The Electronic Ceramics Department is active in the research of the synthesis, properties and applications of materials for electronics and energetics, mainly complex multifunctional materials and structures. The materials of interest include ceramic piezoelectrics, ferroelectrics, relaxors, multiferroics and conductive oxides. The emphasis is on creating the properties by the synthesis and structure on the nano-, micro- and macro-levels. The group also works on the principles of the basic technologies of ceramic pressure sensors, ceramic MEMS and flexible electronics.

In the framework of lead-free piezoelectric materials we were particularly interested in alkali-niobate-based ceramics, which are still considered as one of the most important candidates for the replacement of lead-based piezoelectrics in piezoelectric applications. In collaboration with Keio University from Japan we developed a new synthesis method for the preparation of fine and single-phase potassium sodium niobate (K_{0.5}Na_{0.5}NbO_3) powders. The method consists of the attrition milling of fine Nb_2O_5 particles suspended in an ethanol solution of sodium and potassium acetates. We obtained a single-phase KNN powder by calcining the milled powder twice at temperatures as low as 450-650°C, which are 100-200°C lower than those typically used during the conventional solid-state synthesis of KNN.

Using optical dilatometry and a detailed microstructural analysis we studied the sintering behaviour of sodium niobate (NaNbO_3) powders with particles of nanometre and submicrometre sizes. We found that the initial particle size did not affect the evolution of the microstructure upon annealing, suggesting a key role of the mechanisms responsible for the grain growth in the initial stage of the sintering. By measuring the specific surface area of the specimens, which were annealed at different temperatures, we found that the observed grain growth is due to the surface diffusion. Owing to the low activation energy (50-60 kJ/mol), in fact, this grain-growth mechanism is activated in the initial stage of the sintering and, thus, decreases the driving force for the sintering and prevents any further densification of the powder compact. NaNbO_3 ceramics with a relative density of 98% and an average grain size of 0.7±0.29 μm were successfully prepared by hot pressing at 1150°C. The results significantly contribute to the general understanding of the sintering of alkali-niobate-based ceramics and suggest ways to control the microstructure of this important group of lead-free piezocermics.

Within the activities on lead-based piezoelectric ceramics, we focused on the solid-state synthesis and characterization of the Pb(Zr,Ti)O_3 (PZT) ceramics, mechanically toughened by tetragonal-stabilized zirconia (TZ) particles. In order to achieve a homogeneous distribution of TZ grains within the PZT matrix, we developed a modified solid-state synthesis procedure, consisting of pre-milling, pH adjustment and a modification of the surface of the TZ powder. According to the Voronoi-diagram analysis of the microstructures of the ceramics, the modified synthesis route provided a more homogeneous TZ distribution in the PZT matrix, as compared to the composites processed by conventional means (figure 1). The R-curve measurements, performed at the Technische Universität Darmstadt, however, did not show a measureable difference in the fracture behaviour of the two PZT-TZ composites.

Within the 7FP EU project CERAMPOL and in collaboration with the company HIPOT-RR we continued our work on the integration of piezoelectric PZT actuators in waste-water cleaning systems. Based on the vibration measurements of a corundum substrate with integrated piezoelectric actuators, we were able to evaluate the influence of various parameters, such as the type of the piezoelectric material and the position of the actuators, on the amplitude and frequency of the substrate vibration resonances. A numerical analysis of the different substrate/actuator structures showed trends in the vibration behaviour. A combination of the numerical analysis and the experimental verification made it possible to identify the main parameters of the vibration system, like those mentioned above, which will be further optimized within the project.
The 0.57Pb(Sc1/2Nb1/2)O3–0.43PbTiO3 (PSN-PT) is a perovskite material that can be used in various piezoelectric applications, including sensors, actuators and ultrasound transducers. The integration of such functional materials onto substrates in the form of thin or thick films often results in thermal stresses in the film, which have their origin in the mismatch between the thermal expansion coefficient of the active layer and the substrate, and may significantly affect the functional response of the material. In order to understand and control these stresses, the linear expansion coefficient of the PSN-PT must be known, in both the unpoled and poled states. We found that the thermal expansion coefficient of PSN-PT increases from 30°C up to the Curie temperature of 260 °C, where it reaches 2.08 · 10⁻⁶ K⁻¹. The phase transition was identified as an anomaly in the expansion between 260 °C and 280 ° C. The coefficient of thermal expansion then increases with a further increase in the temperature, reaching 9.66 · 10⁻⁶ K⁻¹ at 400 °C. These data will be essential for the integration of PSN-PT in thin- or thick-film structures.

