atomic volume, and glass characteristic temperatures (the glass transition,  $T_g$  and the crystallization  $T_x$ ) were measured. Both  $T_g$  and  $T_x$  decrease with increasing sodium content  $x$ .

The glasses belong to  $\text{Na}^+$  ionic conductors as deduced from the  $^{22}\text{Na}$  Tracer diffusion measurements. The room temperature conductivity increases by  $\sim 5$  orders of magnitude from  $2.20 \times 10^{-16} \text{ S.cm}^{-1}$  to  $4.6 \times 10^{-11} \text{ S.cm}^{-1}$  over 4 orders of magnitude in the sodium content  $y$ , between  $y_{\min} = 0.004 \text{ at.\% Na}$  ( $x = 10^{-4}$ ) and  $y_{\max} \approx 16.3 \text{ at.\% Na}$  ( $x = 0.35$ ). Meanwhile, the conductivity activation energy shows an overall decrease by 5 factors from  $\sim 1.05 \text{ eV}$  ( $x = 0.0$ ) to  $\sim 0.56 \text{ eV}$  ( $x = 0.35$ ). Two different ion transport regimes were distinguished: (a) critical percolation domain at low sodium content ( $\leq 1\text{-}2 \text{ at.\% Na}$ ) and (b) modifier-controlled domain at higher sodium content.

The structural investigations were carried out using Raman scattering and neutron diffraction measurements and ion transport changes in  $\text{Na}_2\text{S}-\text{As}_2\text{S}_3$  glasses in relation to structural changes are studied.

## Lead sulphide PbS-As<sub>2</sub>S<sub>3</sub> chalcogenide glass system: macroscopic, electric and structural properties

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**Keywords:** Lead chalcogenide glasses, macroscopic properties, thermal properties, Raman, Conductivity, HE-XRD

Amorphous chalcogenide glasses are well suited materials for various applications in the electronics, photonics and sensor fields. The later field is the object of my PhD research activity. In this frame, we seek to elaborate a new, proficient and cost-effective potentiometric chemical sensor destined to the detection of Pb<sup>2+</sup> traces in aqueous solutions. Before such sensor elaboration can take place, a thorough approach to establish the composition–transport–structure correlations is necessary because the enhanced response of the sensors is in the long run directly correlated to all these characteristics and properties.

In this regard, glasses were synthesized in the lead sulphide PbS-As<sub>2</sub>S<sub>3</sub> system using both the classical melt-quenching and the ball-milling methods. The Macroscopic property measurement including density, X-ray diffraction (XRD), and differential scanning calorimetry (DSC) were performed. The glass-forming range for xPbS·(1-x)As<sub>2</sub>S<sub>3</sub> compositions extends up to x = 0.6. The density increases with increasing PbS content from 3.18 (x = 0.0) to 5.24 g cm<sup>-3</sup> (x = 0.6). The glass transition temperature, T<sub>g</sub>, slightly changes with x and the single T<sub>g</sub> indicates a homogeneous glass nature on both macroscopic and mesoscopic scale. Evolution of the total electrical conductivity was also studied using a high resistance meter. The lead sulfide (PbS) addition to the As<sub>2</sub>S<sub>3</sub> host glass leads to a monotonic conductivity increase.

The resulting Raman spectra of the xPbS·(1-x)As<sub>2</sub>S<sub>3</sub> glasses were also studied. The As<sub>2</sub>S<sub>3</sub> host glass (x = 0.0) exhibits a broad poorly resolved multimodal feature centered at 340 cm<sup>-1</sup> corresponding to symmetric and asymmetric As–S stretching modes in corner-sharing AsS<sub>3/2</sub> pyramids and As–S–As bridges. Additional new peak appears at 360 cm<sup>-1</sup> and its intensity increases with increasing lead sulfide content x in the glasses. Also, a weak but distinct feature exists at 230 cm<sup>-1</sup> and increases in intensity with PbS content. This feature shifts to lower frequencies and becomes broader upon adding the lead sulfide to the host glass. Finally, high-energy X-ray diffraction experiments were carried out at Diamond facility and preliminary results in relation to structural motifs will be presented.

## Strong emission at 1000 nm from Pr<sup>3+</sup>/Yb<sup>3+</sup>-codoped multicomponent tellurite glass

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**Keywords:** tellurite glasses, lathanide ion codoping, index of refraction, absorption, emission. down-conversion

We have investigated the spectroscopic properties of Pr<sup>3+</sup>-doped and Pr<sup>3+</sup>/Yb<sup>3+</sup>-codoped tellurite glass with the molar composition 78TeO<sub>2</sub>-10Nb<sub>2</sub>O<sub>5</sub>-5PbO-1PbF<sub>2</sub>-5Li<sub>2</sub>O-1La<sub>2</sub>O<sub>3</sub>. The ellipsometric data have provided a Sellmeier-type dispersion relation of the refractive index of the investigated glasses. The measured absorption spectra of both doped glasses reveal the presence of many absorption bands assigned to transitions from the <sup>3</sup>H<sub>4</sub> ground state of Pr<sup>3+</sup> ion to cosecutive excited states and, in case of Pr<sup>3+</sup>/Yb<sup>3+</sup>-codoped glass, the only absorption band corresponding to the <sup>2</sup>F<sub>7/2</sub>-><sup>2</sup>F<sub>5/2</sub> transition. Analysis of the absorption data has allowed us to calculate the radiative lifetimes of <sup>3</sup>P<sub>0</sub> excited state of Pr<sup>3+</sup> ions and <sup>2</sup>F<sub>5/2</sub> excited state of Yb<sup>3+</sup> ions as being equal to 9.43 and 416.4 μs, respectively. These values appear to be much higher than those obtained from the lifetime measurements indicating the presence of various energy transfer mechanisms. This conclusion is supported by analysis of the emission spectra obtained for doped glasses under the 445 nm excitation; the visible spectra consist of only Pr<sup>3+</sup> transitions, while the near infrared spectrum of Pr<sup>3+</sup>/Yb<sup>3+</sup>-codoped glass demonstrates a strong emission from the <sup>2</sup>F<sub>5/2</sub> excited state of Yb<sup>3+</sup> ion around 1000 nm. This emission is a result of the Pr<sup>3+</sup> - Yb<sup>3+</sup> down-conversion energy transfer and its efficiency for our Pr<sup>3+</sup>/Yb<sup>3+</sup>-codoped glass is estimated as 27%. For potential applications, it is important to increase this efficiency and further studies are desirable, in particular an optimal choice of Pr<sup>3+</sup> and Yb<sup>3+</sup> concentrations to minimize non-radiative energy transfers between the former ions through cross-relaxation and energy migration processes. Analysis of the absorption data of doped samples within the Judd-Ofelt approach has allowed us to determine the intensity parameters and fluorescence spectra have been analyzed in terms of the standard Judd-Ofelt theory along with the photoluminescence decay of the <sup>3</sup>P<sub>0</sub> and <sup>4</sup>S<sub>3/2</sub> for levels of the Pr<sup>3+</sup> and Er<sup>3+</sup> ions. The absorption and emission spectra of infrared transition have been analyzed within the McCumber theory to yield the peak emission cross-section and figure of merit (FOM) for the amplifier gain.

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## Structural features in mercury thioarsenate glasses and their relation to various properties

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**Keywords:** Mercury chalcogenide glasses, Conductivity, Raman, Neutron diffusion, HE-XRD diffraction

Mercury-doped chalcogenides show a large spectrum of property making them good candidates for modern optoelectronic and spintronic applications. Yet, despite their technological interest for electro-optical devices, the number of studies performed on such mercury-doped systems is relatively low. For this purpose, the mercury thioarsenate  $\text{HgS-As}_2\text{S}_3$  glasses were synthesized and characterised.

The glass-forming range for  $x\text{HgS} \cdot (1-x)\text{As}_2\text{S}_3$  compositions was found to be limited to  $x \leq 0.5$ . The measured and modelled Raman spectra, over the entire range, reveal initially a hybrid  $(\text{HgS}_{2/2})_n$  chain/ $\text{AsS}_{3/2}$  pyramidal network. DSC measurements show that the glass transition temperature ( $T_g$ ) decreases with increasing  $x$  and this is coherent with the progressive replacement of the stiff corner-sharing CS-As-S pyramids by the more supple Hg-S chain fragments.

In addition, the data obtained from pulsed neutron and high-energy X-ray diffraction, their RMC modelling as well as from the DFT simulations of mercury species supply evidence to the existence of a second mercury bonding pattern which is the tetrahedral  $\text{HgS}_{4/4}$  units. The total electrical conductivity, studied using a high resistance meter, shows that the conductivity decrease at  $x \leq 0.3$  and the trend is reversed with increasing  $x$ . The non-monotonic change in electronic transport properties backs up the dual structural role of mercury, i.e., the presence of Hg-S chain-like and tetrahedral dimorphous forms.

## Ionic transport and structural features of alkali halide doped $\text{Ga}_2\text{S}_3\text{-GeS}_2$ glasses

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**Keywords:** chalcogenide glasses, macroscopic properties, electrical conductivity, Raman spectroscopy, diffraction studies

The incorporation of metal halides into chalcogenide glassy matrix allows new functional materials to be obtained with the unique optical and electrical properties such as wide transmission range extended in the both infrared and visible spectral regions, high linear and non-linear refractive indices, low phonon energies, photosensitivity and high ionic conductivity. Actually, lithium and cesium containing chalcogenide glasses are investigated most extensively but only few papers are devoted to sodium, potassium and rubidium glasses. In this work we present the systematic study of the MY- $\text{Ga}_2\text{S}_3\text{-GeS}_2$  systems ( $M = \text{Na, K, Rb}$ ;  $Y = \text{Cl, Br, I}$ ) including glass-forming regions, macroscopic properties, ionic transport and structural investigations as a function of alkali concentration, MY chemical composition and  $\text{Ga}_2\text{S}_3/\text{GeS}_2$  ratio.

Two composition lines were studied: Series A -  $(\text{MY})_x(\text{Ga}_2\text{S}_3)_{0.2-0.2x}(\text{GeS}_2)_{0.8-0.8x}$  with a constant  $\text{Ga}_2\text{S}_3/\text{GeS}_2$  ratio and Series B -  $(\text{MY})_x(\text{Ga}_2\text{S}_3)_{0.2+0.2x}(\text{GeS}_2)_{0.8-1.2x}$  where the concentration of gallium sulfide increases simultaneously with alkali halide addition. The glass-forming region broadens progressively and monotonically in Series B with the increase of alkali radius up to 66.7 mol.% in case of RbCl. The addition of metal halide leads to a strong decrease of the glass transition temperature,  $T_g$ , from 426 ( $x = 0$ ) to 237 °C for  $(\text{RbCl})_{67}(\text{Ga}_2\text{S}_3)_{33}$  sample. The room temperature dc conductivity increases with cation concentration but a clear saturation is observed at higher ion fraction for all studied glasses. With the increase of the alkali radius, the conductivity decreases due to the large differences in their activation energies. The  $\text{Ga}_2\text{S}_3/\text{GeS}_2$  ratio and the halide nature affect the conductivity weakly.

The structural analysis based on Raman and diffraction data for the  $\text{NaY-Ga}_2\text{S}_3\text{-GeS}_2$  ( $Y = \text{Cl, Br, I}$ ) glasses reveals that the  $\text{Ga}_2\text{S}_3\text{-GeS}_2$  vitreous matrix is different from  $\text{GeS}_2$ -like disordered network in two aspects: (i) the presence of Ga-S triclusters containing 3-fold coordinated sulphur  $\text{S}_{3F}$ , and (ii) the ethane-like  $\text{ETH-Ga}_2\text{S}_{6/2}$  units with homopolar Ga-Ga bonds. Alloying with sodium halides, the  $\text{ETH-Ga}_2\text{S}_{6/2}$  units disappear while the mixed  $\text{GaYS}_{3/2}$  tetrahedra grow with increasing NaY content. Sodium cations neighbouring the mixed tetrahedra also appear to be mixed-coordinated. In average, each sodium has two halide and two sulphur nearest neighbours.

## Energy transfer from silver to rare-earth ions (Er, Tm, Ho) and near-infrared photoluminescence enhancement in zinc-silicate glasses

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**Keywords:** Silver, Erbium, Holmium, Thulium, Silicate glass, Photoluminescence

This presentation focuses on the study of the effect of various silver species, such as ions, molecular clusters and nanoparticles on the near-infrared photoluminescence properties of rare-earth-doped zinc-silicate glasses. Rare-earth (RE) ions such as  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$  or  $\text{Ho}^{3+}$  are perspective luminophores for use in photonics.  $\text{Er}^{3+}$  ions display emission at 1.5  $\mu\text{m}$ , which corresponds to the 3rd telecommunication window, and are therefore used in optical fiber amplifiers.  $\text{Ho}^{3+}$  and  $\text{Tm}^{3+}$  with strong emission around 2  $\mu\text{m}$ , corresponding to absorption of water, have application in the construction of fiber lasers for medicine, atmospheric sensing, or materials processing. In order to achieve the best photoluminescence performance of RE ions, the choice of a suitable host matrix is of great importance. Silicate glasses are frequently used in practical applications due to excellent material properties (resistance against mechanical stress, thermal shock, or chemical corrosion). However, the spectroscopic properties of RE ions in silicate glasses are severely limited by high phonon energy of silica network and low solubility of RE ions.

Transition metals such as silver are perspective sensitizers for the photoluminescence of RE ions in silicate glasses. Silver nanoparticles can enhance the photoluminescence of RE ions via surface plasmon resonance (SPR) effect, whereas silver ions and molecular clusters (dimers) can participate in energy transfer to RE ions. Majority of studies in this field have been so far limited to  $\text{Er}^{3+}$  ions, while the research concerning the effect of silver on photoluminescence of  $\text{Ho}^{3+}$  or  $\text{Tm}^{3+}$  ions remained relatively scarce and focused mainly of photoluminescence in visible region.

In this work, zinc-silicate glasses doped by  $\text{RE}^{3+}$  ions (RE = Er, Ho, Tm) were prepared by standard melt-quenching technique. Silver was introduced in the glasses using the ion-exchange method, its oxidation state was controlled by employing different heat treatment programs. The effect of silver in various oxidation states and forms (ions, molecular clusters, and nanoparticles) on the near-infrared photoluminescence properties of RE ions was evaluated, the mechanism of energy transfer was studied in detail, and will be discussed.

