

# DEPARTMENT FOR ADVANCED MATERIALS

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*At the Advanced Materials Department, we investigate novel materials through an understanding of the mutual dependence of their structural, microstructural and functional characteristics. Modern technologies that enable the synthesis of materials with atomic- and microscale precision are used to prepare pre-designed structural 3D materials, thin films and nanoparticles with the desired crystal structure, chemical composition, microstructure and morphology. Among our important objectives is the development of i) novel functional oxides for electronic applications and energy conversion, ii) antibacterial and piezoelectrical biocompatible materials and iii) heat-insulation materials with improved properties and sustainability.*

## Novel functional oxides

In the scope of the HarvEnPiez M-era-Net Project and the studies of ferroelectric perovskite particles with defined morphologies for piezoelectric applications, the research was focused on the elucidation of experimental conditions for controlling the composition, crystal structure and preferential orientation to obtain  $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ -based platelets with improved ferroelectric/piezoelectric characteristics. In the topochemical microcrystal conversion (TMC) from  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  to the target  $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$  perovskite platelets the incorporation of Ca was found to be limited ( $\leq 1.5$  at.% at nominal  $x=0.1$ ) and accompanied by considerable Bi remains (up to 2 at.%). Both types of cations are incorporated at the A-site of the single crystalline complex  $\text{Ba}(\text{Ca},\text{Bi})\text{TiO}_3$  perovskite structure of the platelets. Additionally, defects such as dislocations enriched with Ca (Figure 1) and inclusions containing Bi are also present in the crystal. It was found that the general principles for the formation of  $\text{BaTiO}_3$ -based platelets with high tetragonality and high (001) preferential orientation already changed for low Ca substitutions (i.e.  $x=0.01$ ). While for  $\text{BaTiO}_3$  platelets, prolonged annealing times at 600–900 °C (12 hours) and a slow cooling rate (1 °C/min) favoured high (001) preferential orientation. These conditions led to a pseudocubic structure for the composition with  $x=0.01$ . Shorter annealing times (2 hours at 900 °C) and fast cooling rates ( $>10$  °C/min) enabled a long-range-ordered tetragonal structure for the Ca, Bi-containing platelets ( $x=0 \Rightarrow \text{Ba}_{0.96}\text{Bi}_{0.07}\text{Ti}_{0.97}\text{O}_3$ ,  $x=0.01 \Rightarrow \text{Ba}_{0.92}\text{Ca}_{0.016}\text{Bi}_{0.09}\text{Ti}_{0.97}\text{O}_3$  and  $x=0.05 \Rightarrow \text{Ba}_{0.89}\text{Ca}_{0.056}\text{Bi}_{0.09}\text{Ti}_{0.96}\text{O}_3$ ). For these platelets piezo-response force microscopy (PFM) revealed the presence of  $\sim 500$ -nm-sized ferroelectric domains and local  $d_{33}$  values of 20–80 pm/V. A low-temperature X-ray diffraction examination of  $\text{Ba}(\text{Ca},\text{Bi})\text{TiO}_3$ -based perovskite platelets revealed that small contents of Bi (1.4 at.%) and Ca (0.3 at.%) inhibit the low-temperature tetragonal-to-orthorhombic phase transition (present in pure  $\text{BaTiO}_3$  at 5–10 °C), while these substitutions do not significantly influence the tetragonal-to-cubic phase transition at 125–135 °C. Broadening of the temperature range of tetragonal phase stability down to very low temperatures ( $\leq -120$  °C) implies less-temperature-dependent ferroelectric/piezoelectric properties in the temperature range  $-120$  °C  $\leq T \leq 100$  °C.

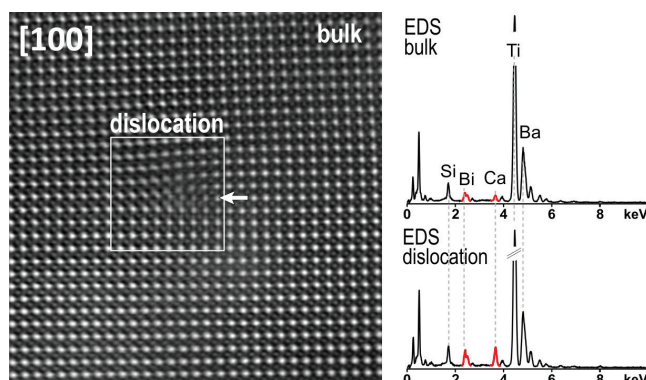
We studied the epitaxial growth of  $\text{SrTiO}_3$  and  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  nanoplatelets under hydrothermal conditions to prepare the  $\text{SrTiO}_3$  and heterostructural  $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{SrTiO}_3$  nanoplatelets with different ratios of  $\text{SrTiO}_3$  and  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ . The processes that accompany this topochemical conversion (TC) and its mechanism were explained. The epitaxially grown layers of  $\text{SrTiO}_3$  protect the template against premature and uncontrolled dissolution, thus presumably decisively influencing the retention of the platelet after the completion of the conversion. Consequently, the finished  $\text{SrTiO}_3$  platelets after the conversion, as well as partially converted  $\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{SrTiO}_3$  composites, acquire the mesocrystalline structure. According to the literature, mesocrystalline and hetero-structures can enhance the photocatalytic activity of the  $\text{SrTiO}_3$  particles for  $\text{H}_2$  evolution from water splitting. The prepared mesocrystalline nanoplatelets were tested for photocatalytic  $\text{H}_2$  production without the use of co-catalysts and confirmed the positive influence of the heterostructure on the efficiency of the photocatalytic reaction. The study of epitaxial growth and TC mechanism was broadened to the conversion of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  to other  $\text{MTiO}_3$  ( $\text{M}=\text{Ba}$ ,



Head:

**Asst. Prof. Matjaž Spreitzer**

**We found that the minor incorporation of both Ca and Bi in  $(\text{Ba},\text{Ca},\text{Bi})\text{TiO}_3$  perovskite platelets significantly broadened the temperature range of the tetragonal phase with ferroelectric properties stability (from below  $-120$  to  $135$  °C), compared to that of pure  $\text{BaTiO}_3$  (5 to  $125$  °C).**



**Figure 1:** HR-STEM image of the  $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$  platelet cross-section with the Ca-rich dislocation in single crystalline bulk (left) and EDS spectra of bulk (top-right) and dislocation (bottom-right).