In collaboration with the Ecole Polytechnique Fédérale de Lausanne, Switzerland, we studied the elastic properties of Pb(Mg₁/₃Nb₂/₃)O₃–0.3PbTiO₃ (PMN) ceramics. It was shown that the PMN ceramics exhibit true anelastic relaxor behavior with the parameters of the Vogel-Fulcher equation similar to those for dielectric relaxation.

We continued our research on multiferroic BiFeO₃ ceramics, focusing on the (Bi,RE)FeO₃ (RE=Sm, Gd, Dy) compositions, which exhibit morphotropic phase boundaries. By combining the milling of the starting powders in ethanol with the addition of polyacrilic acid and subsequent mechanochemical activation, we succeeded in preparing homogeneous powders with the sintering temperatures as low as 800°C. The powders were then used to prepare homogeneous and dense bulk ceramics. Like in the case of BiFeO₃, the ceramics modified by the RE oxides exhibited large electric-field induced strains, which exceeded 0.3%. The advantage of these modified ceramics over the unmodified BiFeO₃ is that the strain shows little dependence on the driving electric-field frequency; as compared to unmodified BiFeO₃, the response of RE-modified ceramics is thus more stable.

Using the inkjet printing of water-based dispersions of submicron lead zirconate titanate (PZT) particles we prepared films with thicknesses of a few micrometres. We confirmed the local piezoelectric response of such PZT films by means of piezo-response force microscopy.

In collaboration with the Department for Condensed Matter Physics we studied the electrocaloric (EC) response of 0.7Pb(Mg₀.₃₃Nb₀.₆₆)O₃–0.3PbTiO₃ bulk ceramics, processed from mechanochemically activated powders. The highest temperature change of 2.7 K was observed in the vicinity of the critical point, i.e., at 430 K, and under an applied electric field of 90 kV/cm. In addition, we investigated the EC response of the environmentally friendly lead-free relaxor K₀.₇Na₀.₃NbO₃SrTiO₃ (KNN-STO) ceramics. The results confirmed the large EC response in the vicinity of the dielectric anomaly. The EC temperature change at room temperature is comparable to that measured in lead-based ceramics.

In the framework of lead-free ferroelectric thin films prepared by Chemical Solution Deposition, we collaborated with the Ecole Centrale Paris, France, and investigated the phase transitions of KNN thin films deposited onto (111)Pt/TiO₂/SiO₂/Si substrates. The purpose was to compare the phase-transition behaviour of the KNN films with two different microstructures, i.e., columnar and granular. Raman spectroscopy and X-ray diffraction analysis confirmed the presence of both phase transitions as observed in the KNN powder, i.e., the monoclinic-to-tetragonal (Tₐ→ₐ) and the tetragonal-to-cubic (Tₐ→ₐ) transition. Whereas the Tₐ→ₐ transition of the film with the columnar microstructure was similar to that observed in the KNN powder, the Curie temperature (Tₐ→ₐ) was slightly lower. We attribute this lowering of the Tₐ to the presence of tensile stresses, which develop as a consequence of the thermal expansion coefficient mismatch between the film and the substrate.

Within the project FERROPATCH in the frame of the program JP PECS of the European Space Agency (ESA) we prepared Ba₀.₆Sr₀.₄TiO₃ (BST) thin-film varactors on alumina substrates. Single-phase and dense films with homogenous microstructures and thicknesses between 70 nm and 600 nm were prepared by annealing the as-deposited films at temperatures up to 900°C. The highest dielectric permittivity was measured in the 170-nm-thick sample and was 1310 at 100 kHz and 1210 at 10 GHz. In addition, we also studied the synthesis of BST nanoparticles.
which were prepared via the thermal degradation of acetylacetone precursors in oleylamine under the presence of stearic acid, used as surfactant. The particles were amorphous and crystallized into the perovskite phase after annealing at 700 °C.

The work within the 7FP EU ORAMA project was concentrated on the synthesis of oxide semiconductors and dielectrics for transparent electronics. CuAlO₂, which is a p-type semiconductor, was synthesized by annealing a stoichiometric mixture of nano-boehmite (AlOOH) and Cu₂O at 1100°C in an argon atmosphere. In contrast to the conventional synthesis from a mixture of oxide powders, this synthesis method represents an efficient way toward the phase-pure delafossite. By sintering the as-prepared powder compacts at 1100°C for 2 hours in air, we succeeded in preparing X-ray-diffraction phase-pure ceramics with 86% of relative density, which can be used as sputtering targets (figure 2).

