In the Department for Advanced Materials 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 micro-scale precision are used to prepare pre-designed structural ceramics, 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 oxide materials for various electronic applications, ii) new materials with improved antibacterial and photocatalytic effects, and iii) new oxide materials for efficient high-temperature thermoelectric energy conversion.

Functionalized oxides for electronic applications

Ferroelectric perovskite nanoparticles with well-defined anisotropic shapes are attracting increasing attention because of their unique shape- and size-dependent properties at small dimensions (below 200 nm). In addition, these particles with well-defined shapes and uniform size distributions have the potential to be used as the building blocks for the fabrication of functional nanodevices.

The shape, size and orientation engineering of perovskite ferroelectric particles were the focus of a study of the in-situ topochemic transformation in the molten salt from Aurivillious Bi$_4$Ti$_3$O$_{12}$ template plates into BaTiO$_3$ perovskite plates with a maintained shape. In the first step we investigated the principles for controlling the size of the Bi$_4$Ti$_3$O$_{12}$ plates, with the main emphasis being on the conditions for the preparation of nanoplates with a homogeneous size distribution. In the continuation, we managed to prepare various sizes (100 nm to 2 µm) of plate-like BaTiO$_3$ particles by controlling the size of the initial Bi$_4$Ti$_3$O$_{12}$ template plates. We systematically investigated how the conditions of the topotactic transformation, in addition to the initial template size, influenced the shape, size, tetragonality and orientation of the formed BaTiO$_3$ plates. The results showed that the shape of the Bi$_4$Ti$_3$O$_{12}$ nanoplates (< 500 nm) was the most preserved during the topotactic transformation into BaTiO$_3$ at 650–700°C, while the larger template plates (1 µm) disintegrated into smaller blocks (<500 nm) at this temperature due to the strains, which are a consequence of the misaligned growth of BaTiO$_3$ on the parent Aurivillious structure. The 1-µm-sized Bi$_4$Ti$_3$O$_{12}$ plates transformed into the ‹001› preferentially oriented BaTiO$_3$ plates at 800–900°C (Figure 1). The degree of preferential orientation was higher in the case of a homogeneous size distribution of the parent Bi$_4$Ti$_3$O$_{12}$ plates, an excess of Ba, slow cooling and heating rates and a defect-free surface. An understanding of the in-situ topotactic transformation from Bi$_4$Ti$_3$O$_{12}$ into BaTiO$_3$ represents the basis for engineering the morphology and orientation of other perovskite ferroelectrics (Ba$_{1-x}$Sr$_x$TiO$_3$ and Ba$_{1-x}$Ca$_x$Ti$_{1-y}$Zr$_y$O$_3$) with good piezoelectric properties.

Ferroelectric (FE), antiferroelectric (AFE) and relaxor materials with a perovskite lattice all exhibit characteristic domain structures, which are a result of the lattice strains from phase transformations into lower-symmetry phases. When external fields (electrical or mechanical) are applied to these materials, changes to the crystal lattice dimensions (intrinsic contribution) and/or changes to the domain structure (extrinsic contribution) can be detected. In order to determine the extrinsic effects on the tunable materials from the Pb$_{1-x}$La$_x$(Zr$_{1-y}$Ti$_y$)$_{1/4}$O$_3$ (PLZT) system, in-situ environmental scanning electron microscopy (ESEM) was employed for the first time. With the in-situ ESEM method the movement of domain walls during pressing or applying an electric field can be directly observed. From these experiments we determined that the mechanical force has the most influence on the domain structure of AFE materials, whereas the domains of FE materials are mainly affected by an electric field. Thus, extrinsic effects play an important role in the electromechanical response of FE and AFE materials. In relaxors, on the other hand, the main contribution to the enhanced electromechanical properties was determined to be intrinsic, from the distortion of the crystal lattice.

In the scope of an investigation of the phase relations in ternary oxide systems where new compounds and solid solutions form and exhibit interesting electric properties, we determined the phase equilibria in La$_2$O$_3$–TiO$_2$–GeO$_2$ at 1000°C. The samples were prepared by the wet-precipitation method from a
soluble precursor in order to achieve good homogenization of the starting compositions. We identified in the system a new compound and several solid solutions and determined their crystal structures and ranges of solid solubility. We found that in the compound $\text{La}_{10-x}\text{Ge}_x\text{O}_{26}$ with an apatite crystal structure that forms in the $\text{La}_2\text{O}_3-\text{GeO}_2$ system and exhibits high ionic conductivity, it is possible to incorporate Ti, resulting in the solid solution $\text{La}_{9.33}\text{Ge}_x\text{Ti}_x\text{O}_{26}$ that is stable for $0 \leq x \leq 4$.