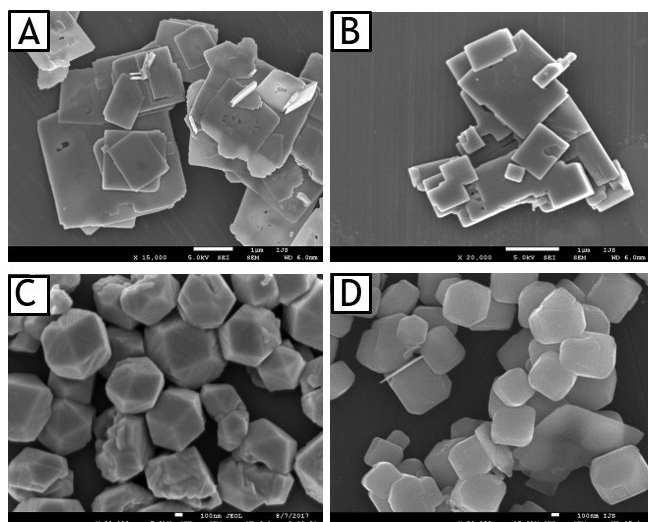


Figure 2: From the  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BIT) templates,  $\text{SrTiO}_3$  (A),  $\text{CaTiO}_3$  (B) and  $\text{BaTiO}_3$  (C and D) particles were prepared under hydrothermal conditions. In the latter, the anisotropic shape of the template was not preserved.

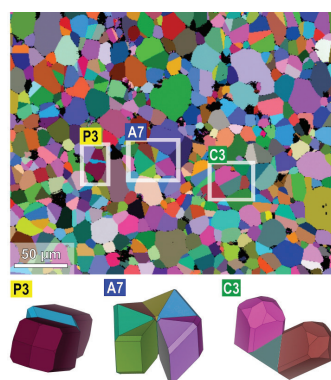


Figure 3: EBSD image of  $\text{SnO}_2$ -based ceramics with many cassiterite twins. The analysis revealed the presence of crystallographically different types of multiple twins: polysynthetic, alternating and coplanar; schematic models of the twins with a different number of twin domains are shown below the microstructure.

Ca). The mechanism proceeds on the same principle, but for the case of  $\text{BaTiO}_3$  we were unable to determine such conditions that would allow the preservation of the anisotropic shape (plate-like shape). It is assumed that the reason is a larger ionic radius of  $\text{Ba}^{2+}$ . In this case, the growth on the surface of the template occurs in the form of island formation and does not completely cover and thereby protect the entire surface of the template. The template therefore dissolves in the reaction and the plate-like shape in this case is diminished (Figure 2).

In the frame of the national research project J1-9177 we studied the microstructure development and electrical properties of  $\text{SnO}_2$ -based ceramics doped with oxides of cobalt and niobium. Characteristic for this system is the development of a dense microstructure that contains a high fraction of contact and multiple twins of cassiterite  $\text{SnO}_2$ . In collaboration with Géosciences Montpellier (France) we analysed the microstructures using electron-backscatter diffraction (EBSD) to reveal the crystallography of multiple twins. We identified three types of twins with different crystallographic settings: polysynthetic or lamellar twins and two types of cyclic twins, coplanar and alternating (Figure 3). Based on phase-equilibrium studies of the  $\text{SnO}_2$ - $\text{Co}_3\text{O}_4$ - $\text{Nb}_2\text{O}_5$  system we found that the formation of twins is related to the oriented growth of cassiterite on structurally related Co-Nb-oxides with the columbite- and corundum-type structures. In

addition to these crystallographic characteristics, the ceramic also exhibits interesting functional properties. At low doping levels, it has promising dielectric properties, while at higher doping levels, it shows nonlinear current-voltage dependency, which is excellent for varistor applications. The results are published in the Journal of the European Ceramic Society.

We continued to study the growth and properties of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$  (PMN-PT) thin films. Previous analyzes have shown that films prepared by pulsed laser deposition (PLD) using Pb-rich targets exhibit a surplus of Pb and Mg deficiency. Therefore, we prepared targets with different excess amounts of Pb and Mg. The chemical composition of the films at the macroscopic level was examined by wavelength-dispersive X-ray spectroscopy. The composition of the sample prepared from the target with 20 mol.%  $\text{PbO}$  excess and 20 mol.%  $\text{MgO}$  excess, was the closest to stoichiometric, but the sample in question did not exhibit superior functional properties. Based on the results of the microscopic analysis and on literature data, we assume that the main reason for this is a different local stoichiometry of the films resulting from extended  $\text{PbO}$  defects and/or a different local chemical environment affecting the response of individual species in the material upon the application of an electrical field. The structure of the PMN-PT thin films with different concentrations of the PT component around the morphotropic phase boundary was also studied. The structure of the epitaxial thin films was found to differ strongly from that of bulk PMN-PT, with the tetragonal phase being stabilized on  $\text{SrTiO}_3$  substrates. We found that the composition with the highest piezoelectric response is shifted towards higher PT contents in the thin films.

A large part of research was focused on the integration of  $\text{SrTiO}_3$  with graphene oxide-buffered silicon surfaces. We investigated the interface reactions between silicon and  $\text{SrTiO}_3$ , with and without a graphene oxide buffer layer. Also, the key parameters for the PLD growth of  $\text{SrTiO}_3$  were optimized.  $\text{SrTiO}_3$  of optimum quality was used as a pseudo-substrate for the growth of piezoelectric  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  (PZT) thin film. The characterization of the functional properties revealed  $d_{33}$  values comparable to PZT grown on  $\text{SrTiO}_3$  prepared by molecular beam epitaxy method. The results demonstrate the high applicative potential of the studied integration method.

We collaborate with Institute of Geotechnics, Slovak Academy of Sciences (Košice, Slovakia) and CRISMAT-CNRS Laboratory (Caen, France) on the topic of next-generation thermoelectric materials based on copper-rich sulphides. We have shown that an efficient, ecologically safe and scalable approach using a combination of high-energy milling and spark plasma

sintering (SPS) can be used for the synthesis of thermoelectric sulphides with complex crystal structures, like tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ) and colusite ( $\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$ ), compounds that exhibit excellent thermoelectric performance. In our recent work we studied phase changes during milling and the SPS of elemental precursors for the synthesis of tetrahedrite. We found that the formation of targeted compound proceeds via several intermediate phases and that only under certain conditions, the product is single-phase tetrahedrite with an excellent figure of merit (ZT of  $0.67@700\text{K}$ ), as a consequence of a high power factor ( $1.07 \text{ mWm}^{-1}\text{K}^{-2}$ ) and a low thermal conductivity ( $1.12 \text{ Wm}^{-1}\text{K}^{-1}$ ). The excellent performance of the samples was interpreted based on the results of microstructural and nanoscale characterisation. The results are published in Journal of the European Ceramic Society.