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## Materials screening for Anderson localization in disordered chalcogenides

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**Keywords:** chalcogenides, Anderson localization,

Disorder-induced Anderson localization and metal-insulator transition have been a central topic in both condensed matter physics and materials science in the past 60 years. Recently, Anderson localization has been observed in Ge-Sb-Te alloys forming a metastable rocksalt-like phase with high concentration of atomic vacancies (~10%). This phase is obtained by rapid crystallization from the amorphous state in phase-change memory devices and, thus, is of considerable technological importance. For demanding applications in phase-change electronics or photonics, it is crucial to have a pool of materials with tunable electronic and transport properties, including band gap size and electron localization length. Therefore, it is of pressing need to carry out a systematic search for compounds exhibiting Anderson localization features.

Here, we demonstrate by ab initio simulations and transport experiments that the parent compound of Ge-Sb-Te alloys -Sb<sub>2</sub>Te<sub>3</sub>- is also an Anderson insulator in the rocksalt-like structure, and elucidate why such disordered crystalline phase can form, extending the exploration of Anderson insulators to binary chalcogenides. We then carry out a systematic ab initio computational screening over all binary and ternary chalcogenides with V<sub>2</sub>VI<sub>3</sub> and IVV<sub>2</sub>VI<sub>3</sub> compositions and identify 47 (meta-)stable rocksalt-type compounds that can sustain a high degree of disorder. Our large-scale electronic structure calculations reveal that most of these disordered chalcogenide crystals are Anderson insulators. Moreover, we obtain an in-depth understanding of the critical factors that affect the stability of the rocksalt structure, namely, sp<sup>3</sup> mixing and atomic radius ratio, and distinguish (meta-)stable compounds from unstable ones in a rationalized materials map.

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## Er<sup>3+</sup>/Yb<sup>3+</sup> co-doped oxyfluoro-tellurite glasses: Investigation of excited state dynamics and optical temperature sensing based on FIR technique

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**Keywords:** Glass, Up-conversion, Down-conversion, Optical thermometry, FIR technique.

Temperature (T) is a thermodynamic parameter and its accuracy is important in both the scientific and industrial fields. The conventional contact temperature measurement technique, which is usually used, requires the thermal transfer and heat balance between sensor and object. It usually takes a longer time, so that the real temperature of the sample may change during the measurement, especially when the size of the sample is comparable to the sensor head or even smaller. It is therefore highly desirable to perform temperature measurements with high temperature and spatial resolution. Recently, a novel non-contact temperature sensor based on FIR technique has attracted considerable attention due to its promising applications in electromagnetically and/or thermally harsh environments [1, 2]. This technique uses the intensity of two closely spaced energy levels called thermally coupled energy level (TCEL) to monitor the temperature.

In this context, we prepared a series of Er<sup>3+</sup>/Yb<sup>3+</sup> co-doped oxyfluoro-tellurite (TZYN) glasses and examined the effect of the concentration of Yb<sup>3+</sup> (0, 0.25, 0.5, 1.0 and 2.0 mol%) on the relaxation dynamics of the excited states of Er<sup>3+</sup> ion using excitation and luminescence spectroscopy. The up-conversion luminescence spectra were studied as a function of temperature in the 298–633 K range, and luminescence intensity ratio (FIR) for green bands attributed to the <sup>2</sup>H<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> transitions of Er<sup>3+</sup> ion against temperature was determined. The temperature sensing performance of TZYN: Er<sup>3+</sup>/Yb<sub>3+</sub> glasses was studied using the fluorescence intensity ratio technique (FIR) up to 633 K. The maximum absolute (S<sub>a</sub>) and relative (S<sub>r</sub>) sensitivity of about 0.00246 K<sup>-1</sup> at 413 K, and 0.72% K<sup>-1</sup> at 323 K, respectively, were established for TZYN: 0.5Er<sup>3+</sup>/1.0 Yb<sup>3+</sup> glass.

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# Intrinsic and activated thermoluminescence in $\text{LiMgPO}_4\text{:RE}$

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**Keywords:**  $\text{LiMgPO}_4$ , rare-earth ion, dosimetry, nonradiative transitions

Olivine-type phosphate  $\text{LiMgPO}_4$  doped with rare-earth elements is currently considered as a new dosimetric material suitable for both OSL and TSL applications and able to compete with top commercial detectors. In this work, the samples of  $\text{LiMgPO}_4\text{:RE}^{3+}$  (RE- Nd, Gd, Dy, Tb, Sm, Er, Ho, Tm) were synthesized by the conventional solid state reaction method. We studied X-ray luminescence, thermally and optically stimulated luminescence and UV–vis spectra in  $\text{LiMgPO}_4\text{:RE}^{3+}$  in detail. We showed that the thermoluminescence spectra of irradiated  $\text{LiMgPO}_4$  doped with majority of RE ions consist of the components caused by the 4f-4f transitions in RE ions, but for some RE they do not contain any 4f-4f lines, but coincide with the spectrum of the phosphate matrix with two broad bands at 360 nm and 650 nm. We discovered a high OSL and TSL output in these samples, despite the nonradiative deexcitation of RE ions. In this case the 4f-4f transitions are not a source of TSL or OSL in doped  $\text{LiMgPO}_4$ . The double-humped spectra indicate that the recombination centers in undoped and some doped phosphates are of the same origin and, apparently, are associated with defects formed both during synthesis and upon irradiation. Thus, some RE ions in  $\text{LiMgPO}_4$  act as sensitizers enhancing stimulated luminescence.

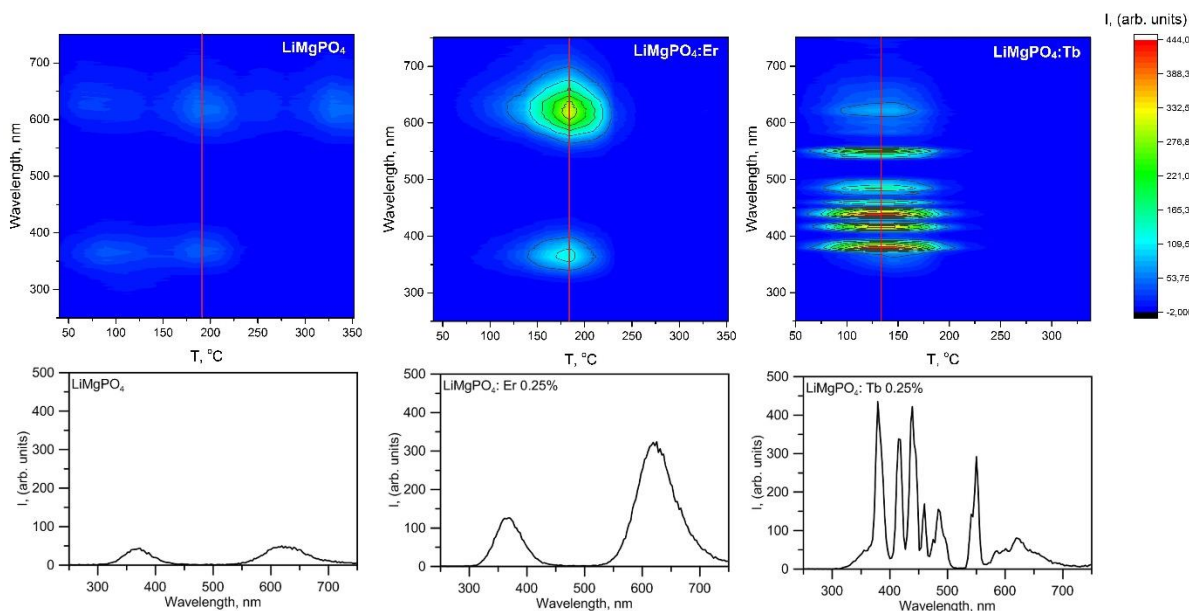


Fig. 1. Contour plots of TSL spectra recorded for  $\text{LiMgPO}_4$ ,  $\text{LiMgPO}_4\text{:Er}$  and  $\text{LiMgPO}_4\text{:Tb}$  and cross sections at the temperatures of peak intensity (indicated by red lines)

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## Intriguing light effects on ion transport in hybrid halide perovskites

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**Keywords:** ion conduction; photo-enhancement; halide perovskites; photovoltaics; electrochemistry.

Recently, hybrid halide perovskites have attracted great attention for their potential use as light-harvesters in solar cells, due to their exceptional photo-electrochemical properties (Shi et al., 2015; Stoumpos et al., 2013) that can yield device efficiencies above 25%. However, to understand the relevant features underlying these high performances, one must consider not only the electronic transport, but also the significant ion conduction present in this class of materials (Xiao et al., 2015; Yang et al., 2015).

In this contribution, we study the nature of such ionic conductivity in methylammonium lead iodide (MAPbI<sub>3</sub>), the archetypal halide perovskite, applying many electrochemical and nuclear magnetic techniques (Senocrate et al., 2017). We observe a substantial ion conductivity under equilibrium conditions, and we identify the dominant electronic and ionic charge carriers as electron holes and iodine vacancies (Senocrate et al., 2018).

Interestingly, by performing similar measurements under illumination we observe, for the first time, a striking enhancement of ionic conductivity by more than 2 orders of magnitude in MAPbI<sub>3</sub>, which happens alongside the expected increase in electronic conductivity (Kim et al., 2018, 2021). We discuss these intriguing results with respect to equilibrium conditions, and in the context of simple defect chemical models. This leads us to the proposal of a mechanism for the photo-enhanced ion conduction that relies on electron-ion interactions (Kim et al., 2018, 2021).

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## Ion Transport in Li<sub>2</sub>O and Li<sub>2</sub>S

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**Keywords:** defect chemistry, antiferroite, conductivity, SEI, film

Lithium oxide (Li<sub>2</sub>O) and lithium sulfide (Li<sub>2</sub>S) are interesting for both battery applications and fundamental science. Here, the transport properties of the two compounds are characterized in bulk and film samples as a function of temperature and doping. The bulk results are explained by a model based on Frenkel disorder and vacancy-dopant association. The thermodynamic and kinetic parameters for Li<sup>+</sup> transport in antiferroite Li<sub>2</sub>O and Li<sub>2</sub>S show remarkable agreement with the analogous parameters for F<sup>-</sup> transport in fluorite compounds such as CaF<sub>2</sub>, which reflects a strong analogy between the antiferroite and fluorite structures. Nanocrystalline films of Li<sub>2</sub>O and Li<sub>2</sub>S show an ionic conductivity which is enhanced by 3-4 orders of magnitude relative to that of bulk samples. The evidence points to grain boundaries and/or dislocations as enabling the faster transport, which may also be the mechanism for ion transport through various SEI passivation layers in batteries.(1-4)

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## Resistive switching with metal doped chalcogenide thin film

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**Keywords:** chalcogenide, thin film, resistive switching

The resistive random access memory is promising to replace the traditional memory technology [1]. The unique photo-induced solid state chemical reaction between metal and amorphous chalcogenides is used to form ionic conductive film. The switching mechanism of metal doped chalcogenide thin film involves the redox of ions, leading to the formation and dissolution of metal filaments. Such memory cell is referred as programmable metallization cell (PMC) or conductive bridging RAM (CBRAM) [2]. The chalcogenide based resistive cell owns excellent storage performance, for instance, low operative voltage, low operative current, fast response and long term data storage [3]. In this presentation, a switching cell based on Ag or Cu doped Ge-Se electrolyte is introduced. And its relevant property and potential application are discussed.

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## Solution processed chalcogenide glass thin films

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**Keywords:** chalcogenide glasses, spin-coating, thin films, solution processed thin films

Chalcogenide glasses have been intensively studied materials for many decades. Main focus of the research is aimed on the optical properties of bulk glasses and especially the thin films. Due to the large transmission window IR and high refractive index, chalcogenide glasses are attractive materials for optical applications (e.g. waveguides, diffractive elements, microlens arrays, etc.). Frequent sensitivity of chalcogenide glasses (usually in a thin film form) to various kinds of radiation (such as UV-VIS, electron beam, X-ray and others), often leading to selective etching, significantly simplifies preparation of the optical elements and even allows usage of chalcogenide glass thin films as resists for lithography.

Thin films of chalcogenide glasses are usually deposited through physical vapor deposition methods such as vacuum thermal evaporation or sputtering. Alternative way for chalcogenide thin films preparation lies in dissolution of the source bulk glass in appropriate volatile solvent and thin film deposition by proper coating technique (such as spin-coating, spiral-bar coating, electrospray, etc.). Subsequent evaporation of the solvent forms solid thin film in specular optical quality.

Solution processed thin films of chalcogenide glasses have been intensively investigated by our group for many years. In comparison with traditional physical vapor deposition techniques, solution based deposition methods allow modifications of the thin film composition and even structure without the need for preparation of new bulk glass. In solution state, chalcogenide glasses can be altered in composition by addition of pure elements or by mixing of multiple glass solutions (even of different compositional systems). Exact composition of the thin film can be easily tailored by simple changing of the volume ratio of different glass solutions. Furthermore, structure of the thin film can be modified as well by proper annealing treatment and even by introduction new components (e.g. nanoparticles or nanotubes) into the glass solution resulting in composite material. New functionalities such as fluorescence can be introduced to the thin film.

Structuring of solution processed thin films can be performed directly (without the need of the photoresist) by UV-VIS or electron beam lithography due to their frequent sensitivity. Hot embossing structuring method can be applied as well and with good advantage – many of solution processed chalcogenide glass thin films can be structured at temperatures below the  $T_g$  of the glass.

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## Advanced characterisation techniques

## Glass surface inspected by the microscopic and spectroscopic methods

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**Keywords:** silicate glass, surface, spectroscopy, microscopy, Molecular Dynamics

Knowledge of the glass surface is of paramount importance for many applications in science and industry: it is intimately related with problems and development in chemical and mechanical resistance, bio-compatibility, surface coating and functionalising to name a few. Therefore, it is surprising how little is known about the glass surface, despite of significant physical, chemical, and structural differences from bulk. The lack of data is often justified by the limitations of experimental techniques with regard to their surface sensitivities and treacherousness of theoretical calculations due to small energy differences between different surface configurations.

The contribution reviews some of the results obtained for both model and commercial glass surfaces. The presented experimental findings were obtained from Scanning Electron Microscopy (SEM), Electron Probe Microanalysis (EPMA), Raman Spectroscopy (RS), Time-of-Flight Secondary Ion Mass Spectrometry (TOF SIMS), Atomic Force Microscopy (AFM), and X-Ray Photoelectron spectroscopy (XPS) and are supplemented with Molecular Dynamics calculations. Questions about the surface: “What is it?” and “How to prepare it?” are tackled. The advantages and drawbacks of the mentioned methods and their ability to answer basic questions about the glass surface are discussed and accompanied with examples.

