DEPARTMENT FOR ADVANCED MATERIALS K-9

The primary activities of the department are the development of new materials, and new processes for the preparation of such materials, in the form of nanostructures and nanocomposites. The main objective of the current projects is the synthesis of new, environmentally friendly materials with special electrical and optical properties, with the emphasis on tunable materials that exhibit a dependence of the electric polarization on external electric, mechanical or magnetic fields and, furthermore, the development of new dielectrics and semiconductors that can be exploited for their microwave and optical properties.

Head:
Prof. Danilo Suvorov

Development of tunable materials

We have investigated the structural and electrical characteristics of the $Na_{0.5}Bi_{0.5}TiO_3$-$SrTiO_3$ ceramic system. The end-members of the system have already been thoroughly investigated with respect to their various characteristics; however, their solid-solution has very seldom been the focus of research. $Na_{0.5}Bi_{0.5}TiO_3$ is a complex perovskite with relaxor characteristics, related to the compound's compositional disorder. Recently, it has been tested frequently for applications in electronic devices, mainly as an ecological alternative to lead-containing relaxors. $SrTiO_3$ is a well-known incipient ferroelectric and therefore enables a shift of the $Na_{0.5}Bi_{0.5}TiO_3$ phase transitions towards lower temperatures. In this way we were able to control the samples` polar order and the intensity of the dielectric relaxations at room temperature. We observed that samples with intermediate compositions have the most intense relaxation and thus exhibit a pronounced stress tunability. Moreover, samples with a higher $SrTiO_3$ concentration have smaller dielectric losses and still a marked DC-bias dependence of the dielectric constant. These samples are therefore attractive for voltage-tunable applications, such as varactors, phase shifters, etc.

In addition, we focused on perovskite ceramics in the form of the $(Na_{1-x}K_x)_{0.5}Bi_{0.5}TiO_3$ solid solution system (NBT-KBT). NBT crystallizes in the rhombohedral R3c polar structure, whereas KBT exhibits the tetragonal P4mm polar structure. At a concentration of 80 mol% of NBT in the NBT-KBT solid solution the samples consist of coexisting tetragonal and rhombohedral crystal structures, which are both thermodynamically stable and form a morphotropic phase boundary. We performed transmission electron microscopy and electron diffraction experiments of the local structure of pure KBT and found that the grains consist of typical differently oriented transformation domains separated by <100> and <110> twin boundaries.

We found that during the synthesis of $K_{0.5}Bi_{0.5}TiO_3$ the volatilization of the potassium and bismuth components occurs, followed by a thermal decomposition of the matrix phase during annealing at temperatures higher than 1000°C This leads to the formation of potassium polytitanate and bismuth-rich phase $K_{0.5}Bi_{4.5}Ti_4O_{15}$ with an Aurivillius-type crystal structure. In contrast, some papers report single-phase ceramic samples, sintered from powders prepared by different methods. Therefore, we started with investigations of materials prepared by the hydrothermal and molten salt methods.

Measurements of the uniaxial stress dependence of permittivity in lead-free $Na_{0.5}Bi_{0.5}TiO_3$-based materials showed the most favorable results for relaxor compositions. These materials exhibit the highest change in the permittivity. Moreover, the change of permittivity was reversible above the temperature of the permittivity maximum. Thereafter, relaxor compositions from the $Na_{0.5}Bi_{0.5}TiO_3$– $SrTiO_3$ system with an even higher dielectric constant were investigated. Measurements of the stress dependence of the permittivity for compositions with 50 and 70 mol% of $SrTiO_3$ showed a decrease in the relative permittivity of 400 and 900, respectively, at an applied pressure of 200 MPa and a measuring frequency of 1 kHz. The change of the permittivity was reversible, which gives potential applications of these materials in pressure sensing