**We stabilized single-phase and stoichiometric thin films of piezoelectric PMN-PT, epitaxially aligned with various oxide single crystals.**



Organic pollutants such as azo dyes and phenolic compounds in wastewater pose a serious environmental problem, as they are difficult to decompose with traditional water-treatment methods. However, the photocatalytic degradation process of these pollutants could achieve reductions in their harmful effects in a clean and sustainable manner. Therefore, within the framework of nano-structured materials, we focused on the synthesis and photocatalytic activity of the hollow  $\text{TiO}_2$  sphere (Ti-HS). In a typical Ti-HS synthesis, carbon spheres (CSs) were added to a solution of Ti (OBu) 4 and ethanol under vigorous stirring. The obtained Ti @ CS product was calcined at various temperatures between 450 and 800 °C to form Ti-HS, which were about 800 nm in size and a shell thickness of about 100 nm. The samples fired <725 °C retained the anatase structure, while firing of samples at > 725 °C produces a mixture of anatase and rutile. Measurements of the band gap of the Ti-HS showed that its value decreased from 3.2 eV for samples with anatase (450-650 °C) to 3.1 eV for the sample fired at 725 °C. However, the samples fired at 750 °C and 800 °C showed values of about 3.0 eV, which are typical of the rutile structure. The photocatalytic activities of Ti-HS were monitored by the decomposition of methyl blue under the influence of UV light in an aqueous solution. A pronounced photocatalytic effect was detected for Ti-HS, which were calcined between 650 and 725 °C and was better or comparable to the commercial nano-powder of Degussa P25 (Figure 4).

In the scope of investigation of the phase relations in ternary metallic systems that can be found in technically very important materials such as strong magnets, based on  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , we investigated high-temperature phase relations in the Nd-Dy-Cu system. During the recycling process of  $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based magnets, some particular elements are added in order to improve their magnetic properties, such as Dy and Cu. The added elements can incorporate into the crystal structure of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  compound or are located at the grain boundary and thus form new phases. Our investigations showed that in the investigated system the intermetallic compounds based on Nd-Cu and Dy-Cu systems form solid solutions over an extended concentration range.

#### Antibacterial and piezoelectric biocompatible materials

Within the project "Piezoelectric biomaterials for electrostimulated regeneration" we investigated the influence of electrostimulation to bacteria. In contrast to the ultrasonic stimulation of planktonic bacteria which did not significantly affected bacterial growth using selected ultrasonic parameters, the presence of piezo-PLLA films during stimulation provided a strong bactericidal effect. Similarly, bacteria in biofilms grown on the top of piezo-PLLA films also confirmed the strong bactericidal effect (Figure 5). This was not the case for biofilms grown on non-piezoelectric PLLA films (with DR 1). The same processing procedure using an external ultrasonic field repeated in red blood cells showed the absence of signs of toxicity. Morphologically cells had the normal discoid shape, without detectable changes in the membrane and without a tendency to aggregate. The study demonstrated the ability to design biomaterials and to use electro-mechanical stimulation as a tool for obtaining antimicrobial properties. The strategy is an antibiotic- and nanoparticle-free solution. It excludes any releasing components and could be extremely important when antibiotic-resistant strains are concerned.

In the field of designing magnetic antimicrobials within the structure of cobalt-ferrite (CFO) we performed partial substitution of  $\text{Fe}^{3+}$  with  $\text{Ga}^{3+}$  ions. The samples were phase pure with a cubic spinel structure and contained sphere-like nanoparticles with a mean diameter of  $\sim 6 \pm 1$  nm and 25–27 wt.% of absorbed oleic acid, indicating the formation of a complete monolayer on the surface. By adding gallium in the CFO structure the Me-O stretching mode of the tetrahedral sites moved towards higher values, indicating a gradual substitution of the iron ions by gallium ones. The change in the spinel structure was also confirmed by Raman spectroscopy. Magnetic measurements revealed the influence of heteroatoms on the saturation magnetization and magnetic anisotropy, showing for all the samples superparamagnetic behaviour at room temperature. Mössbauer spectra evidenced the modification of the inversion degree, with iron in

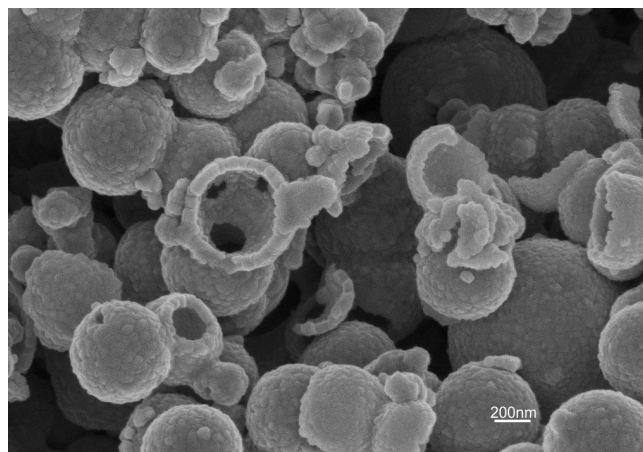


Figure 4: Hollow  $\text{TiO}_2$  spheres after firing at 725 °C, with photocatalytic properties better than Degussa P25.

**We have developed innovative antimicrobial materials (in form of organic piezoelectric films and ion-doped magnetic nanoparticles) and confirmed their ability to effectively decompose and destroy bacterial formations.**

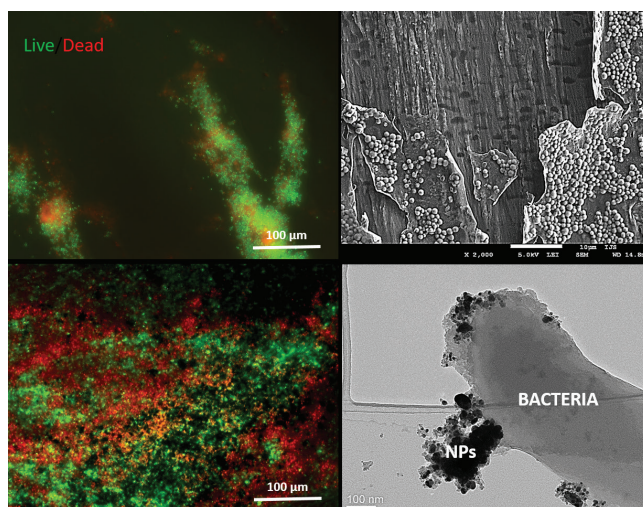


Figure 5: Bacterial viability (Live Dead® assay) and their morphology (SEM images) after interaction with sonicated piezo-PLLA films (a,b) and CFO NPs (c,d).

the tetrahedral site, which decreases with the increase of the Ga content. The substitution of  $\text{Fe}^{3+}$  ions with  $\text{Ga}^{3+}$  leads to a change in the chemical composition and cationic distribution of CFO and consequently to a variation of its magnetic properties that can be tuned for different applications. The nanoparticles were confirmed to destroy the bacterial membrane producing strong bactericidal effect.