### 3D ED for structure determination of inorganic materials

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**Keywords:** electron diffraction, structure solution, titanyl sulfate dihydrate

Crystallography of nanocrystalline materials has witnessed a true revolution in the past 10 years, thanks to the introduction of protocols for 3D acquisition and analysis of electron diffraction data (3D ED). This method provides single-crystal data suitable for structure solution and refinement, allowing the atomic structure determination of those materials that remained hitherto unknown because of their limited crystal size. Several experimental protocols exist, which share the common idea of sampling a sequence of diffraction patterns while the crystal is tilted around a non-crystallographic axis, the goniometer axis of the TEM sample stage (Gemmi, 2019). Structure refinement using dynamical diffraction theory has brought structure determination from 3D ED data to the level of single-crystal X-ray diffraction analysis (Palatinus, 2015).

As an example, the structure determination of titanyl sulfate dihydrate - TSD ( $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ ) will be presented. The structure of TSD has eluded researchers for years mainly due to two reasons – small crystals and quite large unit cell causing severe reflection overlaps in powder diffraction data (English, 2016). Using 3D ED we were able to solve and determine the structure including the positions of hydrogen atoms (Klementová, 2017).

The structure of TSD is monoclinic  $Pn$  with lattice parameters  $a = 5.54(2) \text{ \AA}$ ,  $b = 16.77(9) \text{ \AA}$ ,  $c = 18.74(10) \text{ \AA}$ ,  $\beta = 90.5(3)^\circ$ . The structure is composed of two symmetry independent helices of corner sharing  $\text{TiO}_6$  octahedra extending along  $a$  direction. Each pseudotrigonal helix is held together by  $\text{SO}_4$  tetrahedra that share corners with odd/even  $\text{TiO}_6$  octahedra. The helices are held together by  $\text{H}_2\text{O}$  molecules. Both hydrogens in each water molecule form hydrogen bonds toward oxygens of two different  $\text{SO}_4$  tetrahedra. One H-bond points to the oxygen of  $\text{SO}_4$  tetrahedra from the same helix (intra-chain bond), while the other H-bond points to the oxygen of  $\text{SO}_4$  tetrahedra from the neighbouring helix (inter-chain bond).

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## Investigation of surface-enhanced Raman scattering on gold nanoislands substrates with different geometrical parameters and analytes

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**Keywords:** gold nanoislands; surface-enhanced Raman scattering; plasmonics, photonic devices; sensors

In this work, the process of surface-enhanced Raman scattering (SERS) was studied on gold and silver nanoisland arrangements. Systematic investigations were carried out on different gold and silver nanoisland samples to determine how SERS enhancement depends on the morphology (particle size, gap distance) and optical parameters (plasmon wavelength) of the nanostructures.

For this purpose, the metallic nanostructures were created by annealing thin film layers of gold and silver deposited by vacuum thermal evaporation onto glass substrates. The heat treatment (solid-state dewetting) took place at different temperatures (400 °C, 450 °C, 500 °C, and 550 °C) for different periods (15, 30, 60 and 120 minutes), resulting in a variety of geometrical parameters (e.g. particle diameter, interparticle distance). The parameters of the created nanoislands, such as equivalent particle diameter, gap distance, and plasmon wavelength on the SERS enhancement efficiency were studied. The SERS capabilities of the samples were evaluated by measuring an analyte solution of benzophenone, riboflavin, and rhodamine with three different excitation laser wavelengths (473, 532, and 633 nm). Scanning electron microscopy was used to measure the average particle size and average interparticle distance to correlate them with the obtained SERS enhancements. The influence of the geometric parameters of metallic nanoparticles and the laser wavelength on the surface-enhanced Raman process was evaluated. Furthermore, we have examined the effect of the analyte on the process of Surface-Enhanced Raman Scattering (SERS). The enhancement factor was obtained for the analytes, and the influence of the analytes was studied as well. SERS EF showed a positive linear correlation with nanoparticle size and a negative exponential relationship with interparticle distance for both types of nanomaterials. This is due to the higher scattering efficiency (larger particle size) and the higher density of near-field hot spots on tightly packed particles. Besides it, the results have shown the result of analytes on their plasmon peak position and so on the SERS EF as well.

### Acknowledgments

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## Raman / Second Harmonic Generation Correlative Imaging

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We have developed a correlative Raman / Second Harmonic Generation (GSH) optical microscopy technique using a commercial confocal Raman microscope, allowing a Raman image (giving structural information) to be coupled with a GSH image (giving information on non-linear optical, structural or electro-optical properties). GSH microscopy is performed in polarization with near IR excitation, the vertical, radial or azimuthal linear polarization of which can be modified as required.

This correlative imaging has been successfully applied to analyze glass-ceramics, and for numerous studies on the structuring of glasses by thermal polarization and laser writing.

## Materials for renewable energy production and storage

## Yet another new frontier for photovoltaic power generation: Selectively absorbing highly transparent organic photovoltaic solar cells"

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**Keywords:** solar energy, transparent organic photovoltaic solar cells

Almost 55% of solar energy is in the visible region (380nm-780nm). Contributions of ultraviolet (280nm-380nm) and near infrared (780nm-2500nm) regions are ~ 4% and~ 41% respectively. Thus at the first glance the idea of “converting solar energy by photovoltaic process via transparent solar cells” might seem to be a bit controversial. However, the most cutting-edge research and technological development efforts on new transparent organic photovoltaic (TOPV) solar cell have shown that this new field has a great potential to change the game in photovoltaic industries. Combining PV solar energy generation and transparency opens up new applications for variety of industries such as; construction, transport, electronics, display technologies etc. Thus progress in (TOPV) has been exponential and dynamically reviewed (1,2). Recently it is demonstrated that transparent organic photovoltaic cells with a power conversion efficiency of 10.8% and visible transparency of ~50% (3).

This work would be concentrated on TOPV and solar windows only. There is a common belief that when TOPV field reaches to technological and commercial maturity, solar windows would replace the most of the traditional glass windows and facades in commercial and domestic buildings. This would overcome problems related to large land parcels or roof spaces for PV conversion. It is estimated that the size of the current glass facades in USA is about 5 to 7 billion square meters and installing transparent solar cells on windows and the facades might provide 40% of energy demand.

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# Polymer-derived SiCH organic-inorganic hybrid membranes for solar hydrogen production via photoelectrochemical water-splitting

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**Keywords:** Hydrogen, Membrane, Hydrophobicity, Polycarbosilane, Inorganic-organic hybrid

Solar hydrogen production via the photoelectrochemical water-splitting reaction is attractive as one of the environmental-friendly approaches for producing H<sub>2</sub>. Since the reaction simultaneously generates H<sub>2</sub> and O<sub>2</sub>, this method requires immediate H<sub>2</sub> recovery from the syngas including O<sub>2</sub> under high-humidity conditions around 323 K, and membrane separation is one of the candidate processes for the H<sub>2</sub> recovery.

In this study, superhydrophobic membranes composed of ternary SiCH organic-inorganic hybrid were formed on a mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-modified  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> porous support by using polycarbosilane (PCS) as a starting polymer precursor. The water vapor adsorption-desorption isotherm analysis at 298 K revealed that the PCS-derived hybrids showed excellent hydrophobicity compared to sol-gel derived SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which have been often used for H<sub>2</sub>-selective microporous ceramic membranes (Kubo et al., 2020). Moreover, the PCS-derived SiCH hybrids exhibited a unique H<sub>2</sub> affinity, and the SiCH hybrid membranes showed a good H<sub>2</sub>-selectivity under various water partial pressures up to RH=100 % at 323 K. The H<sub>2</sub> affinity of the SiCH hybrids was characterized by measuring preferential H<sub>2</sub> adsorption onto a thin film of the SiCH hybrid using a quartz-crystal microbalance (QCM) (Kubo et al., 2020), while the dominant mechanism for the H<sub>2</sub>-selective permeation through the SiCH hybrid membrane was studied by using a solid-state diffusion model (Kubo et al., 2021), and some parameters such as number of solubility sites per area [m<sup>-3</sup>], vibrational frequency of the gas molecules in the passageways between the sorption sites [s<sup>-1</sup>] and activation energy [kJ mol<sup>-1</sup>] for the H<sub>2</sub> permeation were estimated. These results will be shown and discussed aiming to develop novel hydrogen separation membranes for solar hydrogen production systems.

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# Polymer-derived SiCH organic-inorganic hybrid membranes for solar hydrogen production via photoelectrochemical water-splitting

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In this study, superhydrophobic membranes composed of ternary SiCH organic-inorganic hybrid were formed on a mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-modified  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> porous support by using polycarbosilane (PCS) as a starting polymer precursor. The water vapor adsorption-desorption isotherm analysis at 298 K revealed that the PCS-derived hybrids showed excellent hydrophobicity compared to sol-gel derived SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which have been often used for H<sub>2</sub>-selective microporous ceramic membranes (Kubo et al., 2020). Moreover, the PCS-derived SiCH hybrids exhibited a unique H<sub>2</sub> affinity, and the SiCH hybrid membranes showed a good H<sub>2</sub>-selectivity under various water partial pressures up to RH=100 % at 323 K. The H<sub>2</sub> affinity of the SiCH hybrids was characterized by measuring preferential H<sub>2</sub> adsorption onto a thin film of the SiCH hybrid using a quartz-crystal microbalance (QCM) (Kubo et al., 2020), while the dominant mechanism for the H<sub>2</sub>-selective permeation through the SiCH hybrid membrane was studied by using a solid-state diffusion model (Kubo et al., 2021), and some parameters such as number of solubility sites per area [m<sup>-3</sup>], vibrational frequency of the gas molecules in the passageways between the sorption sites [s<sup>-1</sup>] and activation energy [kJ mol<sup>-1</sup>] for the H<sub>2</sub> permeation were estimated. These results will be shown and discussed aiming to develop novel hydrogen separation membranes for solar hydrogen production systems.

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## Additive manufacturing

## Additive Manufacturing of Ceramics using Preceramic Polymers

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**Keywords:** polymer derived ceramics, SiOC, silicone elastomer

Preceramic polymers are precursors for ceramic phases of different composition. They convert into nano-structured ceramic materials in the system  $\text{Si(X)OCN}$  (with  $X = \text{Al, Ti, Zr, etc.}$ ), also called PDCs or Polymer-Derived-Ceramics, by high temperature pyrolysis. The resulting materials can have useful structural and functional properties.

This talk will discuss the fabrication of (mainly) porous structures starting from pure preceramic polymers (e.g. silicone resins) or silicone resins plus reactive fillers to produce advanced silicate ceramic phases, including bioceramics and Ceramic Matrix Composites, suitable for different potential applications.

Different types of additive 3D manufacturing techniques were employed, including: a) direct printing using a fused deposition printer (FDM); b) direct printing using an ink extrusion printer (DIW); c) indirect printing using a powder bed-based printer (BJ); d) indirect printing using a stereolithographic printer (DLP); e) indirect printing with sub-micron resolution using 2 Photon Polymerization fabrication (TPP).

Furthermore, we developed a novel hybrid approach to fabricate SiOC ceramic structures with feature sizes ranging from sub-micron to millimeter size, by combining 3D macrostereolithography (DLP) with 2-Photon-Polymerization (TPP).

Finally, we are currently using silicone elastomers to fabricate simple shapes that can be further processed into complex architecture by post-printing folding and pyrolysis. Advantages and disadvantages of the different processing techniques employed, in relation to the use of preceramic polymers, will be discussed, and examples of produced and characterized porous structures for potential use in different applications will be presented.



## Present state of 3D printing from glass

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**Keywords:** additive manufacturing, producing technologies, 3D printing, glass, defects

This paper deals with the issue of additive technologies using glass. At the beginning, our research dealt with a review of the current state and specification of potentially interesting methods and solutions. At present, this technology is being intensively and actively developed and studied in glass research. Although “additive technology” in the sense of adding materials has been used in glass manufacturing since the beginning of the production of glass by humans, the term additive technology nowadays refers to 3D printing.

Currently, there are several approaches to 3D printing of glass that have their advantages, but also limitations. The resulting products very often have a high degree of shrinkage and rounding (after sintering), or they have specific shape structures (after the application of layers) and also generally have a large number of defects (especially bubbles). Some technologies do not lead to transparent glass. Therefore, we cannot use the optical properties used in glass. Nevertheless, these technologies bring interesting new features and applications.

We cannot expect that the technology will produce goods that are price competitive to goods produced by conventional technologies. If 3D glass printing is to be successful as an industrial or highly aesthetically valuable technology, then it must bring new and otherwise unreachable features and properties, as with 3D printing of plastic, metal or ceramics.

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## **2D materials, surfaces, interfaces, hybrid- and nanostructured solids**

## Hybrid Layered Double Hydroxide Materials: an adapted functionalized filler in a sustainable approach

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**Keywords:** layered double hydroxides, filler

Much attention is now focused on layered double hydroxides (LDHs), also known as anionic clays or hydrotalcite-like materials. These materials are described with the general formula  $[M^{II}_{1-x}M^{III}_x(OH)_2](A^{n-}_{x/n}) \cdot mH_2O$ , where  $M^{II}$  is a divalent cation (like Mg, Zn, Ni, Cu or Co) and  $M^{III}$  is a trivalent cation (like Al, Cr or Fe), and  $A^{n-}$  represents inorganic anion such as  $NO_3^-$ ,  $CO_3^{2-}$  or an organic anion. These metal cations  $M(OH)_6$  form the positively charged layer by edge-sharing their octahedra, and with diverse charge-compensating anions present in the interlayer space. By combining both cation and anion versatilities, the resulting compositions are limitless in designing new hybrid LDH assemblies. Often designed as toolbox, such organo-modified LDH may be adapted as nano-fillers for polymer including polymer of interest for sustainable development.

Two examples are selected to picture the invited lecture: one from organo-modified LDH fillers endowing multi-functionality to bio-based poly(butylene succinate) and showing the possible transfer from the lab to the market, and a second focusing on wide-open LDH structure hosting InP/ZnS quantum dots and showing a new route toward efficient and photo-stable red-emitting phosphor when loaded into silicone for possible LED application.