We used the pulsed-laser deposition (PLD) technique to grow Pb[\text{Mg}_{1/3}\text{Nb}_{2/3}]\text{O}_3–\text{PbTiO}_3 (PMN-PT) thin films on TiO$_2$-terminated (001) SrTiO$_3$ (STO) substrates from single-crystal and ceramic targets with compositions in the vicinity of the morphotropic phase boundary (MPB). We prepared the ceramic targets in our laboratories via the columbite method, and we systematically added varying proportions of PbO excess (10–20%). PbO excess compensates for the loss of highly volatile lead in syntheses at high temperatures, which are necessary for the formation of the perovskite PMN-PT. By using PbO excess and by optimizing the remaining process parameters we managed to avoid the occurrence of the non-ferroelectric pyrochlore phase. Specifically oriented single-phase layers of PMN-PT on STO represent a good starting point for the preparation of multilayered structures for integration into piezoelectric micro-electromechanical systems (piezo MEMS). Namely, the values of the piezoelectric $d_{33}$ constant in rhombohedral PMN-PT single crystals are five times higher than the ones in lead zirconate titanate (PZT). PMN-PT is furthermore distinguished by very low dielectric losses and a high electromechanical factor $k_{33}$. By optimizing the conditions of the syntheses, and by using appropriate buffer layers and oxide electrodes, these properties can be transferred into the form of thin films.

In the scope of pulsed-laser deposition (PLD) we focused on the epitaxial integration of SrTiO$_3$ (STO) with Si(001). The high-quality epitaxial growth of STO thin films on a Si platform is essential for many technological applications, since it serves as an excellent template for the growth of different functional oxides. The Si surface is first cleaned by flash annealing up to 1200°C, following the deposition of metal Sr. The growth of epitaxial STO on the bare Si(001) surface is not feasible because of the high oxygen reactivity with the clean Si surface. However, the deposition of a Sr ultra-thin layer passivates the Si surface and enables the further epitaxial growth of STO. The process of PLD deposition of a Sr buffer layer with a coverage up to $1/2$ ML has been studied: we have confirmed that Sr grows with the characteristic two-domain $(2\times3)+(3\times2)$ pattern at $1/6$ ML Sr coverage and $(1\times2)+(2\times1)$ pattern at $1/2$ ML Sr coverage. Furthermore, we have been optimizing the parameters for the epitaxial growth of STO on such a template, using techniques like Reflection High-Energy Electron Diffraction (RHEED), X-Ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM) and X-Ray Diffraction (XRD). Satisfactory values for parameters like the Ar background pressure, laser fluency and frequency, as well as the recrystallization temperature and the sample’s suitable film thickness for a recrystallization step have been determined. The PLD system has been modified for the use of an ultra-high vacuum (UHV) suitcase that enables in-situ studies of the different stages of the process by surface techniques, like Scanning Tunneling Microscopy (STM) or XPS. A Temperature Programmed Desorption (TPD) system is also being implemented in order to extract additional chemical information about the investigated sample.

Thermoelectric materials

In the scope of the research on new materials for energy conversion we synthesized new thermoelectric materials based on compounds with a layered crystal structure. Weak interlayer bonding in such compounds enables the intercalation of various atoms, ions and molecules, which contributes to lowering the thermal conductivity and consequently to improving the efficiency of the direct conversion of heat to electricity. Layered structures in which individual layers exhibit a high electrical conductivity are thus suitable for the implementation of the phonon glass–electron crystal concept, which is essential for the development of new, efficient thermoelectric materials. We applied ion exchange as a route to new materials based on layered cobaltates and high-pressure pulsed electric current sintering (PECS) to precisely control the nano-stoichiometry and consequently the intercalation of titanium between the layers of titanium disulphide (TiS$_2$). We were the first to show that using a gas-tight model with PECS, a highly stoichiometric TiS$_2$ with a high degree of texturing can be synthesized (Figures 2 and 3). Such a material is interesting for the
Antibacterial and photocatalytic materials

In 2015 the Biomaterials Group was engaged in research work in the following areas:

1. The development of new antimicrobial biomaterials: We have developed new materials based on Ga-apatite and 1D structures of MgO (Figures 4–6) and showed that they are very effective against *Escherichia coli* (*E. coli*) and *Pseudomonas aeruginosa* (*P. aeruginosa*). We showed that they are nontoxic to human fibroblast cells and do not produce reactive oxygen species (ROS).