### Materials for heat-insulation applications

Glass waste is recognized as a clean inorganic waste that could be implemented in several new industrial products, a model of the circular economy. One of the potential applications of the contaminated glass waste is production of foamed glass, a high added-value product. A major disadvantage of the production is high costs related to the need to adjust its composition to enable the production of a product with superior properties. The foaming

**We showed that good thermal insulation properties can be obtained by preventing the crystallization of the glass and controlling the composition of the gases in the closed pores.**

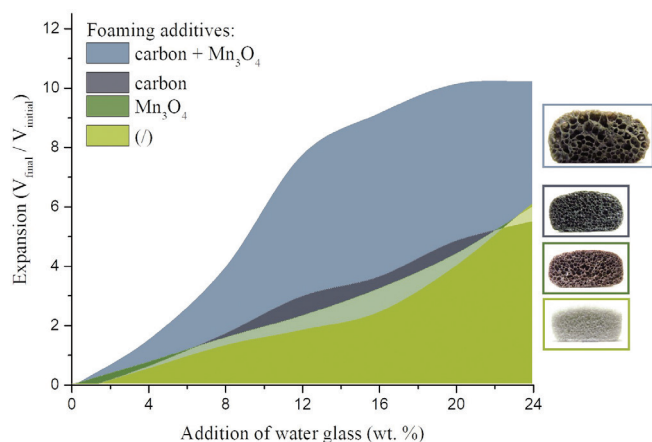
mechanism is heavily influenced by the composition of the used glass, is often hindered by the crystallization process, which is detrimental to the quality of the final product. By adding specific foaming additives, we were able to tune the composition and foaming process of flat glass to avoid crystallization and prepare a foamed glass sample with closed porosity, a small pore size and a low thermal conductivity of  $45 \text{ mW}/(\text{m}\cdot\text{K})$ . On the

other hand, bottle glass with only minor differences in the composition proved to be much more prone to crystallization. To develop an effective foaming process for bottle glass we are looking for alternative foaming additives to tune the glass stability and surface tension.

We studied the crystallization behavior of the container glass cullet supplied by industry in the industrially relevant foaming process, which includes relevant batch compositions and conditions. Usually, surfaces of the milled glass particles act as nucleation centers supporting the crystallization process, so we analyzed waste glass using the DSC and XRD techniques. From the DSC results thermal properties, the glass transformation and glass crystallization temperatures, and crystallization behavior of the glass were determined. Also, different additives, inhibitors of the crystallization were tested. XRD analysis gave an insight into the phase compositions and content of the crystalline phases in the obtained samples. The phase composition was not so much influenced with the additives, the main crystalline phases, quartz and cristobalite only varied in the content. The important properties

of the foamed glass are the density and thermal conductivity, so for the sintered samples density, porosity and thermal conductivity were determined.

In addition to the research on the thermal insulation and mechanical properties of foamed glass, attention was paid to the environmental impact of the required processing conditions. In the study of modified foaming mechanisms that allow foaming in a less-energy-expensive process, we focused on the foaming mixtures that contain water glass. Using water glass, we were able to prepare low-density foamed glass in an air atmosphere. The resulting material has a low thermal conductivity, comparable to products prepared in energy-intensive processes. By comparing the expansions of the samples prepared with different combinations of foaming additives, we determined that two mechanisms mainly contribute to foaming (Figure 6). During the heat treatment, water vapor is released from the water glass up to  $\sim 600^\circ\text{C}$ , which locally creates a less oxidizing atmosphere and inhibits the oxidation of the carbonaceous foaming agent. Furthermore, the addition of water glass lowers the optimum sintering and foaming temperature of the foaming mixture, which favorably affects both the foaming and the energy balance of the process. Due to the apparent usefulness of the water glass, we intend to investigate the possibilities of its use for the preparation of foamed glass from other types of waste glass.



*Figure 6: Expansions of compositions with different combinations of foaming additives depending on the addition of water glass. Expansions of the compositions without one or both additives are very similar and significantly smaller than the expansion of the composition with two additives. The result suggests that the major contribution to the expansion comes from two sources: water glass and the reaction between carbon and  $\text{Mn}_3\text{O}_4$ .*

### Characterization of electrical properties

In 2019 we made improvements to a number of characterization procedures used at our department. The most outstanding was the complete implementation of a Van der Pauw style system for measuring the sheet resistance of thin samples, which allowed us to measure the electrical conductivity of materials such as graphene and thin films of various conductive oxides. Notable improvements were also made to our setup for determining the  $d_{31}$  piezoelectric component of PLLA based polymers. We also upgraded our methods of modeling and measuring the thermal properties of materials, with special emphasis on foamed glass as well as various mineral-wool composites.

## PROJECTS

In the scope of the M-ERA.NET project **HarvEnPiez** we investigated the synthesis of various defined-shape ferroelectric particles with an anisotropic shape (plates, rods) that have controlled preferential orientation. Their self-assembled structures are meant for energy-harvesting applications. Since the  $\text{MTiO}_3$ -type perovskite particles do not show the tendency for anisotropic growth in the shape of plates and rods, we used the topochemical transformation for their preparation. The main focus is on studying the reaction mechanism of topochemical conversion from  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  to  $\text{MTiO}_3$  ( $\text{M} = \text{Ba}, \text{Ca}, \text{Sr}$ ) and their solid solutions in molten salt and under hydrothermal conditions. The project is a cooperation between Slovenia, Latvia and Romania. The Latvian group is involved in *ab initio* calculations and the modeling of piezoelectric properties, whereas the role of Romanian group relates to designing and fabricating of a piezoelectric device. Funding agency: M-ERA.NET European Transnational Agency. Coordinator: dr. Marjeta Maček Kržmanc.