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## Application of holographic lithography for material surface direct nanostructuring

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**Keywords:** holographic recording, azo-benzene containing organic, immersion holography, photo induced birefringence

In this report the state of holographic lithography will be discussed and its comparison with conventional optical lithography technologies will be done. The present state of research and practical application of direct recording photoresists based on photoinduced mass displacement (the surface relief formation occurs during holographic recording) both in organic azo-benzene containing compounds and amorphous inorganic chalcogenides has been examined [1-3]. It is shown, that the value of photoinduced birefringence of recording material plays a major role in the mass photoinduced displacement process [2]. The possibility of improving the photosensitivity of direct recording resists with liquid crystal additives was investigated.

By means of immersion holographic lithography the surface relief gratings with a period of ~150 – 250 nm can be fabricated with a 491 nm laser recording. The grating period for two intersecting light beams in a coupling prism can be expressed as  $\Lambda = \lambda_0 / 2n \sin\theta$ , where  $\lambda_0$  is the wavelength of laser light in vacuum,  $n$  is refractive index of the prism and  $\theta$  is the half-angle between the laser beams inside the prism. The right angle prisms with  $n = 1.5 - 2.6$  were used. A prism serves as an immersion medium and  $n$  times decreases the period of the recorded grating.

It is known that the production of optical range surface plasmon effects in metals and metal oxides involves making surfaces which have features with the sizes of <400 nm. One of the ways to do this is by using holographic lithography technology.

We present preliminary results of direct writing of submicron patterns by the use of laser-photoinduced etching as well as photo-electrochemical etching on metals (Au, Ag, Cu) and metal oxides. In this case intensity modulated holographic recording (s-s or p-p recording beams configuration) simultaneously initiates etching of metal layer in interference pattern maximum places of light intensity. Electro-deposition of metals on conductive ITO layers assisted by holographic recording was also studied. It is believed that this new anisotropic photoetching process may find many lithographic applications in microelectronics and surface science.

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## Plasmonic nanostructures for photonic applications

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**Keywords:** localized surface plasmon resonance, plasmonic nanoparticles

In this work, the performance of plasmonic nanoparticles was investigated for photonic applications. It is widely used for surface plasmon resonance experiments, not in the last place because of the manifestation of optical resonances in the visible spectral region. The localized surface plasmon resonance (LSPR) is rather easily observed in nanometer-sized metallic structures and widely used for measurements, sensing, semiconductor devices, and even in optical data storage.

Firstly, gold nanoparticles on silica glass substrate satisfy the conditions for surface plasmon resonance in the green-red spectral range, where the chalcogenide glasses have the highest sensitivity. The gold nanostructures influence and enhance the optical, structural, and volume changes and promote the exciton generation in gold nanoparticles/chalcogenide layer structure. The experimental results support the importance of localized electric fields in the photo-induced transformation of chalcogenide glasses as well as suggest new approaches to improve the performance of these optical recording media. Results may be utilized for direct, micrometer- or submicron size geometrical and optical pattern formation in the.

Besides that, gold nanoparticles could be added to organic light-sensitive material. The acrylate-based materials are frequently used for the optical, holographic recording of optoelectronic elements due to photo-stimulated structural transformations. The holographic recording process and photo-polymerization effect could be enhanced by the localized plasmon field of the created gold nanostructures.

Finally, gold nanoparticles are widely used for electrochemical and optical sensor applications. Although these NPs can be synthesized in several ways, perhaps one of the simplest methods is the thermal annealing of pre-deposited thin films on glass or silicon surfaces. With this method, the parameters of the annealing process (time, temperature) and the pre-deposited thin film thickness influence and define the resulting size and distribution of the NPs on the surface. LSPR is a very sensitive optical phenomenon and can be utilized for a large variety of sensing purposes (chemical sensors, gas sensors, biosensors, etc.). Surface-enhanced Raman spectroscopy (SERS) is an analytical method that can significantly increase the yield of Raman scattering of target molecules adsorbed on the surface of metallic nanoparticles. The sensitivity of LSPR and SERS-based devices is strongly depending on the used material and also on the size and geometry of the metallic nanoparticles. By controlling these parameters the plasmon absorption band can be tuned and the sensitivity can be optimized. The technological parameters of the generated gold nanoparticles were investigated and influence on the SERS and the LSPR sensitivity was established. It was found that the enhancement factor depends on the size of the nanoparticles and the distance between the particles.

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## Hydrothermal corrosion of polymer derived glass/ceramic coatings

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

Polymer-derived ceramic (PDC) composite coatings are a promising candidate to be used as alternative environmental barrier coatings, e.g. in corrosion protection. In this work, polysilazane-based double layer composite coatings consisting of a PDC bond-coat, and a PDC top-coat containing ceramic passive (8YSZ) and glass (G018-281, Schott) fillers, as well as a specially tailored passive filler ( $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-ZrO}_2$ ) prepared by Pechini method, were developed. The addition of fillers was aimed at the elimination of shrinkage in the course of the polymer-to-ceramic conversion, which could result in crack formation and delamination of the polymer-derived protective coating from the metallic substrate (AISI 441 stainless steel). 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 tested PDC coatings exhibited significant mass loss of up to  $-2.2 \text{ mg/cm}^2$  after 192 h of corrosion tests, which was attributed to the leaching of elements from the coatings to the corrosive medium. Analysis of corrosion liquid by inductively coupled plasma optical emission spectrometry (ICP-OES) confirmed the presence of Ba, Al, Si, Y, Zr, and Cr, as the main component of the steel substrate, in the solution. The microstructure of hydrothermally corroded samples was in detail examined by scanning electron microscopy (SEM) equipped with an EDS detector. SEM examination of the corroded surfaces revealed randomly distributed globular crystallites approximately 3  $\mu\text{m}$  in diameter. EDS analysis of the precipitates showed the presence of Ba, Al, Si, and O. After 192 h of corrosion tests, no significant corrosion damage was observed in the cross-section: the tested coatings showed good adhesion and crack-free microstructure with low porosity. X-ray powder diffraction analysis (XRD) was used to detect any secondary phases, which could result from chemical reactions between the components of the steel substrate, coating, and corrosive agent. The dominant phases detected after corrosion tests by XRD are monoclinic and cubic  $\text{ZrO}_2$ , originating from the used passive fillers. In addition, the crystalline phase of celsian ( $\text{Ba}(\text{AlSiO}_4)_2$ ) was also identified, which is in accordance with the results of EDS analysis of the precipitates formed on the coating surface.

### Acknowledgments



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## High-temperature oxidation behaviour of PDC coatings

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**Keywords:** PDC coatings, oxidation, synthetic air, water vapor

Polymer-derived ceramic (PDC) polysilazane-based double layer composite coatings on stainless steel AISI441 substrates consisting of a PDC bond-coat, and a PDC-based top-coat containing passive (YSZ,  $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ ) and glass (Schott) fillers were developed. The oxidation behaviour of the ferritic stainless steel AISI 441 with and without the PDC coating at temperatures up to 1000 °C in the flow-through atmosphere of synthetic air and in air saturated with water vapor was evaluated. A significant weight gain of the unprotected steel was measured at all temperatures while the oxidation tests of the coated steel showed only a negligible weight gain. The atmosphere with water vapor was more aggressive, which also resulted in higher weight gains of both the uncoated steel and the coated samples. The protective effect of the PDC coatings applied to the stainless steel was confirmed for all experimental conditions and expressed in terms of reduction of the measured weight changes. Detailed X-ray diffraction (XRD) study, and microstructural examination of the oxide products formed at the surface of samples after exposure to air and water vapor at 900, 950, and 1000 °C for 24 and 96 h were carried out. The XRD confirmed extensive oxidation of the uncoated AISI441 stainless steel accompanied by the formation of a  $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $(\text{Mn, Cr})_3\text{O}_4$  spinel containing layer of oxidation products in both atmospheres. In coated samples, m-  $\text{ZrO}_2$ , c-  $\text{ZrO}_2$ , YAG, and crystalline phases  $(\text{Ba}(\text{AlSiO}_4)_2$  - hexacelsian, celsian) were detected. The protective effect of the prepared PDC coatings was observed at the temperature 900 °C, while at a higher temperature (1000 °C) and longer exposure times (96 h) the layer of oxidation products was observed at the interface bond coat/top coat. In the atmosphere of water vapour,  $\text{Cr}^{3+}$  ions diffused through the bond coat, forming the  $\text{Cr}_2\text{O}_3$  layer at the bond coat/top coat interface, but no delamination was observed.

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## From novel oxide thin film matter to device application: SrMoO<sub>3</sub> as highly conducting perovskite enabling agile and energy efficient all-oxide high frequency devices

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**Keywords:** SrMoO<sub>3</sub>, perovskite

In the field of oxide electronics, there has been tremendous progress in the recent years in atomic engineering of functional oxide thin films with controlled interfaces at the unit cell level. However, some relevant devices such as tunable ferroelectric microwave capacitors (varactors) based on Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> are stymied by the absence of suited compatible, very low resistive oxide electrode materials on the micrometer scale. Therefore, we start with the epitaxial growth of the exceptionally highly conducting isostructural perovskite SrMoO<sub>3</sub> having a higher room-temperature conductivity than Pt. In high-frequency applications such as tunable filters and antennas, the desired electrode thickness is determined by the electromagnetic skin depth, which is of the order of several micrometers in the frequency range of a few GHz. Here we report the pulsed laser deposition of a fully layer-by-layer grown epitaxial device stack, combining a several micrometers thick electrode of SrMoO<sub>3</sub> with atomically engineered sharp interfaces to the substrate and to the subsequently grown functional dielectric layer. The difficult to achieve epitaxial thick film growth makes use of the extraordinary ability of perovskites to accommodate strain well beyond the critical thickness limit by adjusting their lattice constant with small shifts in the cation ratio, tuned by deposition parameters. We show that our approach, encompassing several orders of magnitude in film thickness scale whilst maintaining atomic layer control, enables the fabrication of metal-insulator-metal (MIM) varactors based on 50-100 nm thin Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> layers with high tunability above three at Li-ion battery voltage level (3.7 V).

Recent related publications:

P. Salg *et al.*, APL Mater. **7**, 051107 (2019).

P. Salg *et al.*, J. Appl. Phys. **127**, 065302 (2020).

L. Zeinar *et al.*, J. Appl. Phys. **128**, 214104 (2020).

D. Walk *et al.*, 2020IEEE/MTT-S International Microwave Symposium (IMS), Los Angeles, CA, USA, 2020, pp. 139-142, doi: 10.1109/IMS30576.2020.9224035.

## Preparation of protective coatings using polyorganosilazane-derived precursors and cerium as inhibitor to obtain an active protection of Al alloys

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**Keywords:** Al alloys, Corrosion, Cerium, Sol-gel, Polysilazane coatings

In this work, the incorporation of polyorganosilazane-derived precursors to GPTMS ((3-Glycidyloxypropyl trimethoxysilane) silica sols have been considered. The polysilazanes are polymers composed of Si- N- Si network with reactive or inert side groups bound to Si atoms. The influence of synthesis parameters such as reactant's molar ratios, temperature, time, etc., on the sol characteristics have been studied using different techniques such as FTIR, Raman spectroscopy, etc.

The polysilazane/GPTMS sols will be deposited on aluminium alloys by dip-coating at different withdrawal rate. Heat treatment parameters, such as temperature, atmosphere and time, have been also considered to produce SiCN-based ceramic coatings, applicable as environmental barrier coatings, for controlling the oxidation and corrosion of the metal substrate. To achieve active corrosion protection of aluminium alloys, the incorporation of environmentally friendly inhibitors to polysilazane/GPTMS sols have been also studied. The maximum amount of inhibitor that can be incorporated without affecting the stability or morphology of the coatings has been determined. The morphological characterization of the optimized coatings has been carried out using SEM-EDX. Finally, the potentiodynamic polarization method (Tafel) and impedance spectroscopy measurements have been also used to investigate the cathodic and anodic nature and the active corrosion protection in 3.5 % wt NaCl as a function of time.

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## Examination of the Hydrogen Incorporation into Radio Frequency-Sputtered Hydrogenated SiN<sub>x</sub> Thin Films

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**Keywords:** hydrogenated silicon nitride, thin films, radio frequency sputtering

Silicon nitride (SiN<sub>x</sub>) and hydrogenated silicon nitride (SiN<sub>x</sub>:H) thin films have widespread applications, including passivation films for semiconductor devices in microelectronics industry or antireflective layers for solar cells. The most common deposition techniques of SiN<sub>x</sub>:H thin films are different types of chemical vapor deposition methods, such as plasma enhanced chemical vapor deposition (PE-CVD) or hot wire chemical vapor deposition (HW-CVD). Due to the hydrogen content of the precursor gases (most often silane) CVD-deposited films always contain hydrogen and its amount cannot be controlled directly during the preparation process. Therefore, sputtering methods could be interesting as alternative fabrication techniques for controlled hydrogen concentration in direct way from zero by adjusting the applied hydrogen gas flow to the chamber.

In this work amorphous SiN<sub>x</sub> and SiN<sub>x</sub>:H films were deposited by radio frequency (RF) sputtering on single-side and double-side polished crystalline (001) Si wafers. Hydrogen free films were deposited in pure nitrogen, while hydrogenated thin films were fabricated by applying various hydrogen gas to the chamber while all other deposition parameters were kept constant. Optical properties were investigated as a function of hydrogen concentration of the plasma. Structural investigation revealed correlation between hydrogenation process and the layer porosity. 4 at% of bounded hydrogen content was proved by Fourier Transform Infrared Spectroscopy (FTIR) while Elastic Recoil Detection Analysis indicated 6 at% hydrogen which suggests the presence of molecular hydrogen in the films. Annealing measurements showed that molecular hydrogen was released at temperature of ~65 °C while blisters with approximately 100 nm diameter were created on the thin film surface.

## Ink-jet printing of sol-gel based wide band-gap material

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**Keywords:** inkjet printing, wide band-gap, ink formulation, sol-gel, induced gelation

Recent advances in wide band-gap semiconductor materials are enabling a new generation of semiconductor devices beyond the traditional silicon technology<sup>1</sup>. The combination of such semiconductors with an adequate processing method opens up opportunities for a range of novel applications. One such processing method is inkjet printing, which allows for rapid and low-cost manufacture of layered materials. Here, we will report on the processing of several semiconductor materials, like ZrO<sub>2</sub>, SnO<sub>2</sub> and ZnO by using the sol-gel inkjet printing method and subsequent treatment. A commercially available inkjet printer was modified to a flat-bed design in order to print layered microstructures on stiff substrates. The challenging part is to develop an ink suitable for a multi-nozzle commodity printer head. The sol composition was optimized in terms of suitable ink viscosity, surface tension and evaporation properties. Improper ink design leads to lines with bulges or even discrete beads. Solvent-evaporation-induced gelation played an important role in the stability of the printed lines<sup>2</sup>. Taking advantage of the solvent evaporation and sol-gel transition upon substrate heating, we show the evolution of the quality of printed structures. Further solvent evaporation during firing created structures with cracks. The possibility of printing crack-free structures with the sub-critical thickness with the use of polymer additives<sup>3</sup> is also discussed.