2. The development of smart scaffolds as suitable carriers of stem cells and applicable in tissue engineering (in this area we have developed apatite doped with Mg²⁺, Sr²⁺, Ga³⁺ and Zn²⁺ ions, and functionalized its surface using the BMP-2 protein, which promotes the growth of osteoblastic cells). The material was incorporated within the micro- and nano-porous 3D structure of the PLLA polymer. We showed that the developed material slowly released incorporated bioactive components under physiological conditions and confirmed that the release of doped ions brings a strong antimicrobial activity against *E. coli* and *P. aeruginosa*.

3. The development of innovative nanosensors for the detection of bacteria. In this area we have developed nanomaterials based on Au nanoparticles, functionalized their surface with proteins and confirmed the possibility of their specific interactions with *E. coli* and *P. aeruginosa* bacterial cells.

In 2015 we started to work on the development of new antibacterial materials in which we used the antibacterial peptide nisin (Ni) as an antibacterial component. As a carrier of the antibacterial peptide we prepared spherical gold (Au) nanoparticles with an average size of 20 nm. In order to increase the yield of the antibacterial component (Au-Ni), micron-sized carbon spheres (C) were used as supports. Such prepared hybrid materials exhibit improved activity against the bacteria strains *E. coli* and *P. aeruginosa*.

Materials for heat-insulation applications

The aim of our work on foam glass is to develop a new preparation procedure for a foam glass with improved thermal insulation properties. The new method should have a smaller dependence of the foaming process on the composition of the glass cullet. A new preparation procedure was developed that shows a high potential for further improvements. At a density of 150 kg/m³, we reached a thermal conductivity of 40 mW/(m·K), which is almost 20 % better than in a conventional foam glass. A new project on foam glass aims to reach a thermal conductivity of 37 mW/(m·K). This could be achieved with an understanding of the processes and reactions taking place in the softened glass during the foaming process. We continued with research work focused on the investigation of interactions between foaming additives and glass, and optimizing of the viscosity, surface tension and glass stability at the foaming temperature.

Projects

**TDK-Epcos**

For the industrial partner EPCOS OHG, Deutschlandsberg, Austria we work on the project: “Thin-Film-Energy-Storage Devices on the basis of PLZT and Cu-electrodes”, the focus of which was to investigate the growth development of new thermoelectrics that will replace materials based on rare and toxic elements in near-room- and mid-temperature applications.
of Pb$_{1-x}$La$_x$(Zr$_{1-y}$Ti$_y$)$_3$O$_{12}$ (PLZT) thin films using pulsed-laser deposition. The purpose of the project is to develop new materials and technology for advanced energy-storage applications.

**ENPIEZO**

In the scope of the M-ERA.NET project ENPIEZO we develop piezoelectric-based energy-harvesting (EH) devices to provide a remote source of electricity from waste vibrations with countless applications. For instance, EH devices can be powered by a heartbeat to operate pacemakers or it can provide electricity for sensors at remote locations like wind-turbine air blades. We investigate the fabrication-friendly pulsed-laser deposition of high-quality Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_7$-PbTiO$_3$ thin films on silicon, based on the delicate engineering of silicon-oxide interfaces. The study is performed on laboratory- and industrial-scale systems, and it is the first of its kind in the world. In the project, the preparation of EH devices using aerosol deposition is also investigated. The project, which is coordinated by the JSI, brings together four partners with expertise in a very diverse field of research and development.

**SCOPES**

During the realization of the SCOPES 2014–2017 project, the laboratory for biomaterials purchased new equipment for the processing of biomaterials (liofilizator), equipment for the cultivation of bacteria and the simulation of physiological conditions (incubator shaker) and equipment for biological work under sterile conditions (biological safety cabinet, class 2).