Project **CleanTechBlock Basics**, “**Sustainable Multi-functional Building Block Basics**”, addressed heat-transfer in foamed glass and demonstrated the adaptability of the CTB wall solution to different climates. Work was focused on the quantification of the different contributions to the effective thermal conductivity in the foamed glass for which we performed detailed characterization of the microstructure, pore size, open and closed porosity, glass and gas composition, thermal conductivity and developed a vacuum cell for probing the thermal conductivity of the prepared open-porous foamed glass. The testing revealed the contributions of solid conduction, gaseous conduction and the radiation contribution to the effective thermal conductivity in foamed glass. The results were used for the validation of the theoretical calculations, estimating the lower theoretical limit and guidance for new procedures focused on minimizing the thermal conductivity in foamed glasses. Funding agency: M-ERA.NET European Transnational Agency. Coordinator: dr. Jakob König.

Applied project “**Mineral wool composites with improved insulation properties**” is focused on the development of an innovative new preparation procedure for mineral-wool composites with decreased thermal conductivity. Initially, theoretical calculations on the thermal conductivity of the composites were made, followed by experimental validation of the model by measurements performed on test composite samples. The results provided the boundary compositions for the product with targeted insulation properties. In the next stage, the mechanical properties are being addressed by adding a suitable binder through dry and/or wet application process. Funding agency: Slovenian Research Agency. Coordinator: dr. Jakob König.

Project **SIOX** aims to exploit the rich functionalities of oxides and their heterostructures, which show great promise within the emerging field of oxide electronics. For their implementation, the epitaxial integration of oxides with silicon platforms using industrially appropriate technology is urgently needed, and its development represents the main goal of SIOX. Funding agency: M-ERA.NET European Transnational Agency. Coordinator and principal investigator: Asst. Prof. Matjaž Spreitzer.

**BI-RS/18-19-050:** With Nuclear Institute Vinča (Belgrade, Serbia) we collaborate in the frame of bilateral project “**Synthesis of  $\text{R}_2\text{MoO}_6$ :REE luminescent nanopowders and their structural characterization by electron microscopy**”, where we develop novel luminescent nanomaterials for advanced applications. Using cost-effective self-initiated and self-sustained synthesis approach we developed thermally and chemically stable  $\text{Eu}^{3+}$  activated yttrium molybdate, which can efficiently absorb energy in the near-UV region (324–425 nm) and emit in the red region of the spectrum (611 nm). Funding agency: Slovenian Research Agency. Principal investigator: Asst. Prof. Nina Daneu.

**BI-RS/18-19-042:** Project “**Nanostructured and mesoporous functional materials with accentuated photocatalytic properties under the influence of sunlight**” aims to synthesise new functional materials that exhibit solar-light-driven photocatalytic activity in water-pollutant degradation. The synthesis of the following materials is planned: nanostructured  $\text{ZnO}$ ,  $\text{ZnO}/\text{PEO}$  composites,  $\text{ZnO}/\text{SnO}_2$  particles, hierarchically structured  $\text{TiO}_2$  particles with mesoporous nanostructure and large specific surface area, as well as  $\text{BaTi}_{0.9}\text{Sn}_{0.1}\text{O}_3$  particles/ceramics. Funding agency: Slovenian Research Agency. Principal investigator: Asst. Prof. Srečo Škapin.

## Organization of conferences, congresses and meetings

1. Workshop Contemporary characterization techniques for materials within SRIP Factories of the Future & SKD – Section for ceramics, Ljubljana, 18. 4. 2019
2. Workshop on international project M-ERA-NET “SunToChem: Engineering of perovskite photocatalysts for sunlight-driven hydrogen evolution from water splitting”, Ljubljana, 1.–2. 9. 2019
3. Organization of symposium “Ion-related phenomena in nanoscale oxide systems”, E-MRS Fall Meeting 2019, Warsaw, Poland, 16.–19. 9. 2019
4. Workshop on international project M-ERA-NET “SIOX: Engineering of silicon-oxide interface using the pulsed-laser deposition technique”, Goriška Brda, 21.–22. 10. 2019
5. Workshop Chemical and Structural Analysis for Materials, within SRIP Factories of the Future & SKD – Section for ceramics, Dol pri Ljubljani, 28. 11. 2019



## Patents granted

1. Wang Yongli, Boštjan Jančar, Hermann Grünbichler, Franz Rinner, Damjan Vengust, Danilo Suvorov  
Thermoelectric generator comprising a thermoelectric element  
EP2975659 (B1), European Patent Office, 16. 10. 2019.
2. Aleš Mrzel, Damjan Vengust  
Method for the synthesis of metal molybdates and tungstates from molybdenum and tungsten carbides and nitrides  
SI25549 (A), Urad RS za intelektualno lastnino, 31. 05. 2019.

## INTERNATIONAL PROJECTS

1. Investigation of NdDyCoCuFe Rare Earth Alloys Alloys and Related Compounds  
Asst. Prof. Matjaž Spreitzer  
Urban Mining Company
2. Investigation of NdDyCoCuFe Rare Earth Alloys Alloys and Related Compounds  
Asst. Prof. Matjaž Spreitzer  
Urban Mining Company
3. COST CA 17140; Cancer Nanomedicine - From the Bench to the Bedside (NANO2CL)  
Dr. Marija Vukomanović  
Cost Association Aisbl
4. Synthesis of Luminescent Nanopowders of Type R2MoO6:REE and Their Structural Characterization by Means of Electron Microscopy  
Asst. Prof. Nina Daneu  
Slovenian Research Agency
5. Nanostructured and Mesoporous Functional Materials with Enhanced Solar Light Driven Photocatalytic Activity  
Asst. Prof. Srečo Davor Škapin  
Slovenian Research Agency
6. Stoichiometry Engineering of Epitaxial PMN-PT Thin Films  
Asst. Prof. Matjaž Spreitzer  
Slovenian Research Agency
6. Mineral wool composite with improved insulation properties  
Dr. Jakob König
7. Central European SME Gateway to Key-enabling Technology Infrastructures - Sparking new Transnational KET Innovation Ecosystem  
Asst. Prof. Matjaž Spreitzer  
Bay Zoltan Alkalmazott Kutatasi Kozhasznu
8. Innovative ECO plasma seed treatment (for sowing and for human and animal diet/nutrition)  
Dr. Marija Vukomanović  
Ministry of Education, Science and Sport
9. Strategic Research & Innovation Partnership Factories of the Future (SRIP FoF)  
Asst. Prof. Matjaž Spreitzer  
Ministry of Economic Development and Technology
10. Control of crystallization in glass materials for thermal insulation  
Dr. Sonja Smiljanić  
Ministry of Education, Science and Sport
11. HarvEnPiez: Innovative nano-materials and architectures for integrated piezoelectric energy harvesting applications  
Dr. Marjeta Maček Kržmanc  
Ministry of Education, Science and Sport
12. CTB Basics: CleanTechBlock-Sustainable Multi-functional Building Block Basics  
Dr. Jakob König  
Ministry of Education, Science and Sport
13. SIOX: Engineering of silicon-oxide interface using the pulsed-laser deposition technique  
Asst. Prof. Matjaž Spreitzer  
Ministry of Education, Science and Sport
14. SunToChem: Engineering of perovskite photocatalysts for sunlight-driven hydrogen evolution from water splitting  
Dr. Marjeta Maček Kržmanc  
Ministry of Education, Science and Sport
15. XRD Analysis  
Asst. Prof. Matjaž Spreitzer