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**Biomaterials**



## Cu and Sr doped Mesoporous Bioactive Glass: A preliminary study

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**Keywords:** mesoporous bioactive glass, bioactivity, osteogenesis, angiogenesis, antibacterial

Traumatic injuries or infections cause bone loss. Bone degradation and the treatment of bone defects, i.e. restoration, replacement and regeneration of the bone tissue is still a challenging problem.

Mesoporous bioactive glass (MBG) is widely considered as a candidate for bone tissue regeneration application due to its mesoporous structure, large surface area and bioactivity (ability to form bonds with bone). Its properties can be adjusted and tailored by introducing selected therapeutics ions able to play a specific functional and/or biological role [1]. The doping of copper (Cu) and strontium (Sr) offers multifunctional effects in MBG, including stimulation effects on bone formation such as osteogenesis, angiogenesis as well as antibacterial activities [2,3]. In the present study, Sr and Cu co-doped (0-2 mol%) MBG with 80SiO<sub>2</sub>-(15-x) CaO-5P<sub>2</sub>O<sub>5</sub> glass composition and x= 0-4 mol.% were prepared by sol-gel method and evaporation induced self-assembly technique (EISA) using pluronic surfactant P123. The loss of all organic precursors and structure directing agents was completed at around 650°C, as confirmed by DTA-TGA: hence, all samples were calcined at 700°C for 5 h for further study. XRD confirmed the amorphous nature of the glass powders while Raman spectroscopy confirmed the presence of Si-O-Si and P-O bands. Some peak shifts were observed in the Raman spectra of doped glasses. The chemical composition of prepared glasses was verified by ICP-OES, which confirmed the presence of dopant ions in MBG system in the added amounts. However, the amount of phosphorus was determined in lower amounts comparing to the nominal compositions. All the powders scanned by electron microscopy showed cluster-like small cubes morphology and a fringe pattern was observed for all the powders indicating the formation of a highly ordered mesoporous structure in the prepared MBG.

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## Layered rare earth hydroxide nanoparticles for theranostics

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**Keywords:** Theranostics, nanomedicine, drug delivery, fluorescence, layered hydroxide

Theranostics is an emerging field of medicine, and aims to combine diagnostic imaging approaches with therapeutic methods. Layered rare-earth hydroxides are composed of positively charged layers, and are able to reversibly uptake drug anions. The presence of a rare-earth ions allows these materials to act as contrast agents in magnetic resonance and fluorescence imaging. This has been previously demonstrated by our group using layered gadolinium hydroxide, which was shown to be an effective MRI contrast agent.<sup>1</sup>

This work explores layered terbium hydroxide ('LTbH', [Tb<sub>2</sub>(OH)<sub>5</sub>]Cl·yH<sub>2</sub>O, Fig. 1a) as a platform for simultaneous drug delivery and fluorescence imaging. Three novel LTbH- drug intercalates were synthesised, containing diclofenac, ibuprofen, and naproxen anions. Intercalation of the drug anions was confirmed using X-ray diffraction, FTIR spectroscopy, and elemental microanalysis. Drug release experiments (Fig. 1b) revealed that LTbH is able to release drug cargo over approximately 5 h. Fluorescence studies (Fig. 1c) showed that the LTbH materials exhibit a signal characteristic of the Tb<sup>3+</sup> ion <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>5</sub> transition, the intensity of which changes with de-intercalation of the drug ions and can be used to track drug release. Moreover, in-vitro cytotoxicity studies demonstrated that all LTbH materials tested were highly cytocompatible. Overall, the results of the present study show that LTbH has favourable properties for theranostic applications.

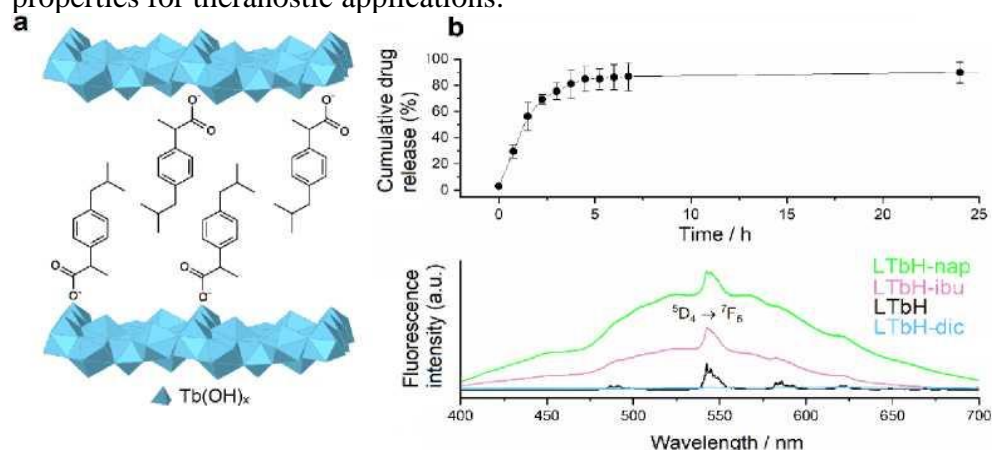


Figure 1: Structure of LTbH intercalated with ibuprofen (a) and the corresponding drug release and fluorescence spectroscopy results (b and c, respectively).

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## Novel Si<sub>3</sub>N<sub>4</sub>/Si<sub>3</sub>N<sub>4</sub>- graphene / hydroxyapatite layered gradient composites

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**Keywords:** Si<sub>3</sub>N<sub>4</sub>, graphene, hydroxyapatite, layered structure

The 400 000 artificial hip joint operations made every year in the world 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, Si<sub>3</sub>N<sub>4</sub> 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 (Si<sub>3</sub>N<sub>4</sub>) could help avoid the rejection from the body in the critical early few days after the operation.

The main trends and fundamental scientific problems about layered bioceramics will be discussed.

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## Development of functional sol-gel coatings on titanium with broad-spectrum properties

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**Keywords:** Titania coating, Sol-gel, Silver, Dip-coating, Antibacterial, Cytotoxicity, In vitro

The titania coatings doped with elements such as silver, calcium and phosphorus, can significantly change the current surface properties of the inert titanium substrate. The metallic material achieves the antibacterial, non-toxic and bioactive properties that are currently required in the field of dental and orthopaedic implantology. The coatings formed by the sol-gel method dip-coating technique are very thin so that they do not change the substrate parameters and at the same time perfectly copy any complicated surface of the substrate. These coatings also have excellent adhesion properties that are important in handling coated substrates. Last, but not least, a great advantage of the titania coating doped with Ag, Ca and P components is the technical simplicity and price. The antibacterial effect was tested against gram-negative *E. coli* and gram-positive *S. epidermidis* for 4 and 24 hours. Coatings on titanium and titanium alloy with two forms of silver ( $\text{AgNO}_3$ ,  $\text{Ag}_3\text{PO}_4$ ) at different concentrations showed an antibacterial effect. The cytotoxicity test with extracts (ISO 10993-5) and also with direct (contact) test was performed using the mammalian cell lines L929 and U-2 OS. Coatings prepared from the sols with a concentration of silver 0.02, 0.06 and 0.09 mol.l<sup>-1</sup> were non-toxic. The adhesion was measured by tape test and all types of titania coatings showed very good adhesion to the titanium and titanium alloy. The *in vitro* test with SBF was used for the testing of bioactive properties of coatings. The hydroxyapatite precipitated on the titania coatings with calcium and phosphate elements under static-dynamic conditions.

## Antimicrobial Soda Lime Silicate Glass Produced by Multi-step Ion Exchange

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**Keywords:** soda-lime silicate, ion-exchange, indentation, strengthening, antimicrobial

Although glass plays a vital role in medical facilities, i.e. countertops or interfaces of equipment, where chemical and mechanical durability is of great concern for such applications, less attention has been paid to developing strong glasses with antimicrobial properties. In the present study, antimicrobial glass is produced by tailoring the strength and surface properties of soda-lime float glass using multi-step ion exchange. Glass samples were subjected to ion exchange processes sequentially in pure potassium nitrate, for 4-24h, and salt baths doped with variable amounts of silver and alkaline earth ions, for 5-15 min. The surface compressive stress was determined using Vickers' indentation, and the penetration depth was measured using Energy Dispersive X-ray Spectroscopy (EDS). The surface chemical composition was analysed by point analyses using Wavelength Dispersive X-Ray Spectroscopy (WDS). The results showed that silver ions penetrated a few microns in the glass surface with no significant surface compression deterioration. The corrosion experiments showed that the silver-rich layer provides the required  $\text{Ag}^+$  leaching essential for the antimicrobial application. Furthermore, silver leaching rate is influenced by the presence of alkali-earth elements in the salt bath.

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## FunGlass Symposium

## Preparation and characterization of electrospun composite fibers with mesoporous bioactive glass nanoparticles: the effect of the amount of nanoparticles and Cu-doping on cell proliferation

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**Keywords:** Bioactive glass, Copper, Electrospinning, Mesoporous, poly( $\epsilon$ -caprolactone)

Due to their 3D porous architecture and the addition of bioactive materials embedded in the soft polymer matrix, electrospun polymeric composite scaffolds became an effective platform for tissue regeneration applications. Therapeutic ion-doped mesoporous bioactive glasses have been studied as novel candidates for incorporation in the polymeric matrix because of their excellent bioactivity, drug loading capacity, and release of therapeutic ions [1]. Recent studies also showed that copper ions ( $\text{Cu}^{2+}$ ) have a significant role in the preparation of biomaterials due to its antibacterial, antimicrobial, angiogenic, and wound healing properties [2]. In this study, we have prepared mesoporous bioactive glass nanoparticles (MBGNs) and Cu-doped MBGNs (Cu-MBGNs) by an emulsion-based sol-gel method. The MBGNs were used to fabricate poly( $\epsilon$ -caprolactone) (PCL)-based electrospun fibrous composites, using optimized parameters of the electrospinning. Fiber mats with different amounts of MBGNs and Cu-MBGNs (5, 10, and 15 wt% with respect to the amount of the polymer) incorporated into the polymer matrix were prepared and characterized. The average diameter of the fabricated fibers was in the range of 190-230 nm.

Afterwards, cell interactions with the composite fibers with different surface roughness and various contents of  $\text{Cu}^{2+}$  ions were studied. The acellular bioactivity (SBF study) of the MBGNs and composite fibers was also investigated. The SEM examination confirmed formation of hydroxyapatite (HA) like crystals *in-vitro* on the surface of MBGNs and Cu-MBGNs. However, *in vitro* mineralisation (HA crystal formation) on composite fibers, with incorporated MBGNs, was not observed. *In vitro* biological study with murine bone marrow-derived stromal cells (ST-2) was performed to investigate the cell attachment and proliferation on the composite mats. Cell viability on the fiber mats was assessed by using the WST-8 assay, using the neat PCL fiber mats as reference. Cell viability decreased significantly by increasing MBGNs content (15 wt%). No significant change of the cell viability was observed for the fiber mat composites with incorporated Cu-doped MBGNs. Fluorescence microscopy and SEM studies of fiber mats with attached cells confirmed the positive role of Cu in cell proliferation.

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## Preparation and characterization of Chitosan-Zn complex films for wound healing applications

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**Keywords:** chitosan, chelation, wound healing, zinc, therapeutic ions

The repair of a wound is one of the most complex biological processes associated with tissue growth and regeneration controlled by various biochemical and cellular mechanisms. It is a dynamic process and involves the interaction of a large number of different types of cells (Boateng and Catanzano 2015). When the wound cannot be repaired itself, the healing processes can be accelerated and stimulated by using various kinds of wound dressings. Among the dressing materials, great interest is being given to chitosan due to its favorable properties such as biocompatibility, non-toxicity, anti-inflammatory, and hemostatic properties. Chitosan as a natural biopolymer is promising material because of the structure similar to glycosaminoglycans which are present in the extracellular matrix. They modulate macrophages, fibroblasts, and endothelial cells by promoting the formation of granulating tissue (Jayakumar et al. 2011; Levensgood et al. 2017). Although chitosan unique properties have been already exploited on commercial basis in products such as Tegaderm, its functionalization is necessary to introduce additional properties for wound healing applications such as antibacterial activity, angiogenesis, and hemostasis. In this study, chitosan was chelated with different ratios of zinc by the in-situ precipitation method previously reported by (Gritsch et al. 2018). Then, chitosan-based films were prepared by solvent casting. The chemical nature of the films was determined by energy-dispersive x-ray spectroscopy and Fourier-transform infrared spectroscopy. MTT assay confirmed the biocompatibility of developed films towards stromal cells (ST-2) and mouse fibroblast cells (MEF) both in indirect and direct contact with the material. In vitro wound scratch test was conducted to evaluate the migration rate of keratinocyte-like cells (HaCaT), with pure chitosan used as the reference. The polysaccharide matrix saturated with 6 % of amino groups of chitosan showed the highest rate of migration at day 3 with 88 % of wound closure. In addition, the antibacterial activity of the films against gram-negative and gram-positive bacteria was carried out to assess their suitability for wound therapy. Chitosan-Zn complex showed superior antibacterial efficiency against *S. aureus*. To evaluate the effect of fabricated complexes on nitric oxide production from macrophages, the cell study was performed using RAW 264.7 cells. The zinc content in the samples affected the NO production: the NO production was slightly reduced with increasing Zn content. The results indicate that the chitosan-Zn complex holds a promise for wound healing applications.