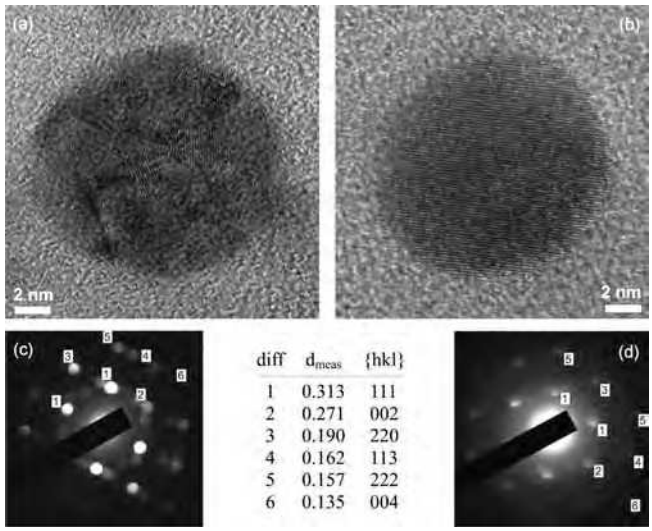

Figure 1: TEM images of (a) a ZnS nanocluster and (b) a ZnS nanoparticle after subsequent recrystallisation, formed in a (PAH/PAA)$_{7.5}$ polyion matrix assembled at pH=3.0 with the corresponding micro-diffraction patterns(c,d)

Development of microwave dielectrics

In the scope of further research on coherent intergrowths between the ordered cubic perovskite $Ba_3CoNb_2O_9$ and polytypes of hexagonal perovskite

In collaboration with Epcos OHG we developed LTCC-technology-compatible ceramic materials with a thermal expansion coefficient that can be tailored in the range 4-12 ppm/K. Regarding the dielectric properties, these materials are superior to those available commercially.

with cation vacancies we investigated the formation of intergrowth phases within the $Ba_3CoNb_2O_9$ – $Ba_5Nb_4O_{14}$ (BCN-5L) system. We found that the intergrown phase forms during the first stage of reaction among the cubic BCN and five-layered hexagonal 5L perovskite. In the second stage the Co diffuses from the cubic into the hexagonal part and in the third phase the Co orders to occupy every eighth (111)c plane. Coherently intergrown phases can thus be understood as a transient phenomenon during ordering into the thermodynamically stable 1:8 ordered hexagonal polytypic phase.

We continued with investigations of the glass-ceramic $MgO\text{-}B_2O_3\text{–}SiO_2$ system and studies of the binary compound $Mg_3B_2O_6$, which crystallizes from the aforementioned ternary system. Nucleating agents (TiO_2 and ZrO_2) were added to the initial oxides from the $MgO\text{-}B_2O_3\text{–}SiO_2$ system with the intention to increase the crystallization rate and to influence the dielectric properties. In both cases the temperature of the peak maximum increases with the amount of added nucleating agent and, furthermore, the Qxf values also increase with the amount of nucleating agent. We assume that the higher Qxf values are the result of a higher degree of crystallization. The highest Qxf values above 160,00GHz were measured for the sample with 7% of added TiO_2.

During the synthesis of the single-phase $Mg_3B_2O_6$ ceramics sintered at 1310°C we observed exaggerated grain growth, which is attributed to the presence of a liquid phase. This could be due to: 1) the melting of the glassy phase, which is often present in systems containing B_2O_3 or 2) the presence of a small amount of $Mg_2B_2O_5$, which according to the reported phase diagram incongruently melts at the temperature close to the sintering temperature of $Mg_3B_2O_6$. The Qxf values increase with the increase in the grain size and the maximum measured values of $Mg_3B_2O_6$, ceramics with or without the addition of $Mg_2B_2O_5$ exceed 220,000GHz. With the use of electron back-scatter diffraction we determined (011) twin boundaries within the exaggeratedly grown grains.

In the scope of the applied project with EPCOS OHG, Deutschlandsberg, Austria, several low-permittivity LTCC materials with temperature expansion coefficients (TCEs) of 4, 6-8, 10-12 ppm/K have been developed. Simultaneous co-firing of materials in the LTCC modules requires their matching in the TCE. The majority of applications requires a low-permittivity substrate with TCE 6-8 ppm/K; however, higher TCE materials are more appropriate in some cases. In contrast to the commercially used glass-based substrates, we managed to sinter the ceramics at the LTCC conditions with small additions of borates. Regarding the dielectric properties, the developed materials exceed those values of the commercially used materials.