Our studies related to thin dielectric films with a high permittivity for transparent electronic components were focused on thin films based on Ta₂O₅ and Ta₂O₅-Al₂O₃-SiO₂, which were prepared by Chemical Solution Deposition. The films, deposited onto glass substrates and processed at temperatures up to 400°C, showed a transmittance of ~80 %, a dielectric permittivity of ~20 and a low leakage current. These films are thus suitable for use in thin-film capacitors or transistors. In addition, we adopted inkjet printing for the deposition of thin films of n-type conducting oxides based on ZnO and SnO₂ onto various substrates.

Within the research on the processing of piezoelectric thick films by electrophoretic deposition (EPD) process, we systematically studied the influence of the polyacrylic acid / organic base ratio on the electrical conductivity of the dispersion and on the thickness uniformity of the as-deposited layers. At the optimal polyacrylic acid / organic base ratio we obtained a stable dispersion of donor-doped PZT particles in ethanol with a low electrical conductivity. The deposited layer had a thickness of 30 μm and was uniform and homogeneous. The dispersions were used for the processing of thick films on curved porous PZT substrates. In the next step and in collaboration with researchers from François-Rabelais University from Tours, France, we fabricated geometrically-focused high-frequency ultrasound transducers (US) for medical diagnoses. With the colleagues from Tours we also investigated the functional properties of 0.65Pb(Mg₁/₃Nb₂/₃)O₃-0.35PbTiO₃ (PMN-PT) thick films for US transducers. The results suggest that the PMN-PT thick-films transducers are superior to those made from the standard Pb(Zr,Ti)O₃ (PZT) piezoelectric material.

We studied the preparation of PZT ceramics with a controlled amount, size and distribution of pores, which could be used as substrates for high-frequency ultrasound transducers. The method consists of the heterocoagulation of PZT and poly(methyl methacrylate) (PMMA) particles.

We developed a procedure for the processing of aqueous dispersions of ceramic particles, suitable for the patterning of thick films by piezoelectric inkjet printing. We reduced the average particle size of a micron-sized PZT powder to a few tens of nanometres by milling and provided an effective dispersion of PZT particles in water by controlling the pH of the dispersion, and the type and amount of dispersant. The ink with an optimized average PZT particle size, surface tension and viscosity was inkjet printed onto platinum-coated condurum substrates. The inkjet printed structures, dried and fired at 1100°C, were dense and ~5 μm thick. The local piezoelectric response of the PZT film was confirmed using an atomic force microscope equipped with a piezoresistance-force module (figure 5).

By optimizing the rheological properties of the ink we improved the procedure for the processing of KNN thick films using screen-printing technology. The films were deposited onto substrates with different thermal expansion coefficients, so that different degrees of in-plane biaxial stresses were induced in the films. The influence of these stresses was reflected in the structural and functional properties of the films. The most important is the phenomenon of ‘self-poling’ of the KNN thick films, the extent of which depended on the mechanical stresses, i.e., on the type of the substrate.

We continued the investigations on LTCC (Low Temperature Co-fired Ceramics), used for the fabrication of 3D structures for different electromechanical (MEMS - Micro Electro Mechanical Systems) and chemical microsystems. In collaboration with the partners from Montanuniversität Leoben, Austria, we studied the influence of the firing conditions on the microstructure and mechanical properties of Du Pont LTCC. We concluded that the porosity has a major influence on the elastic modulus, the fracture toughness, the hardness and the biaxial flexural strength.

We fabricated a ceramic micro reactor with large cavities for the catalytical production of hydrogen from methanol and water by using LTCC technology.
of the LTCC. If the LTCC materials are fired at elevated temperatures for prolonged periods, so that the porosity is reduced, their properties remained unchanged, regardless of the firing temperature and/or firing time. This finding is important for the design and production of ceramic pressure sensors and other MEMS devices, which require relatively long firing procedures at higher temperatures, as compared to the conditions usually required for the processing of LTCC. In 2013 we reinforced the collaboration with KEKO Oprema d.o.o. in the field of materials and technologies based on LTCC.

Traditional co-operation with the research partners from HIPOT-RR and Centre of Excellence NAMASTE continued in all the research projects related to thick-film and LTCC technology. With the group from the company KEKON d.o.o. we continued our research in the field of functional thick-film materials, in particular, we investigated new thick film lead-free resistors as possible sensor elements. We found that the temperature dependence of resistivity of these materials satisfies the needs for the application, however, the “gauge” factors, i.e., the dependence of the resistivity on the deformation, are three times lower than required, so that these materials are not suitable as pressure sensors. We also tested a commercial ESL 3411-I thick-film resistor with a high and linear dependence of resistivity versus temperature and a low sheet resistivity. The results suggested that this material is compatible with LTCC tapes and that it could be used for temperature measurements over large surfaces. This material was successfully used as a sensor for temperature control and regulation in large LTCC chemical reactors.