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## Analysis of the hydrophobic character and reflectance in SiO<sub>2</sub> and SiO<sub>2</sub>-TiO<sub>2</sub> coatings obtained by sol-gel method

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**Keywords:** antireflective coatings, sol-gel, TiO<sub>2</sub>

Antireflective coatings (ARCs), as the media that suppress the undesired reflection effects in multiple applications such as PV solar cells or electro-optical-systems in telecommunications or laser systems, are still an area of great interest<sup>1,2</sup>. ARCs are developed by different approaches such as multilayers coatings, porous layers, coatings incorporating nanoparticles, etc. Different preparation methods can be used to obtain ARC such as chemical or physical deposition techniques (CVD, PVD, etc.)<sup>3</sup> and wet techniques (spray coating, brush casting, spin coating, dip coating, etc.). Wet deposition techniques are suitable processes for the successful preparation of homogeneous coatings of multi-phase materials. Sol-gel processes involve the preparation of a precursor mix (sol) which transforms into a solid-like material after aging and evaporation. This process allows the microstructure of the final film to be controlled by varying the parameters of the synthesis<sup>4</sup>. Dip-coating is one of the most common methods used for the preparation of thin films in combination with the sol-gel process since it offers a good control on the coating thickness.

In this work, (1-x)SiO<sub>2</sub>/xTiO<sub>2</sub> (where x = 0, 0.75, 0.5, 0.25 and 1) sols were prepared and deposited on glass substrate by dip-coating process at different withdrawal rates, ranging from 2.1 to 14.2 cm/min. Moreover, silica sol of composition TEOS - OTES - H<sub>2</sub>O - HNO<sub>3</sub> - IPA was also synthesized and deposited by dip-coating on glass substrate to obtain hydrophobic and antireflective coatings. Finally, a multilayer system was performed combining a SiO<sub>2</sub>-TiO<sub>2</sub> coating with a SiO<sub>2</sub> ARC layer. The obtained films were treated at 450 °C.

The hydrophobic character of the coatings was analyzed by measuring the contact angle. For the multilayer system, values over 100° were obtained confirming the hydrophobic character of the double layer. The thickness and transmittance properties of SiO<sub>2</sub> - TiO<sub>2</sub> and Silica ARC coatings were also measured at 550 nm, and maximum transmittance of 94.1 % was obtained for a molar ratio of 0.5SiO<sub>2</sub>:0.5TiO<sub>2</sub>. Similarly, the double-layer SiO<sub>2</sub>-TiO<sub>2</sub>/SiO<sub>2</sub> ARC achieved a maximum transmittance of 99.1 % at 550 nm. Preliminary results open the way to develop multilayer coatings combining different systems to achieve a system with maximum transmittance.

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## Structure and Fluorescence Properties of Dy doped Borophosphate Glasses

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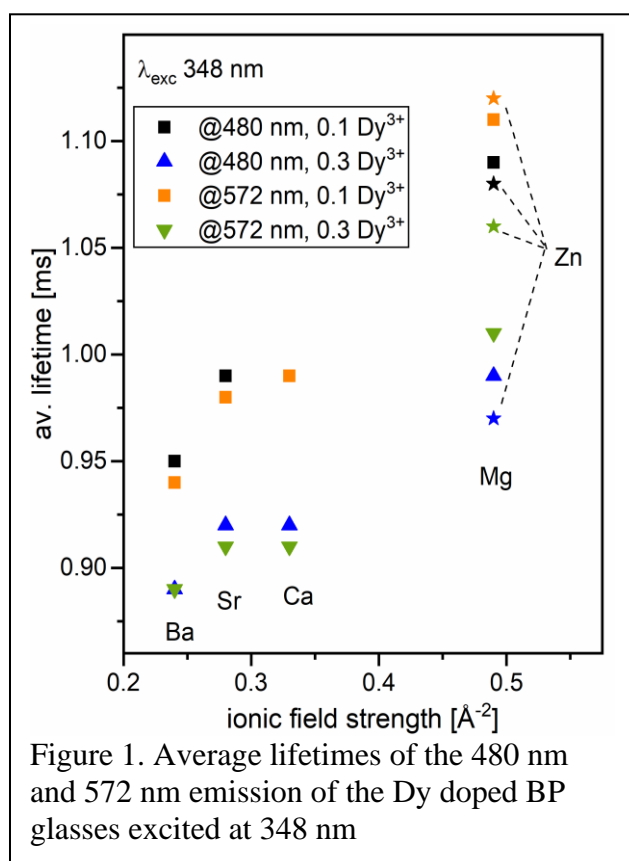
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**Keywords:** Borophosphate, Luminescence, Structure, Glass, NMR, FTIR, Raman

Rare earth doped glasses are potential materials for the production of photonic devices such as solid-state lasers, lighting, optical amplifiers and sensors. Doping with Dy<sup>3+</sup> is particularly interesting for the generation of white light, due to its two emission bands in the blue and yellow part of the visible spectrum.



Borophosphate (BP) glasses are promising host matrices for Dy<sup>3+</sup> ions, as they show comparatively high solubility for rare earth ions, have low melting points and low dispersion and a lower sensitivity to water when compared to pure phosphate glasses.

Dy doped BP glasses containing network modifiers such as Ba<sup>2+</sup> or Zn<sup>2+</sup> have been investigated with respect to their structural and fluorescent properties. We present structural analysis results obtained by infrared, Nuclear Magnetic Resonance and Raman spectroscopy, showing the influence of the different network modifiers on the structure of the BP glass matrix. The Dy emission lifetime and emission spectra are recorded and correlated to structural aspects of the glasses. It was found that the Dy emission lifetime increases with increasing network modifier field strength which can be explained by stronger M-O bonding and rearrangement of the local Dy environment.

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## Additive manufacturing of Ca-Mg silicate scaffolds supported by flame-synthesized glass microspheres

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**Keywords:** Ca-Mg silicates, flame spheroidisation, solid glass microspheres, additive manufacturing technology - DLP, 3D bioactive scaffolds

The present paper deals with a glass approach to three-dimensional scaffolds based on Ca-Mg silicates, which are among the most promising modern bioceramics. The remarkable crystallization tendency of a glass with åkermanite stoichiometry ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ , i.e. 40 mol% CaO, 20% MgO and 40%  $\text{SiO}_2$ ) was considered twice. In a first step, the crystallization was overcome, by feeding oxygen-methane ( $\text{O}_2/\text{CH}_4$ ) torch with nearly fully crystallized powders, from preliminary conventional melt quenching, with the obtainment of solid glass microspheres (SGMs) - with a diameter of 5-63  $\mu\text{m}$ . In a second step, the crystallization was useful in limiting the viscous flow of SGMs, upon firing of reticulated scaffolds, obtained by digital light processing (DLP) of the same SGMs suspended in a photocurable acrylate binder. The spheroidal shape favoured the adoption of a high solid content, up to 77 wt%. After burn-out of the organic binder, a fast sintering treatment at 950°C, for 30 min, led to scaffolds preserving the macro-porosity from 3D printing model (diamond cell lattice) but with well densified struts. The packing of particles in the printing phase affected the crystallization sequence, favouring merwinite ( $\text{Ca}_3\text{MgSi}_2\text{O}_8$ ) and diopside ( $\text{CaMgSi}_2\text{O}_6$ ) instead of åkermanite. The crystallization led to scaffolds with adequate strength-to-density ratio.

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## Assessment of Alkali activation for Producing Porous Glass Microspheres

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**Keywords:** upcycling/recycling, waste glasses, alkali activation, flame synthesis, porous glass microspheres

Alkali-Activation (AA) is a new generation procedure that has taken a lot of consideration recently. Alkali-Activation materials are materials produced when glass powder is activated by a strongly alkaline solution. Which strengthens and develops materials with high binding properties [1]. In general, any substances that have sufficient quantities of silica and calcia can be applied as a precursor for alkali activation. The most common alkaline solutions that can be applied properly for alkali activation are NaOH, KOH, and sodium silicate hydrates (water glass). Alkali activation begins of such materials with two stages, first, it starts with the destruction of the basic materials and then poly-condensation of the reaction products. Porous glass microspheres (PGMs) are ultra-lightweight inorganic non-metallic material with a hollow structure, and it possesses multipurpose and has extraordinary properties as a new material that produced lately [2]. In this study, different concentrations of the alkaline solution have been applied for glass wastes in order to optimize the formation of porous glass microspheres through the flame synthesis process (oxygen/ methane flame). Many techniques have been used in this study such as differential thermal analysis (DTA) for investigating the thermal effect of the produced activated material, x-ray diffraction (XRD) for checking the exactly formed phases after alkali activation, scanning electron microscope (SEM) for investigating the morphology of the obtained glass microspheres, helium pycnometer for measuring the density of the obtained glass microspheres.

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## Preparation and characterization of PEO/sol-gel composite coatings for corrosion protection of Mg alloys

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*Keywords:* AZ31B Mg alloy, anodization, sol-gel, corrosion performance

Magnesium and its alloys have become a hot research topic for a variety of industries such as electronic, automotive, biomedical, aerospace industries due to its excellent mechanical and physical properties; particularly, low density, easy recyclability, and high strength-to-weight ratio properties. Nevertheless, their high chemical reactivity makes them highly susceptible to corrosion, limiting their use in such areas. The control of corrosion rate through surface modification techniques has attracted an increasing interest for many researchers. Among the alternatives, plasma electrolytic oxidation (PEO) is one of the most important surface techniques based on the creation a natural micro-porous oxide layer by using environmentally friendly electrolytes. However, the oxide layer provides a moderate corrosion protection on metals because the presence of micro-pores acts as potential sites for penetration of corrosive  $\text{Cl}^-$  ions of electrolytic medium. A posttreatment process achieved by the deposition of a sol-gel coating can be a good approach to optimize the surface microstructure by reducing the coating porosity.

Under this perspective, the aim of the work was the optimization of the anodizing condition to obtain PEO coatings, using an alkaline electrolyte (NaOH) modified with the addition of different concentration of sodium metasilicate pentahydrate ( $\text{Na}_2\text{SiO}_3$ ). On the other hand, the preparation and deposition of  $\text{SiO}_2$  sol on the PEO coatings, obtained by hydrolysis and condensation of TEOS (tetraethoxysilane) and GPTMS (3- Glycidyloxypropyl) trimethoxysilane) was also studied to obtain an integrated system. The final coating systems have been characterized by infrared (IR) spectroscopy, optical microscope, x-ray diffraction (XRD), spectroscopic ellipsometer, optical profilometer and water contact angle. The electrochemical properties have been explored in 3.5%wt NaCl solution by potentiodynamic polarization technique and Electrochemical Impedance Spectroscopy (EIS) (Gamry FAS2 Femtostat), revealing that the appropriate anodization electrolyte together with the post-treatment process result in a promising solution to control the corrosion performance.



## Transparent Nd<sup>3+</sup>-doped LaF<sub>3</sub>-SiO<sub>2</sub> glass ceramics films produced by sol-gel and using nano-crystalline suspensions

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**Keywords:** glass ceramic films, sol-gel, xerogel

Glass-ceramics are inorganic non-metallic materials containing one or more functional crystalline phases and a residual glass. Rare earth (RE)-doped fluoride crystal nanoparticles in a sol-gel silica matrix, as well as oxide glass matrices containing fluoride crystals, have gained attention in the last decades due to their attractive optical properties and their use in photonic applications.

Melt-quenching (MQ) is the most frequently used method to prepare these materials.

However, the sol-gel method has increased its impact as a suitable alternative process to prepare oxyfluoride glass-ceramics avoiding the drawbacks of MQ and allowing the preparation of thin films with luminescence emission. The SG method is an appropriate and versatile route compared to other chemical procedures.

The aim of this work was to study the preparation of glass ceramics films using a new sol-gel route based in the preparation of fluoride nanoparticle suspensions doped with Nd<sup>3+</sup> via chemical reaction and their subsequent incorporation in a silica sol-gel matrix. First, stable, and homogeneous suspensions of LaF<sub>3</sub> nanoparticles doped with 1.2 Nd<sup>3+</sup> % wt. were prepared and dispersed with the help of polyvinyl pyrrolidone (PVP). The suspensions were characterized by XRD, HRTEM, Zeta Potential and Nanosizing, to confirm the crystallization of the LaF<sub>3</sub> as unique phase and the well dispersability. Second, LaF<sub>3</sub> nanoparticles suspensions were incorporated into a TEOS-MTES sol and used to obtain xerogels and films. Xerogel was dried in Teflon mold at 450°C and films were prepared by dip-coating. Finally, xerogels and films were heat treated at 150°C and 450°C for 1h to eliminate de organic PVP and to consolidate the structure.

Optical characterization of Nd<sup>3+</sup>-doped LaF<sub>3</sub>-SiO<sub>2</sub> xerogels and films has been performed by the emission spectra of the laser transition and lifetimes of the <sup>4</sup>F<sub>3/2</sub> state. The results confirm the efficiency of the active phase and evidence the Nd<sup>3+</sup> incorporation into the LaF<sub>3</sub> nanocrystals with a well-defined crystal field site for the GCs powders and films heat treated at 450°C/1h.

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## Spark plasma sintering and optical properties of Tm doped NaLaF<sub>4</sub> transparent glass- ceramics

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**Keywords:** Transparent oxyfluoride glass-ceramics, NaLaF<sub>4</sub>, spark plasma sintering (SPS)

Rare-earth doped transparent oxyfluoride glass-ceramics (GCs) are promising materials in the photonics field. The main advantage of these materials is the combination of the good mechanical and chemical properties of oxide glasses with the low phonon energy (300- 500 cm<sup>-1</sup>) of fluoride crystals (Fedorov et al., 2015). In this work, transparent GCs containing NaLaF<sub>4</sub> nanocrystals (NCs) doped with Tm<sup>3+</sup> ions were prepared by Spark Plasma Sintering (SPS). Glass powder pellets were sintered under a vacuum atmosphere, optimizing the processing parameters such as particle size, pressure, temperature, and holding time to obtain full densification (Singarapu et al., 2020) and nanocrystals formation. X- ray diffraction (XRD) and high- resolution transmission electron microscopy (HR-TEM) have been used for the structural characterization of the GCs. The structural properties have been correlated with the optical properties of the glasses and GCs including transmittance measurements, near infrared (NIR) emission spectra and the corresponding lifetimes. The GCs obtained by SPS show similar properties to those prepared through conventional heat treatment (De Pablos-Martín et al., 2010) but involving shorter treatment times.