## RESEARCH PROGRAMME

1. Contemporary Inorganic Materials and Nanotechnologies  
Asst. Prof. Matjaž Spreitzer

## R & D GRANTS AND CONTRACTS

1. Synthesis and characterization of alkali activated foams based on different waste  
Asst. Prof. Srečo Davor Škapin
2. Piezoelectric Biomaterials for Electro-stimulated Regeneration  
Dr. Marija Vukomanović
3. Nanoscale investigations of diffusion controlled topotaxial phase transformations in rutile-corundum host systems  
Asst. Prof. Nina Daneu
4. Engineering of oxides on silicon for future electronics  
Asst. Prof. Matjaž Spreitzer
5. Mineral inclusions in garnet from macroscopic to atomic scale: Opening the petrogenetic archive  
Asst. Prof. Nina Daneu

## NEW CONTRACTS

1. Determination of potential structural changes of proteins using the following analytical techniques: UV-Vis-NIR spectrometry, fluorescence spectrometry, X-ray diffraction and circular dichroism  
Asst. Prof. Matjaž Spreitzer  
Lek d. d.
2. Mineral wool composite with improved insulation properties  
Dr. Jakob König  
Knauf Insulation, d.o.o., Škofja Loka

## VISITORS FROM ABROAD

1. Dr José-Alberto Padron Navarta, Géosciences Montpellier, CNRS, Montpellier, France, 1. 1.-8. 1. 2019.
2. Prof. Gertjan Koster, University of Twente, Enschede, Netherlands, 22.-25. 4. 2019.
3. Dr Nadežda Stanković, Dr Jelena Luković, Dr Branko Matović, Vinča Nuclear Institute, Belgrade, Serbia, 19.-25. 5. 2019.
4. Prof. Davide Peddis, University of Cagliari, Monserrato, Italy, 5.-8. 6. 2019.
5. Prof. Rick Ubb, Micron School of Materials Science and Engineering, Boise State University, Idaho, USA, 23. 6.-27. 7. 2019.
6. Dr Manal Benyoussef, Laboratoire de Physique de la Matière Condensée (LPMC), Amiens, France, 1. 7.-30. 8. 2019.
7. Prof. Peter Baláž, Slovak Academy of Sciences (SAS), Bratislava, Slovakia, 1.-5. 7. 2019.
8. Dr Ivan Kozenkov, Laboratory of Novel Magnetic Materials, Immanuel Kant Baltic Federal University, Kaliningrad, Russia, 8. 7.-2. 8. 2019.
9. Dr Leonid Rusevich, Institute of Solid State Physics, University of Latvia, Riga, Latvia,

- Dr C.S. Jeffrey Wu, Dr Wen Yueh Yu, Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, 1.-2.9. 2019.
10. Dr Sarah Risquez, Dr Adrien Piot, Dr Jaka Pribošek, Dr Heimo Müller, Silicon Austria Labs GmbH, Graz, Austria, 12. 9. 2019.
11. Prof. Heli Jantunen, University of Oulu, Oulu, Finland, 11.-15. 11. 2019.
12. prof. Dr Eric Bousquet, Dr Wen Yi, University of Liège, Liège, Belgium, Dr Bin-Bin Chen, Fudan University, China, 21. 10. 2019.
13. Dr Vladislav Rac, prof. Dr Vesna Rakić, Poljoprivredni fakultet Beograd, Belgrade, Serbia, 1.-3. 12. 2019.

### Visiting Researcher

14. Dr Jamal Belhadi, Laboratoire de Physique de la Matière Condensée (LPMC), Amiens, France, 1. 3. 2019-29. 2. 2020.

## STAFF

## Researchers

1. Asst. Prof. Nina Daneu
  2. Heli Maarit Jantunen, B. Sc.
  3. Zoran Jovanović
  4. Dr. Jakob König
  5. Dr. Gertjan Koster
  6. Dr. Špela Kunej
  7. Dr. Marjeta Maček Kržmanc
  8. Asst. Prof. Matjaž Spreitzer, Head
  9. Asst. Prof. Srečo Davor Škapin
  10. Dr. Marija Vukomanović
- Postdoctoral associates
11. Dr. Urška Gabor, on leave 01.08.19
  12. Dr. Sonja Jovanović
  13. Sonja Smiljanić, B. Sc.

## Postgraduates

14. Alja Čontala, B. Sc.
15. Uroš Hribar, B. Sc.
16. Nina Kuzmić, B. Sc.
17. Tjaša Parkelj Potočnik, B. Sc.
18. Lea Udovč, B. Sc.