Within the programme JE PECS of the European Space Agency (ESA), we continued our work on the CERACON project, together with the partners from the Department of Systems and Control, and the National Institute of Chemistry. The topic of the project was the design and fabrication of LTCC-based micro reactors and the necessary periphery for the high-temperature catalytic transformation of methanol and water into hydrogen. It is worth mentioning that we succeeded in designing and constructing two reactors, i.e., one for the steam reforming and the other for the removal of the residual carbon monoxide from gas products. Both reactors had large buried cavities where the chemical reactions take place; the volume of the reformer and the reactor for CO removal was 18.7 cm³ and 5.4 cm³, respectively. These, rather extreme dimensions for LTCC technology, were fabricated in order to satisfy the required production of 85 litres of hydrogen per hour. The realisation of these particularly large cavities required special LTCC lamination procedures and a controlled firing process. The final dimensions of the reformer and the reactor for CO-removal were, respectively, 90 mm × 90 mm × 9.2 mm and 90 mm × 36 mm × 9.2 mm (figure 4).

In collaboration with the company ETI d.d. Izlake we investigated various silicate materials, i.e., steatite and cordierite, which are used in electrical engineering as heat or electrical insulators. We systematically studied the influence of raw materials on the microstructure, mechanical and electrical properties of the ceramics. At the optimal amount of selected raw materials and at the optimal milling conditions we prepared a new type of dense, alkaline steatite with a high flexural strength (~185 MPa) and a high specific electrical resistivity (~0.8 MΩm). The resulting material was prepared on a production scale in the company and is now used for the fabrication of electrical fuses.

Some outstanding publications in the past year


Organization of conferences, congresses and meetings

1. COST Training school on characterization of materials, Ljubljana, Slovenia, 28.–29. 1. 2013

Patent granted


INTERNATIONAL PROJECTS

1. 7FP - ORAMA: Oxide Materials Towards a Matured Post-silicon Electronics Era
   European Commission
   Prof. Barbara Malič

2. 7FP - CERAMPOL: Ceramic and Polymeric Membrane for Water Purification of Heavy Metal and Hazardous Organic Compound
   European Commission
   Asst. Prof. Danjela Kuščer Hrovatin

3. 7FP - PI: The Pizio Institute - European Expertise Centre for Multifunctional and Integrated Piezoelectric Devices
   European Commission
   Prof. Barbara Malič

4. CERACON: Integration and Control of Liquid Fuel processor based on Ceramic Micro-Systems
   COST Office
   Asst. Prof. Marko Hrovat

5. COST MP9094; SIMUFER: Single- and Multiphase Ferroics and Multiferroics with Restricted Geometries
   COST Office
   Prof. Barbara Malič

6. FERRO-PATCH: Frequency and Polarisation Agile Microstrip Patch Antenna based on Ferroelectric Varactors
   ESA/ESTEC
   Prof. Barbara Malič

7. Solution Processing of Thin Films for Transparent Electronics (TRANS)
   Slovenian Research Agency
   Prof. Barbara Malič

8. Dielectric Spectroscopy and Tunability of Low-Temperature Recessed Complex Perovskites
   Slovenian Research Agency
   Prof. Barbara Malič

R&D GRANTS AND CONTRACTS

1. Nanostructures for High-Efficiency Solar Cells and Photovoltaics
   Prof. Barbara Malič

2. Oxide-Based Components for Transparent Electronics
   Prof. Barbara Malič

3. Tunable Ferroelectric Thin Film Capacitors for Agile Microwave Antennas
   Prof. Barbara Malič

4. High-performance Piezoelectric Materials for Sensors and Actuators in High-temperature Applications
   Asst. Prof. Tadej Rojač

5. Textured Ceramic Films for Sensors and Actuators
   Asst. Prof. Tadej Rojač

6. Materials and Technologies for Chemical Microsystems
   Asst. Prof. Andreja Benčan Golob

7. PhScI SN80 5:031-PTG03 Thin Films for Sensor and Actuator Applications
   Dr. Nana Utčič Nemevič

NEW CONTRACTS

1. Evolution of Microstructure in Non-porous Bulk Ceramics with Selected Properties for Applications in Low Temperature Co-fired Ceramic (LTCC) structures
   Keko – Oprema, d. o. o., Žužemberk
   Prof. Barbara Malič

2. Materials and Technologies for Chemical Microsystems
   Keko – Oprema, d. o. o., Žužemberk
   Asst. Prof. Andreja Benčan Golob