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## Poster session

## Behavior of molybdenum in calcium phosphate glasses

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**Keywords:** phosphate glasses; molybdenum; structure;  $^{31}\text{P}$  MAS NMR; ESR

Transition metals are often used as an electropositive part of phosphate glasses, but their chemistry in high temperature melts is often not given enough attention. While for the s- and p-metals their interaction with the phosphate glassy network can be predicted with a high probability, in the case of transition metals (d-elements) the situation is more complicated, as they can occur in several oxidation states and form various complex ions, which can come in to the formation and strengthening of the glass-forming network by means of coordination bonds. For these reasons, it is not possible to predict unambiguously the chemical behavior of transition metals in the phosphate melt. It is therefore appropriate to pay more detailed attention to the chemistry of transition metals in phosphate melts, as the literature data are often contradictory and not entirely sufficient. One of the elements that can occur in different oxidation states and form different complex cations is molybdenum. In glasses, this should normally occur in two oxidation states,  $\text{Mo}^{\text{VI}}$  ( $d^0$  system) and  $\text{Mo}^{\text{V}}$  ( $d^1$ ) and can form molybdenyls  $(\text{Mo}^{\text{X}}\text{O}_2)^{(\text{X}-4)+}$  and  $(\text{Mo}^{\text{X}}\text{O})^{(\text{X}-2)+}$ , where X is 6 or 5.

A series of glasses in which the composition changes from calcium metaphosphate to molybdenum pyrophosphate  $(\text{Mo}^{\text{V}}\text{O})_4(\text{P}_2\text{O}_7)_3$ , i.e.  $x\text{MoO}_3-(50-0.875x)\text{CaO}-(50-0.125x)\text{P}_2\text{O}_5$ ,  $x = 0, 1, 10, 20, 30, 40, 45, 50$  and 57.14, was used for this work. Homogeneous glasses were prepared over the whole compositional line. The composition of glasses was checked by XRF. The Mo free glass ( $x=0$ ) was colorless and transparent and the addition of Mo produces a gradual coloration of glasses changing from light to dark green indicating by that the reduction of Mo(VI) to Mo(V) during synthesis ( $d^0$  to  $d^1$  system). The degree of reduction of molybdenum and the symmetry of its coordination polyhedron were derived from electron paramagnetic resonance measurements. The amount of reduced Mo did not exceed 3%, only in the case of the two highest concentrations of  $\text{MoO}_3$  the reduction was higher  $\sim 7\%$ , which is still a very low degree of reduction.

The phosphate base of glassy network was characterized by  $^{31}\text{P}$  MAS NMR and correlated with Raman spectra. It has been found that  $\text{Ca}^{2+}$  is gradually being replaced by molybdenyl  $(\text{MoO}_2)^{2+}$  and thus starting metaphosphate network of  $\text{Ca}(\text{PO}_3)_2$  remains maintained as much as possible and only a significantly increasing O/P ratio leads to the partial formation of pyrophosphates. It has been found that like in aqueous solution, reduction of  $\text{Mo}^{\text{VI}}$  is almost negligible in the glass-forming phosphate melts and that composition of phosphate glassy network is primarily controlled by the presence of divalent cations. Unlike calcium, molybdenyl is incorporated into the glass network structure by four covalent bonds which, in addition to forming a cation-anion network, also allows the involvement of small pyrophosphate anions, i.e.  $(\text{O}_3\text{P}-\text{O}-\text{PO}_3)^{4-}$  units in the glass network and thus improves the glass forming ability of the studied system even with complete replacement of calcium by molybdenum.

## Borate and silicate glasses doped with $\text{Ce}^{3+}$ and $\text{Mn}^{2+}$ ions for UV-VIS spectral shifting

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**Keywords:** photoluminescence, silicate, borate, glass, cerium, manganese

This study is aimed to investigate the possibilities of spectral shifting of light radiation by using the combination of  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$  ions in glasses. We focused on the possibility of shifting the radiation from green region of spectra (470-550 nm) to red (650-730 nm) or blue (370-450 nm) regions. The combination of  $\text{Ce}^{3+}$  and  $\text{Mn}^{3+}$  ions has been shown to manifest this kind of shifting in special types of crystalline matrices [1-3], however it is yet to be investigated in glasses. The type of used matrix and method of preparation can influence the oxidation state of doped ions and their photoluminescence properties (shape and position of emission spectra, photoluminescence lifetime). The use of glasses also has several benefits over crystals in practical applications such as low cost and easy preparation.

To study the influence of glass matrix on photoluminescence, we prepared several types of glasses doped by mixture of  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$  ions. First, two glasses with completely different matrices – silicate and borate – were prepared to study their suitability as host matrix for both ions. In addition, a set of borosilicate glasses with varying contents of  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$  were prepared and reducing agents were added to the batch to preserve cerium and manganese in +III and +II oxidation state, respectively. The glasses were prepared by a standard melt-quenching technique. Basic optical and physical properties of the glasses were measured, such as refractive index by m-line spectroscopy, density by pycnometric measurement and glass transition temperature by differential scanning calorimetry. Structure of the glasses was studied by Raman spectroscopy. XPS and EPR measurements were carried out to study the oxidation state of doped elements in the glass. Spectroscopic properties were evaluated by absorption spectroscopy and photoluminescence measurements in UV-VIS.

The results indicate that borate and borosilicate glasses are suitable hosts for incorporation of  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$  ions, which results in 650 nm luminescence under UV excitation. However, pure borate glass displayed poor chemical resistance against water. Silicate glasses were chemically stable, but failed to manifest clear luminescence of  $\text{Mn}^{2+}$  ions in the region of 650 nm. Borosilicate glasses were prepared to combine the advantages of both types of glasses and the best ratio of  $\text{B}_2\text{O}_3/\text{SiO}_2$  content was studied. Reducing agents were found to preserve  $\text{Mn}^{2+}$  ions in the glass and therefore enhance  $\text{Mn}^{2+}$  photoluminescence. The studied glasses are promising candidates for the use in photobioreactors for enhancing a growth of various bio-organisms such as algae.

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## Isomorphous Substitutions in the Electron-Ion Conductor $\text{Pr}_5\text{Mo}_3\text{O}_{16+\delta}$

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**Keywords:** molybdates, rare-earth elements, fluorite, solid solutions, solid electrolytes, electrical conductivity

Solid ionic oxygen conductors are interesting functional materials due to the possibility of using them in fuel cells, gas sensors, and devices for producing pure oxygen. Compounds  $\text{Ln}_5\text{Mo}_3\text{O}_{16+\delta}$  exhibit high oxygen-ion conductivity at medium temperatures. These molybdates have a fluorite-like structure and crystallize in the  $\text{Pn-3n}$  space group. The initial fluorite structure is distorted as a result of the presence of cations significantly different in size and charge. It leads to the displacement of oxygen ions from the ideal fluorite positions and the formation of  $\text{MoO}_4$  tetrahedra.

The conductivity of the oxidized  $\text{Ln}_5\text{Mo}_3\text{O}_{16+\delta}$  molybdates is proportional to the REE size, which is due to an increase in interatomic distances and, as a consequence, to a decrease in steric obstacles due to the oxygen ions movement. The cubic fluorite-like structure is formed under oxidizing conditions only for praseodymium and neodymium molybdates. Praseodymium may have variable oxidation states in  $\text{Pr}_5\text{Mo}_3\text{O}_{16+\delta}$ , which determines the presence of electronic conductivity and the possibility of using  $\text{Pr}_5\text{Mo}_3\text{O}_{16+\delta}$  as electrode material in fuel cells [1]. The value of electronic conductivity is insufficient for practical use, but it can be improved through heterovalent isomorphous substitutions with charge compensation of elements in lower oxidation states for praseodymium and molybdenum according to the schemes:  $2\text{Pr}^{+3} \rightarrow \text{M}^{+2} + \text{Pr}^{+4}$ ;  $\text{Mo}^{+6} + \text{Pr}^{+3} \rightarrow \text{M}^{+5} + \text{Pr}^{+4}$ . However, other schemes with charge compensation are valid:  $\text{Pr}^{+3} + 1/2\text{O}^{2-} \rightarrow \text{M}^{+2} + 1/2\text{V}_\text{o}$ ;  $\text{Mo}^{+6} + 1/2\text{O}^{2-} \rightarrow \text{M}^{+5} + 1/2\text{V}_\text{o}$ . To verify this, in this research we studied isomorphous substitution of calcium for praseodymium and niobium for molybdenum in the  $\text{Pr}_5\text{Mo}_3\text{O}_{16+\delta}$ .

Samples of the  $\text{Pr}_{5-x}\text{Ca}_x\text{Mo}_3\text{O}_{16+\delta}$  ( $x = 0 - 1$ ) and  $\text{Pr}_5\text{Mo}_{3-x}\text{Nb}_x\text{O}_{16+\delta}$  ( $x = 0 - 2$ ) systems were obtained by solid-phase synthesis. The unit cell parameters were calculated by full profile analysis, the conductive properties were measured, and the morphology of the ceramic surface was studied using scanning electron microscopy for the obtained samples. The elemental composition is confirmed by energy dispersive x-ray spectroscopy.

The phase with a cubic structure exists in the whole concentration range in the  $\text{Pr}_{5-x}\text{Ca}_x\text{Mo}_3\text{O}_{16+\delta}$  system after calcination at  $1100^\circ\text{C}$ . Single-phase samples obtained in the composition up to  $x = 0.5$ . A phase with calcium molybdate structure appears at a higher concentration of the modifying element. The unit cell parameter decreases with the introduction of calcium to  $x = 0.5$  and does not change at higher  $x$  values which indicates the substitutional limit of calcium for praseodymium in the structure of praseodymium molybdate. In the  $\text{Pr}_5\text{Mo}_{3-x}\text{Nb}_x\text{O}_{16+\delta}$  system, the homogeneous region of single-phase samples was found up to  $x = 1.2$ .

It was shown that the substitution of calcium for praseodymium and niobium for molybdenum leads to a decrease in total conductivity. It suggests that praseodymium stays in the oxidation state of +3 in the solid solutions and charge compensation is achieved through the formation of oxygen vacancies.

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## Precipitation of cobalt molybdates on activated carbons for catalytic applications

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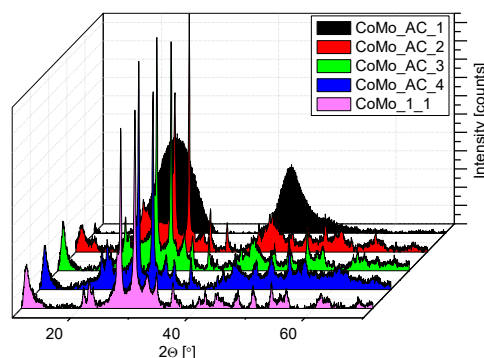
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**Keywords:** activated carbon, catalytic applications, cobalt, molybdenum

In order to meet economical requirements for industrial processes, transition metals nitrides are being investigated as a new generation of catalysts. Their purpose is to replace expensive noble metals [1]. Typical industrial processes, which could use nitrides, are hydrotreatment reactions, oxidation and ammonia synthesis. The latter one, currently based on the Haber-Bosch process, uses a Fe-based catalyst and requires pressures near 200 bar and temperatures above 673 K. Nowadays, it is responsible for approximately 2% of global energy demand. Therefore, new catalysts are required to optimise this technology. Cobalt molybdenum nitrides are possible catalysts to reduce energy consumption by  $\text{NH}_3$  synthesis [2]. This research presents a preparation procedure for cobalt molybdate supported on activated carbon, which could be transformed into a nitride form.

Following materials were used:  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  and activated carbon (AC) Organosorb 10CO as a support. According to the previous study [3], AC was washed with water to remove soluble inorganic compounds. The final precipitation step was performed in the presence of supporting material. Samples with different ratios of cobalt and molybdenum compounds to AC were prepared.

Materials were analysed with the XRD technique, which confirmed successful precipitation of the cobalt molybdate phase on the AC, thus sufficient dispersion of a precursor is possible to obtain via the presented method.



**Figure 1.** XRD results of obtained materials. CoMo\_AC\_X is a supported material, where higher X means a higher load of catalyst on the carbon support.

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## Influence of various annealing atmospheres on excitonic and defect photoluminescence properties of single-crystal ZnO

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**Keywords:** annealing, atmospheres, ZnO, defects, luminescence

In the last decade, ZnO has been intensively studied as a II-VI type semiconductor thanks to its excellent electro-optic, acousto-optic and piezoelectric properties, high electric conductivity and physical as well as chemical stability. ZnO is a crystal material with wurtzite structure, its most prominent properties include wide band gap and large binding energy. Properties which are interesting for photonics include wide transparency region and high refractive index. Moreover, ZnO exhibits intrinsic photoluminescence in the UV-VIS region, which is related to ZnO crystal structure defects such as oxygen vacancies or zinc and oxygen interstitials. Recently a tailoring of the band gap of ZnO has also become an important topic since ZnO material can be utilized in new-generation nanoscale photonics devices. Multiple studies have established a relationship between oxygen defects in ZnO structure and intrinsic photoluminescence and it has also been shown that the concentration of defects may be modified by using different annealing atmospheres. However, a systematic study focusing on the creation and migration of defects in various crystallographic cuts during annealing has been so far missing in literature. In this work, we present a systematic study of the behavior of defects in different crystallographic cuts of ZnO under different annealing atmospheres and its influence on intrinsic photoluminescence.

In our experiment, various ZnO crystallographic orientations were used, i.e. Z (0001), X (11-20) and Y (10-10). The dimensions of the samples were 1.0×1.0×0.3 mm. Thoroughly pre-cleaned wafers were annealed in vacuum or in oxygen and argon atmospheres for 1 hour at the temperature of 600 °C. The structural modifications of the ZnO single crystal structure after the annealing process were determined by Raman spectroscopy, X-Ray Diffraction (XRD) and Rutherford Backscattering Spectroscopy (RBS) and RBS/Channeling measurements. Photoluminescence measurements were performed at a room temperature in the range of 250–1000 nm for visible and near-infrared regions (VIS-NIR). The relationship between annealing conditions, structural changes and photoluminescence was evaluated. Obtained results confirmed the possibility of modifying the photoluminescence of ZnO connected to oxygen defects by using different crystallographic cuts and annealing atmospheres.

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## Preparation of spin-coated thin film using mixtures of separately dissolved chalcogenide glasses of various compositions

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**Keywords:** spin-coating, chalcogenide glasses, thin films, optical properties, wet etching

Chalcogenide glasses are materials well-known for their desirable optical properties such as a wide transparency in infrared region, high refractive index and frequent sensitivity to various kinds of radiation, mainly in thin film form [1]. Chalcogenide thin films are usually deposited using vacuum based deposition techniques such as vacuum thermal evaporation, sputtering or laser ablation [2]. Perspective alternative way is deposition of thin films from source bulk glass solution in volatile organic bases, usually the aliphatic amines.