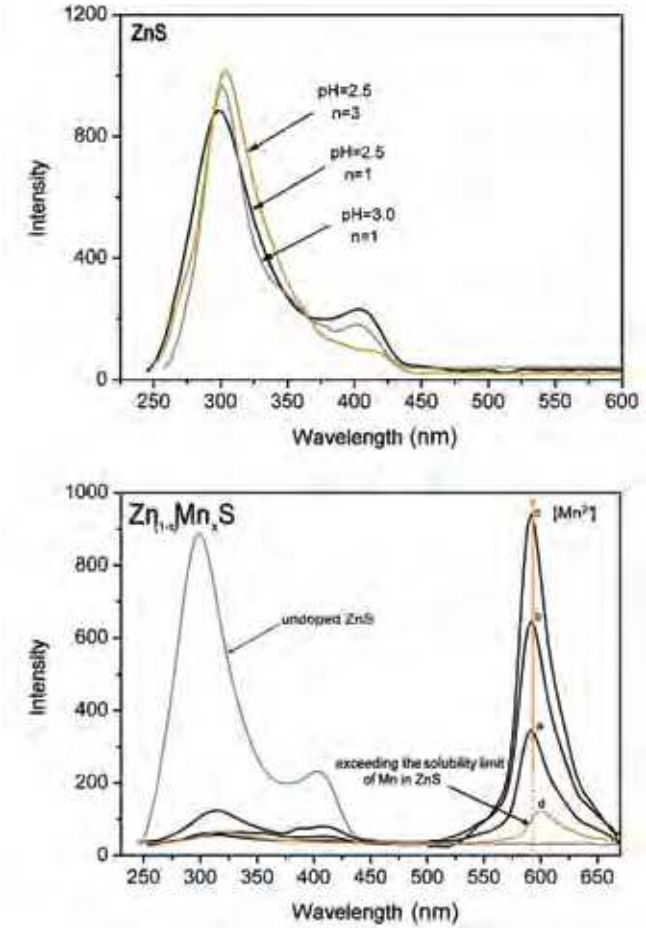

Figure 2: Photoluminiscence (PL) spectra of ZnS nanoparticles synthesized with n=1 and n=3 reaction cycles in $(PAH/PAA)_{2.5}$ polyelectrolyte multilayers assembled at a pH value of 2.5 and at a pH of 3.0 and the PL spectra of undoped and Mn-doped ZnS nanoparticles in a polyion matrix assembled at a pH value of 2.5, n=1, exposed to the various concentrations of Mn solution (a) 0.001M, (b) 0.0015M, (c) 0.002 and (d) 0.003M.

Research of nanostructured materials and nanocomposites

Research of nanomaterials has been focused on investigations of low-dimensional titanate nanostructures, the synthesis of nanopowders of the relaxor perovskite $Na_{0.5}Bi_{0.5}TiO_3$ and high-surface-area nanopowders of TiO_2.

Hydrothermally synthesized layered titanate-based nanotubes (din = 4–5 nm, dout = 8–10 nm, L = 100 nm – several 100 nm) were introduced in further hydrothermal reactions as a template material for the preparation of nanotubes with modified properties (i.e., photocatlytic activity) and as a precursor for the synthesis of the nanostructured perovskite $CaTiO_3$. The hydrothermal intercalation of calcium into the structure of the precursor at 100°C for 5 days led to the formation of nanotubes with the maximum amount of incorporated calcium. The Ca^{2+}-exchanged nanotubes inherited the dimensions of the precursor and exhibited improved photocatalytic activity as compared to the template nanotubes. The hydrothermal treatment of the precursor in the presence of a source of calcium at 150°C yielded the formation of clusters of nanosized crystals of orthorhombic $CaTiO_3$. The crystals were 100–300 nm wide and 500–800 nm long. The crystals grow in the [010] direction and have edges curled perpendicular to the growth direction, which suggests the influence of the precursor's morphology on the formation of nanosized $CaTiO_3$ crystals.

The hydrothermal method was employed for the preparation of nanosized $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) particles, suitable for further thin-film fabrication. Under the hydrothermal conditions of the selected precursors several different solid phases can form, besides NBT, 1-D sodium titanate and bismuth titanate phases of various stoichiometry. Therefore, the focus of our study was the correlation between the chemical-thermodynamic parameters applied in the synthesis and the phase composition and morphology of the obtained powders. Furthermore, we introduced organic surface-active agents and polymers into the hydrothermal reactions, in order to control the particle size. Polymers and surfactants can be used to facilitate the dispersion of inorganic particles in a given solvent; in addition, they may also control the process of nucleation and inhibit the crystal growth through adsorption on the growing facets. Best results were obtained by the employment of an SDS surfactant (sodium dodecyl sulfate) combined with polymer PVP (polyvinyl pyrrolidone). With this surfactant/polymer-assisted synthesis we obtained NBT particles of small size (~50 nm) and a narrow size distribution.

We developed a synthesis process that enables control of the size and consequently the optical properties of semiconducting ZnS nanoparticles within a polyelectrolyte matrix.