3. Nanomaterials in Ceramics-Feasibility Study
   RE, eNoM
   Prof. Barbara Malič

RESEARCH PROGRAM

1. Electronic Ceramics, Nano-, 2D and 3D Structures
   Prof. Barbara Malič

VISITORS FROM ABROAD

1. Julian Walker, School of Materials Science & Engineering, University of New South Wales, Sydney, Australia, 1. 1.–31. 7. 2013
2. Prof. Liliana Mitoseriu, University “Al. I. Cuza”, Faculty of Physics, Iasi, Romania, 23.–30. 1. 2013
3. Dr. Denis Schütz, CD-Lab for Advanced Ferroic Materials, Graz, Austria, 27. 1.–14. 4. 2013
4. Dr. Nadejda Horchidan, University “Al. I. Cuza”, Faculty of Physics, Iasi, Romania, 27. 1.–22. 2. 2013
5. Andre-Pierre Abellard, Université François Rabelais, Tours, France, 2.–29. 3. 2013
7. Prof. Dragom Damjanovic, Swiss Federal Institute of Technology - EPFL, Lausanne, Switzerland, 6.–9. 3. 2013
8. Dr. Marco Deluca, Institut für Struktur- und Funktionskeramik, Montanuniversität Leoben, Materials Center Leoben Forschung GmbH, Leoben, Austria, 15. 3. 2013
9. Naima Benyagoub, Magali Leger, Prof. Marc Lethiecq, Prof. Franck Levassort, Université François Rabelais, Tours, France, 24.–29. 3. 2013
10. Dr. Marko Budimir, Institute for Nuclear Technology-INETEC, Zagreb, Croatia, 13. 5. 2013
11. Prof. Jürgen Rödel, Technische Universität Darmstadt, Darmstadt, Germany, 16.–17. 5. 2013
12. Prof. Klaus Reichmann, Graz University of Technology, Graz, Austria, 17. 5. 2013
13. Prof. Angus I. Kingon, Brown University, Rhode Island, USA, 9.–17. 6. 2013
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Postgraduates
1. Dr. Gregor Trefalt, University of Geneva, Geneva, Switzerland, 9.–13. 9. 2013
2. Dr. Vassilios Binas, Foundation for Research & Technology Hellas (FORTH), Institute for Electronic Structure and Laser (IESL), Crete, Greece, 8.–25. 9. 2013
10. Alja Kupec, Tanja Pečnik, B. Sc.
12. Tanja Pečnik, B. Sc.
13. Alja Kupec, B. Sc.
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16. Tina Ručigaj, B. Sc.
17. Silvo Drnovšek, B. Sc.
18. Jernej Pavlič, B. Sc.
PUBLISHED CONFERENCE CONTRIBUTION (IMITED LECTURE)


3. Hana Uršič, Franc Levassort, Janzˇna Holc, Marc Letheiç, Marija Kosec, "0.65Pb(Mg1/3Nb2/3)O3-0.35PbTiO3 thick films for high-frequency piezoelectric transducer applications", Jpn. j. appl. phys., vol. 52, no. 5, pp. 055502-1-055502-6, 2013.


REVIEWS


PUBLISHED CONFERENCE CONTRIBUTION (INVITED LECTURE)


6. Hana Uršič, Franck Levassort, Janzˇna Holc, Marc Letheiç, Marija Kosec, "0.65Pb(Mg1/3Nb2/3)O3-0.35PbTiO3 thick films for high-frequency piezoelectric transducer applications", Jpn. j. appl. phys., vol. 52, no. 5, pp. 055502-1-055502-6, 2013.


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15. Tanja Pečnik, Sebastian Glinšek, Brigita Knet, Barbara Malič, "Microstructure and kHc and kGh range dielectric properties of polycrystalline Ba0.8Sr0.2TiO3 thin films", In: 2013 Joint UFFC, EPTF and PFM Symposium, International Ultrasonics Symposium (IUS), Joint IEEE International Symposium on the Applications of Ferroelectrics (IAF) and Piezoresponse Force Microscopy and Nanoscope Phenomena in Polar Materials (PMP), Joint International Frequency Control Symposium (IFCS), and European Frequency and Time Forum (EFTF), 21-25 July 2013, Prague, Czech Republic, [S. L.], IEEE Ultrasonics, Ferroelectrics, and Frequency Control Society, 2013, pp. 235-238.


INDEPENDENT COMPONENT PART OR A CHAPTER IN A MONOGRAPH


PATENT APPLICATION


PATENT


MENTORING