Solution based deposition techniques circumvent the problem of possible fractionation occurring in the preparation of thin layers of more complex compositions by vacuum based techniques [2] and allow tailoring of thin film properties through incorporation of (nano)materials via source solution doping [3,4]. Doped thin film may have significantly modified physico-chemical properties or some new can be introduced such as photoluminescence [4] or photoconductivity [5].

In our work, we present the study of quaternary As-Ge-Sb-S spin-coated thin films prepared from mixtures of separately dissolved As<sub>40</sub>S<sub>60</sub> and Ge<sub>20</sub>Sb<sub>5</sub>S<sub>75</sub> glasses. Thin films of all studied compositions ((As<sub>40</sub>S<sub>60</sub>)<sub>x</sub>(Ge<sub>20</sub>Sb<sub>5</sub>S<sub>75</sub>)<sub>100-x</sub>; where x = 0, 25, 50, 75 and 100) showed high optical quality and close composition to the target one. The structure, organic residual content, thickness, optical properties and chemical resistance of prepared thin films were studied in dependence on both annealing temperature and the film composition.

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# Model Description of the Viscosity of Glass-Forming Chalcogenides

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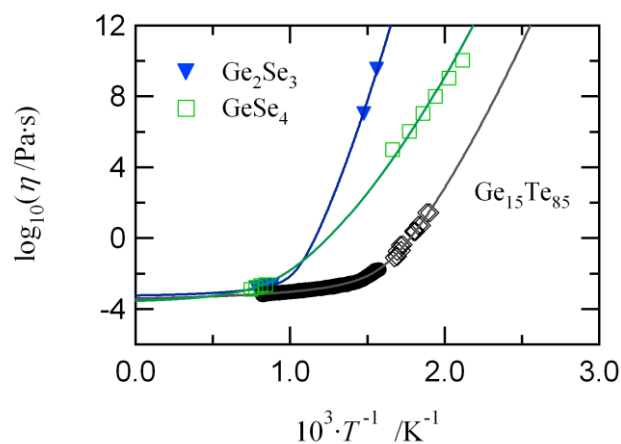
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**Keywords:** viscosity, chalcogenide, glass, fragility, fragile-to-strong transition, BSCNF model

Understand the viscosity behaviour is of primordial importance in the processing of glass-forming materials. Concerning the temperature dependence of the viscosity, many theories and models have been proposed till now [1]. Some years ago, we proposed the Bond Strength-Coordination Number Fluctuation (BSCNF) model [2]. This model describes the temperature dependence of the viscosity or relaxation time in terms of the mean bond strength, mean coordination number and their fluctuations of the structural units that form the melt.

Recently, the model was applied to describe the unusual temperature dependence of the viscosity of metallic glass-forming liquids [3]. These systems have the propensity that at high temperature the viscosity exhibits a very low activation energy, while at low temperature it exhibits an Arrhenius type behaviour. Interestingly, such kind of behaviour has been also observed in some type of chalcogenide systems [4]. Some authors discuss the unusual behaviour in connection with phase change materials and fragile-to-strong transition [4]. In order to understand better the nature of such behaviour, we analysed the temperature dependence of the viscosity of chalcogenide systems based on our BSCNF model. A part of the result is shown in the Figure. Here, the full lines denote the description based on the BSCNF model [3]. By comparing the result obtained in other systems enable us to discuss what could be the origin of the peculiar viscosity behaviour reported in some glass-forming systems.



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## TMA measurements of the viscous flow changes in glasses induced by illumination

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**Keywords:** viscous flow, thermomechanical analysis, penetration method, laser induced changes, glass

The viscous flow is important property of glassy materials that influences many processes (e.g. structural relaxations) and even the industrial applications (e.g. preparation of fibres) (Košťál, Shánělová, & Málek, 2020). The viscous flow can be influenced by photons with appropriate intensity and energy (e.g. in chalcogenides for example Se (Repka, Frumar, & Hrdlicka, 2007) or As<sub>2</sub>S<sub>3</sub> (Tanaka, 2002)).

This work is focused on the study of the viscous flow changes induced by different laser beams covering gap and sub-gap wavelengths ( $\lambda = 532, 650$  nm) at various temperatures below the glass transition temperature ( $T_g$ ) in the model bulk As<sub>2</sub>S<sub>3</sub> glass ( $E_g^{\text{opt}}$  of As<sub>2</sub>S<sub>3</sub>  $\sim 2.4$  eV). The viscous flow and its photo-induced changes were measured by modified Thermomechanical analyzer using penetration method with optically transparent hemispherical indenter made from the optical quality silica glass (focusing of laser beam onto a sample).

Changes of non-illuminated and illuminated viscous flow were compared. The illumination of samples led to the increasing of the viscous flow and thus to the changes of the penetration rate of the indenter into the sample. It was found that the laser emitting at  $\lambda = 650$  nm (sub-gap photons) caused the higher photo-induced viscous flow changes due to the higher optical penetration depth leading to the larger light-affected volume of the glass. It was observed from cyclic measurements (illumination-dark-illumination) that the influence of photons on the viscous flow was only temporary - it vanished when laser was switched off and the viscous flow returned to its original state. Furthermore, the photo-induced viscous flow decreased with increasing temperature.

The research was extended on the oxide glassy system PbO-ZnO-P<sub>2</sub>O<sub>5</sub> modified by CoO. The role of photons, absorbed by different way (d-d transitions), on the viscous flow was studied as well.

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## **Ion implantation of Gd, Er and Au into various crystallographic cuts of ZnO single crystals - structural vs. photoluminescence properties**

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**Keywords:** ion implantation, Gd, Er, Au, ZnO, luminescence

Ion implantation is an efficient tool for ZnO doping with various ions. Previous results show the importance of ZnO surface crystallographic orientation towards the ion beam, which influence the process of recombination of Zn/O interstitial and vacancy positions. But recently the defect removal seem to be complicated and unknown. By varying the concentration and position of the oxygen vacancies as well as by changing the band gap structure luminescence of ZnO is significantly influenced. Therefore, luminescence spectroscopy is a suitable tool for monitoring mentioned changes.

In this contribution, the single-crystal ZnO wafers with (0001), (10-10) and (11-20) crystallographic planes were implanted by Gd<sup>+</sup>, Er<sup>+</sup> and Au<sup>+</sup> ions accelerated to 400 keV. The ion-implantation fluences used for the mentioned single-crystal ZnO were  $5 \times 10^{14}$  and  $1 \times 10^{15}$  ions/cm<sup>2</sup>. The implanted samples were subsequently annealed in O<sub>2</sub> at 600 °C for 1 hour. The ion concentration-depth profiles as well as disorder-depth profiles caused by ion implantation and subsequent annealing were examined by Rutherford backscattering spectrometry (RBS) and RBS/channelling (RBS/C) measurements. Additionally, the Raman spectroscopy was performed to study the ZnO structure changes. The main attention of our work was focused on the investigation of luminescence properties. We focused particularly on the relationship between the two main intrinsic luminescence bands of ZnO at around 375 and 530 nm and studied in detail the possibility of controlling the luminescence properties of ZnO by varying the position of the short-wavelength bands. The results showed different structural damage reflected in shifts of wide defect-related luminescence band (DLE, i.e. deep level emission) of ZnO. The resulting luminescence properties of ZnO depended significantly on the choice of dopants and crystallographic cuts of ZnO as well as on the conditions of subsequent annealing. The practical results were also compared with theoretical simulations of various dopant positions in ZnO structure performed by density functional theory (DFT) simulations.

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## Solid state synthesis and characterization of $\text{La}_2\text{Ce}_2\text{O}_7$ powder as a candidate material for thermal barrier coatings

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**Keywords:** solid-state reaction, lanthanum cerium oxide, TBC

Lanthanum cerium oxide,  $\text{La}_2\text{Ce}_2\text{O}_7$  (LC), has attracted increasing interest as a promising material for thermal barrier coatings (TBC) because of its high phase stability and potential capability to be operated above 1250 °C [1]. Moreover, LC exhibits lower thermal conductivity and higher thermal expansion coefficient than the conventional yttria partially-stabilized zirconia [2]. In this work, LC powder was synthesized by solid-state reaction method using commercial  $\text{La}_2\text{O}_3$  and  $\text{CeO}_2$  binary oxides. The synthesized LC powder was heat treated at the temperatures of up to 1400 °C for 6 hours and investigated as a material for TBC applications: powder morphology, chemical composition, crystal structure and thermal stability were systematically studied. Scanning electron microscopy (SEM) of the prepared powder revealed agglomerated structure consisting of finely and uniformly distributed grains with size up to 10  $\mu\text{m}$ . The fluorite structure of the LC powder after annealing at 1400 °C was confirmed by X-Ray diffraction analysis (XRD) showing intensive peaks corresponding to the pure  $\text{La}_2\text{Ce}_2\text{O}_7$  phase. No additional peaks belonging to  $\text{La}_2\text{O}_3$  were observed, confirming the formation of solid solution of  $\text{La}_2\text{O}_3$  in  $\text{CeO}_2$ . The thermal behavior 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 high phase stability of the LC powder and its suitability for TBC applications.

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## Solid-state synthesis and *in vitro* characterization of Mg-doped ZrO<sub>2</sub> bioceramics for dental applications

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**Keywords:** bioceramics, zirconia, solid-state synthesis, XRPD, ICP-AES, SEM/EDS

ZrO<sub>2</sub>-based bioceramics have been successfully used in recent years as a dental biomaterial due to their excellent properties as biocompatibility, good mechanical properties, and chemical inertness in the oral environment. ZrO<sub>2</sub> presents three types of crystalline structures at ambient pressure: the monoclinic phase (*m*-ZrO<sub>2</sub>), stable from room temperature up to 1170 °C which exhibits poor mechanical properties, the tetragonal phase (*t*-ZrO<sub>2</sub>), which is stable in the temperature range 1170-2370 °C and has good mechanical properties, and the cubic phase (*c*-ZrO<sub>2</sub>), which is stable above 2370 °C and has moderate mechanical properties [French et al, 1994; Denry & Kelly, 2008]. To prevent the volume expansion during cooling, ZrO<sub>2</sub> can be stabilized with different oxides like MgO, CaO, Y<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, using different methods of synthesis.

In this work, Zr<sub>2-x</sub>Mg<sub>x</sub>O<sub>2</sub> (x = 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3) was synthesized by solid-state reaction at high temperature, followed by their *in vitro* characterisation. The analysis of the amount of Zr<sup>4+</sup> and Mg<sup>2+</sup> ions dissolved in the Xerostom<sup>®</sup> saliva substitute gel after two months exposure times, using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) technique, showed dissolution of Mg<sup>2+</sup>. The XRPD (X-ray powder diffraction) technique was employed to investigate the phase transformations occurring during the degradation process in Xerostom<sup>®</sup>. The results revealed that the *t*-ZrO<sub>2</sub> is the predominant phase for all the prepared compositions. The coexistence of both *t*- and *m*-ZrO<sub>2</sub> phases on the x = 0.1 composition was evidenced. Moreover, an examination by SEM/EDS (scanning electron microscopy/energy dispersive X-ray spectroscopy) showed interconnected grains in the sintered ceramics and confirmed the presence of Mg, Zr, and O, with a homogenous distribution throughout the samples.

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## The influence of test conditions on zinc release from the 45S5 bioactive glass

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**Keywords:** bioactive glass, dissolution, test condition, 45S5+Zn, simulated body fluid

The 45S5 Bioglass (BG) (Hench, 1971) is a bioactive material that stimulates bone repair. In an aqueous environment, this material undergoes a series of reactions to create a surface layer of hydroxyapatite (HA) and hydroxy-carbonate apatite (Filgueiras, 1993). The incorporation of ions in BG can enhance the therapeutic effects of the material. Zinc is a co-factor for over 400 enzymes, a key mediator of bone matrix mineralization and plays a significant role in bone formation (Lakhkar N.J., 2013). Additionally, zinc is well known for its antibacterial effects. *In vitro* bioactivity experiments are normally conducted under static conditions, which could lead to local ion saturation and increased pH values (Zhang, 2008). Dynamic dissolution configuration is a convenient alternative to analyze the leaching behavior of bioactive glasses under a continuous flow of a suitable solution simulating conditions in a human body. In this study, the effect of different test conditions on the leaching behavior of 45S5 BG doped with zinc (4 wt%) was investigated. The static and dynamic regimens of bioactivity testing were compared. *In vitro* tests were also carried out under static and dynamic conditions in the simulated body fluid (pH 7.4) (SBF) and deionized water (pH 6.5, conductivity 0.14 µS/cm). During all tests, the temperature was maintained at 37°C. For static dissolution studies, 35 mg of glass particles were added in 25 mL of SBF. Dynamic dissolution studies were performed with a continuous flow-through cell set-up. The sample cell was filled with 550 mg of glass and SBF solution was flowing through glass particles with a rate of 0.66 ± 0.5 ml/min. The solutions were periodically collected for ICP-OES analyses. The release of zinc as a potential antibacterial inhibitor was meeting the limit of quantification in SBF solution during static bioactivity testing. The test revealed a faster dissolution of the material during the dynamic test as well as a detectable amount of zinc released from the glass. The dynamic tests are more suitable to study ion release in an aqueous environment with high ionic strength, where precipitation reactions occur rapidly due to the fast dissolution of a material.

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# Machine Learning Analysis of Microwave Dielectric Properties for Seven Structure Types: The Role of the Processing and Composition

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**Keywords:** microwave dielectric characteristics, materials informatics, descriptors, grain boundaries, machine learning

During the last decades the area of wireless communications experienced the drastic growth demanding the search for new materials with tailored microwave dielectric characteristics. Microwave dielectric properties of ceramic materials have been extensively studied, the comprehensive database of microwave dielectric properties is now available [1, 2]. Several studies involving machine learning approaches have been performed [3, 4].

In this study, machine learning approaches have been used for synthesis-structure-property relationships assessment. The analysis has been performed for several structure types. The new descriptors encapsulating the information on the constituent building blocks, their relative number and connectivity have been introduced. These structure-characterizing parameters, the hybrid of descriptors recently proposed in [5] and [6], can be regarded as a flexible way to describe the inorganic crystal structures using the substructural bottom-up approach comprising both, the symmetry and the connectivity information.

The role of the processes observed at the grain boundaries as well as the re-crystallization processes for the microwave dielectric characteristics is discussed. The impact of the heat-treatment and the composition for the considered structure types is discussed.

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