## Technical officers

19. David Fabijan, B. Sc.
20. Tina Radošević, B. Sc.
21. Damjan Vengust, B. Sc.

## Technical and administrative staff

22. Vesna Butinar, B. Sc.
23. Silvo Zupančič

## BIBLIOGRAPHY

## ORIGINAL ARTICLE

1. Le Minh Nguyen, Huiyu Yuan, Evert P. Houwman, Matthijn Dekkers, Gertjan Koster, Johan E. ten Elshof, Guus Rijnders, "Highly oriented growth of piezoelectric thin films on silicon using two-dimensional nanosheets as growth template layer", *ACS applied materials & interfaces*, 2019, **8**, 45, 31120-31127.
2. Nuria Blanco-Cabra, Karina Vega-Granados, Laura Moya-Andérico, Marija Vukomanović, Andrés Parra, Luis Álvarez de Cienfuegos, Eduard Torrents, "Novel oleanolic and maslinic acids derivatives as a promising treatment against bacterial biofilm in nosocomial infections: an in vitro and in vivo study", *ACS infectious diseases*, 2019, **5**, 9, 1581-1589.
3. Zhandos Shalabayev *et al.* (11 authors), "Sulfur-mediated mechanochemical synthesis of spherical and needle-like copper sulfide nanocrystals with antibacterial activity", *ACS sustainable chemistry & engineering*, 2019, **7**, 15, 12897-12909.
4. Mark Huijben *et al.* (19 authors), "Defect engineering in oxide heterostructures by enhanced oxygen surface exchange", *Advanced functional materials*, 2019, **23**, 13, 5240-5248.
5. Matej Baláž, L'udmila Balážová, Mária Kováčová, Nina Daneu, Aneta Salayová, Zdenka Bedlovicová, L'udmila Tkáčiková, "The relationship between precursor concentration and antibacterial activity of biosynthesized Ag nanoparticles", *Advances in nano research*, 2019, **7**, 2, 125-134.
6. Marcela Achimovičová, Nina Daneu, Elena Tóthová, Matjaž Mazaj, Erika Dutková, "Combined mechanochemical/thermal annealing approach for the synthesis of Co<sub>9</sub>Se<sub>8</sub> with potential optical properties", *Applied physics. A, Materials science & processing*, 2019, **125**, 8.
7. Tjaša Parkelj Potočnik, Erik Zupanič, Wen-Yi Tong, Erik Bousquet, Daniel Diaz-Fernandez, Gertjan Koster, Philippe Ghosez, Matjaž Spreitzer, "Atomic structure of Sr/Si(0 0 1)(1 x 2) surfaces prepared by Pulsed laser deposition", *Applied Surface Science*, 2019, **471**, 664-669.
8. M. Coll *et al.* (56 authors), "Towards oxide electronics: a roadmap", *Applied Surface Science*, 2019, **482**, 1-93.
9. Goran Durn, Srečo D. Škapin, Neda Vdović, Thilo Rennert, Franz Ottner, Stanko Ružičić, Nuša Cukrov, Ivan Sondi, "Impact of iron oxides and soil organic matter on the surface physicochemical properties and aggregation of Terra Rossa and Calcocambisol subsoil horizons from Istria (Croatia)", *Catena*, 2019, **183**, 104184.
10. Violeta N. Nikolić, Marin Tadić, Sonja Jovanović, Vojislav Spasojević, "Tracking of the electronic re-ordering in Fe<sub>3</sub>O<sub>4</sub>/OA nanoparticles using magnetometry", *Ceramics international*, 2019, **45**, 14, 17429-17437.
11. Vuk Uskoković, Eric Huynh, Sean Tang, Sonja Jovanović, Victoria Wu, "Colloids or powders: which nanoparticle formulations do cells like more?", *Colloids and surfaces. B, Biointerfaces*, 2019, **181**, 39-47.
12. Jakob Koenig, Vincenc Nemanič, Marko Žumer, Rasmus R. Petersen, Martin B. Østergaard, Yuanzheng Yue, Danilo Suvorov, "Evaluation of the contributions to the effective thermal conductivity of an open-porous-type foamed glass", *Construction & building materials*, 2019, **214**, 337-343.
13. Ladislav Vrsalović, Ivana Ivanić, Stjepan Kožuh, Borut Kosec, Milan Bizjak, Janez Kovač, Urška Gabor, Mirko Gojić, "Influence of heat treatment on the corrosion properties of CuAlMn shape memory alloys", *Corrosion reviews*, 2019, **37**, 6, 579-589.
14. Alenka Ristić, Matjaž Mazaj, Iztok Arčon, Nina Daneu, Nataša Zabukovec Logar, Roger Gläser, Nataša Novak Tušar, "New insights into manganese local environment in MnS-1 nanocrystals", *Crystal growth & design*, 2019, **19**, 6, 3130-3138.
15. Victor G. Thomas, Nina Daneu, Rudolf I. Mashkovtsev, Aleksander Rečnik, Dmitry A. Fursenko, "The internal structure of hydrothermally grown leucosapphire crystals", *CrystEngComm*, 2019, **21**, 7, 1122-1129.
16. Dragana Jugović, Miloš Milović, Maja Popović, Vladan Kusigerski, Srečo D. Škapin, Zlatko Rakočević, Miodrag Mitrić, "Effects of fluorination on the structure, magnetic and electrochemical properties of the P2-type Na<sub>x</sub>CoO<sub>2</sub> powder", *Journal of alloys and compounds*, 2019, **774**, 30-37.
17. Awais Ikram *et al.* (12 authors), "The sintering mechanism of fully dense and highly coercive Nd-Fe-B magnets from the recycled HDDR powders reprocessed by spark plasma sintering", *Journal of alloys and compounds*, 2019, **774**, 1195-1206.
18. G. Muscas, Sonja Jovanović, Marija Vukomanović, Matjaž Spreitzer, Davide Peddis, "Zn-doped cobalt ferrite: tuning the interactions by chemical composition", *Journal of alloys and compounds*, 2019, **796**, 203-209.
19. S. K. Hasanur Rahaman, Arnab Bhattacharjee, Monisha Chakraborty, Nina Daneu, Jui Chakraborty, "Incorporation of shRNA in bioactive glass coated SS316L implant material and its role in inhibition of the osteoclast activity for better post implantation fixation", *Journal of drug delivery science and technology*, 2019, **52**, 730-737.
20. Hugo Rojas-Chávez, Rurik Farías, Heriberto Cruz-Martínez, J. L. González-Domínguez, Nina Daneu, J. Manuel Juárez-García, A. Ávila-García, R. Román-Doval, "Understanding the growth of ZnTe nanorods by mechanochemical synthesis: the role of structural defects", *Journal of materials science. Materials in electronics*, 2019, **30**, 12, 11291-11300.
21. Marija Vukomanović, Eduard Torrents, "High time resolution and high signal-to-noise monitoring of the bacterial growth kinetics in the presence of plasmonic nanoparticles", *Journal of nanobiotechnology*, 2019, **17**, 21.
22. Sonja Jovanović, Ksenija Kumrić, Danica Bajuk-Bogdanović, Boštjan Jančar, Matjaž Spreitzer, Tatjana Trtič-Petrović, Danilo Suvorov, "Cobalt ferrite nanospheres as a potential magnetic adsorbent for chromium(VI) ions", *Journal of nanoscience and nanotechnology*, 2019, **19**, 8, 5027-5034.
23. Martin B. Østergaard, Rasmus R. Petersen, Jakob Koenig, Michael Bockowski, Yuanzheng Yue, "Impact of gas composition on thermal conductivity of glass foams prepared via high-pressure sintering", *Journal of non-crystalline solids. X.*, 2019, **1**, 100014.
24. Andreja Šestan, Janez Zavašnik, Marjeta Maček, Matej Kocen, Petra Jenuš, Saša Novak, Miran Čeh, Gerhard Dehm, "Tungsten carbide as a deoxidation agent for plasma-facing tungsten-based materials", *Journal of nuclear materials*, 2019, **524**, 135-140.