**Some outstanding publications in the past year**


**Organization of conferences, congresses and meetings**

1. Workshop on NATO Sfp 984091 project “Microwave Tuneable Materials, Composites and Devices”, Ljubljana, 23. 2. – 27. 2. 2015.
2. Workshop on SCOPES project “Intelligent Scaffolds as a Tool for Advanced Tissue Regeneration”, Ljubljana, 26. 5. – 29. 5. 2015.

**INTERNATIONAL PROJECTS**

1. Thin-Film Energy-Storage Device on the basis of PLZT and Ca-Electrodes
   Prof. Danilo Suvorov
   Epcos Obg

2. Technological Characterisation Test of OGK-5 (NBGRES) Ashes for Verification of Usability in the Process of Rock Wool Production
   Prof. Danilo Suvorov
   Enel Ingegneria E Ricerca S.p.a.

3. Investigation of NdBiCuGaFe Rare Earth Alloys and Related Compounds
   Prof. Danilo Suvorov
   Urban Mining Company

4. Production and Characterisation of Coal Ash Fibres
   Prof. Danilo Suvorov
   Enel Ingegneria E Ricerca S.p.a.

5. Microwave Tuneable Materials, Composites and Devices
   Asst. Prof. Boštjan Jančar
   Nato - North Atlantic Treaty Organisation

6. 3D Composite Plasmonic Metal/ Semiconductor Photo-catalyst for Efficient Solar to Fuel Energy Conversion
   Asst. Prof. Srečo Davor Škapin
   Slovenian Research Agency

7. Biomineralization at the Nanoscale: from the Natural Systems to the Laboratory
   Asst. Prof. Srečo Davor Škapin
   Slovenian Research Agency
RESEARCH PROGRAM

1. Contemporary Inorganic Materials and Nanotechnologies
   Prof. Danilo Suvorov

R & D GRANTS AND CONTRACTS

1. Engineering of structural and microstructural characteristics in contemporary dielectrics and ferroelectrics with perovskite and perovskite-like crystal structures
   Prof. Danilo Suvorov
2. Growth of high quality piezoelectric thin films on silicon using pulsed laser deposition
   Dr. Matjaž Spreiter
3. SOFIEP; Intelligent Scaffolds as a Tool for Advanced Tissue Regeneration
   Dr. Marija Vukomanović
   SNF; Swiss National Science Foundation

VISITORS FROM ABROAD

1. Dr. Christoph Aster, TDK EPCOS, Deutschlandsberg, Austria, 10. 2. 2015.
2. Dr. Kerstin Schmolter, TDK EPCOS, Deutschlandsberg, Austria, 10. 2. 2015.
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5. Dr. Tim Jackson, University of Birmingham, Birmingham, Great Britain, 23. 2. – 27. 2. 2015.
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13. Prof. dr. Yun Liu, Research School of Chemistry, Australian National University, Canberra, Australia, 15. 6. – 19. 6. 2015.
14. Dr. Hua Chen, Research School of Chemistry, Australian National University, Canberra, Australia, 15. 6. – 19. 6. 2015.
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17. Dr. Kerstin Schmolter, TDK EPCOS, Deutschlandsberg, Austria, 15. 7. – 15. 7. in 20. 7. – 24. 7. 2015.
20. Dr. Chuan-Liang Kao, National Taiwan University, Taipei City, Taiwan, 23. 8. – 5. 9. 2015.
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24. Prof. dr. Wen-Jong Wu, National Taiwan University, Taipei City, Taiwan, 10. 9. – 14. 9. 2015.
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27. Dr. Kerstin Schmolter, TDK EPCOS, Deutschlandsberg, Austria, 7. 12. – 9. 12. 2015

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1. Prof. dr. Junliang Bian, Department of Inorganic Materials, Shanghai University, Shanghai, China, 2. 6. – 28. 8. 2015.
2. Dr. Jyoti Prosad Guha, Missouri University of Science and Technology, Rolla, USA, 2. 6. – 28. 8. 2015.
3. Prof. Dr. Dragan Uskoković, Institut tehničkih nauka Srbske Akademije Znanosti i Umetnosti, Belgrade, Serbia, 8. 7. – 15. 7. 2015.

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BIBLIOGRAPHY

ORIGINAL ARTICLE


PUBLISHED CONFERENCE CONTRIBUTION


MENTORING