25. Leonid L. Rusevich, Guntars Zvejnieks, Eugen A. Kotomin, Marjeta Maček, Anton Meden, Špela Kunej, Ioana D. Vlaicu, "Theoretical and experimental study of (Ba,Sr)TiO<sub>3</sub> perovskite solid solutions and BaTiO<sub>3</sub>/SrTiO<sub>3</sub> heterostructures", *The journal of physical chemistry. C, Nanomaterials and interfaces*, 2019, **123**, 4, 2031-2036.
26. J. J. Bian, Mojca Otoničar, Matjaž Spreitzer, Damjan Vengust, Danilo Suvorov, "Structural evolution, dielectric and energy storage properties of Na(Nb<sub>1-x</sub>Ta<sub>x</sub>)O<sub>3</sub> ceramics prepared by spark plasma sintering", *Journal of the European ceramic society*, 2019, **39**, 7, 2339-2347.
27. Juliane Moritz, Anže Abram, Miha Čekada, Urška Gabor, Maja Garvas, Irena Zdovc, Aleš Dakskobler, Jasna Cotič, Karolina Ivičak-Kocjan, Andraž Kocjan, "Nanoroughening of sandblasted 3Y-TZP surface by alumina coating deposition for improved osseointegration and bacteria reduction", *Journal of the European ceramic society*, 2019, vol.39, 14, 4347-4357.
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29. Damjan Vengust, Matejka Podlogar, Aleš Mrzel, Mojca Vilfan, "Rapid reaction of Mo<sub>2</sub>N nanowires with Pb<sup>2+</sup> ions in water and its use for production of PbMoO<sub>4</sub> nanoparticles", *Materials chemistry and physics*, 2019, **226**, 20-25.
30. Martin B. Østergaard, Biao Cai, Rasmus R. Petersen, Jakob Koenig, Peter D. Lee, Yuanzheng Yue, "Impact of pore structure on the thermal conductivity of glass foams", *Materials letters*, 2019, **250**, 72-74.
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34. Peter Baláž *et al.* (15 authors), "Photovoltaic materials: Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) nanocrystals synthesized via industrially scalable, green, one-step mechanochemical process", *Progress in photovoltaics*, 2019, **27**, 9, 798-811.
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36. Nenad Ignjatović *et al.* (13 authors), "Rare-earth (Gd<sup>3+</sup>, Yb<sup>3+</sup>/Tm<sup>3+</sup>, Eu<sup>3+</sup>) co-doped hydroxyapatite as magnetic, up-conversion and down-conversion materials for multimodal imaging", *Scientific reports*, 2019, **9**, 16305.
37. Sayantan Ray, Suman Sahay, Rahaman Sk. Hasanur, Arnab Bhattacharjee, Nina Daneu, Zoran Samardžija, Jui Chakraborty, "An in vitro evaluation of the variation in surface characteristics of bioactive glass coated SS316L for load bearing application", *Surface & coatings technology*, 2019, **377**, 124849.
38. Una Stamenović, Vesna Vodnik, Nemanja Gavrilov, Igor A. Pašti, Mojca Otoničar, Miodrag Mitrić, Srečo D. Škapin, "Developing an advanced electrocatalyst derived from triangular silver nanoplates@polyvinylpyrrolidone-polyaniline nanocomposites", *Synthetic metals*, 2019, **257**, 116173.
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1. Vasyl Shvalya, Gregor Filipič, Damjan Vengust, Janez Zavašnik, Martina Modic, Ibrahim Abdulhalim, Uroš Cvelbar, "Reusable copper oxides based plasmonic templates for improved SERS detection", In: *55th International Conference on Microelectronics, Devices and Materials & the Workshop on Laser Systems and Photonics, September 25 - September 27 2019, Bled Slovenia*, Conference proceedings, MIDE, 2019, 14.
2. Janvit Teržan, Petar Djinović, Janez Zavašnik, Iztok Arčon, Gregor Žerjav, Matjaž Spreitzer, Albin Pintar, "Direct propylene oxidation using molecular oxygen using mesoporous silica as the support", In: *Proceedings of the 8th Serbian-Croatian-Slovenian Symposium on Zeolites, Proceedings of the 8th Croatian-Slovenian-Serbian Symposium on Zeolites, Proceedings of the 8th Slovenian-Serbian-Croatian Symposium on Zeolites: [3 - 5 October 2019, Belgrade, Serbia]*, Serbian Zeolite Association, 2019, 29-32.
3. Maruša Borštnar, Sabina Kramar, Nina Daneu, "Potek hidratacije in nastanek hidratacijskih produktov belitno-kalcijevo sulfoaluminatnega cementa pri različnih temperaturah", In: *24th Meeting of Slovenian Geologists, Ljubljana, november 2019*, Treatises, reports, (Geološki zbornik, **25**), 2019, 13-15.

## PATENT APPLICATION

1. Aleš Mrzel, Damjan Vengust, *Method for the synthesis of metal molybdates and tungstates from molybdenum and tungsten carbides and nitrides*, EP3486218 (A1), European Patent Office, 22. 05. 2019.

## PATENT

1. Wang Yongli, Boštjan Jančar, Hermann Grünbichler, Franz Rinner, Damjan Vengust, Danilo Suvorov, *Thermoelectric generator comprising a thermoelectric element*, EP2975659 (B1), European Patent Office, 16. 10. 2019.
2. Aleš Mrzel, Damjan Vengust, *Method for the synthesis of metal molybdates and tungstates from molybdenum and tungsten carbides and nitrides*, SI25549 (A), Urad RS za intelektualno lastnino, 31. 05. 2019.