With the combination of sol-gel and solvothermal synthesis we prepared anatase powders with a high crystallinity and a high specific surface area (up to 335 m^2/g). We established the influence of triblock copolymere P123 as a TiO_2 framework template and phosphorous as a framework stabilizer on crystallinity and the specific surface area of un-annealed and annealed (500–1000°C) anatase powders. We can conclude that by the use of triblock copolymer P123 and phosphorous it is possible to prepare anatase powders with a high crystallinity and a high specific surface area (296 m^2/g) that remains high even after annealing at higher temperatures (500°C, 176 m^2/g). By analyzing samples prepared with and without phosphorous we can presume that the incorporation of the phosphorous into the TiO_2 framework increases the thermal stability of the anatase.

We also synthesized Ca and Ca-Mg carbonate particles in different polyols, where carbonate particles with various morphologies and different crystal structures were formed, depending on the reaction parameters.

It seems that the aragonite particles synthesized in ethylene glycol grow in accordance with an aggregation mechanism and they appear in a sheaf-like shape. However, the calcite particles synthesized in di- and tetraethylene glycol appear in a cube-like and a scalenoeder-like shape.

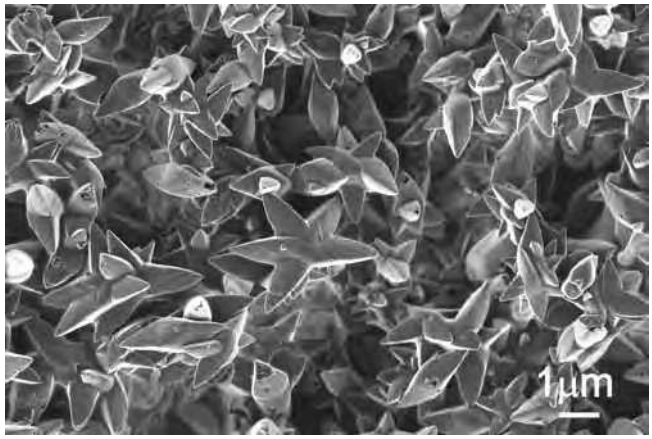

Figure 3: Scalenoeder-shaped calcite particles precipitated from a $CaCl_2$ solution in tetraethylene glycol at 140 °C

In the scope of the research on nanocomposites we synthesized inorganic-organic nanocomposite thin films of ZnS and Mn-doped ZnS. The organic matrix in the form of polyelectrolyte multilayers (PEMs) was fabricated using the layer-by-layer (LbL) self-assembly of weak polyion of polyacryllic acid (PAA) and polyallylamine (PAH) due to the electrostatic interactions between appositively charged polyion chains. The conformational arrangement of the polyion chains induced by a variation in the assembly pH is the key parameter that affects the structural and morphological characteristics of ZnS nanocrystallites. The morphology of the ZnS nanoparticles suggests that the as-formed ZnS clusters are constructed of more primary building particles of different orientations. In order to reduce the high surface energy the primary particles, which are 2–3 nm in diameter, tend to assemble into larger clusters by a random-aggregation mechanism. Within the clusters, primary ZnS particles aggregated in a random manner underwent a subsequent recrystallisation process, resulting in single-crystalline particles. By cycling the absorption-precipitation reaction process, further growth of the initially formed particles by the Ostwald ripening mechanism resulted in an increase in the volume density of ZnS nanoparticles within the polyion matrix. With the ability to obtain control over the size, the size distribution and the density of the surface states on the ZnS nanoparticles, attributed to the surface passivation of the ZnS nanoparticles by the polyion matrix, the tunability of the optical absorption and emission properties of the inorganic/organic nanostructured composite films can be obtained. The surface passivation of the ZnS nanocrystallites within the polyion matrix enables the enhanced radiative emission of ZnS composite films in the UV range, whereas by doping the ZnS nanocrystallites show emission characteristics of the manganese ions in the visible region.

Some outstanding publications in 2009

1. Jana Bezjak, Aleksander Rečnik, Boštjan Jančar, Philippe Boullay, Ivana Radosavljević Evans, Danilo Suvorov, "High-temperature transmission electron microscopy and X-ray powder diffraction studies of polymorphic phase transitions in $Ba_4Nb_2O_9$", J. Am. Ceram. Soc., Vol. 92, No. 8, pp. 1806-1812, 2009.
2. Jakob König, Matjaž Spreitzer, Boštjan Jančar, Danilo Suvorov, Zoran Samardžija, Arkadije Popović, "The thermal decomposition of $K_{(0.5)}Bi_{(0.5)}TiO_3$ ceramics", J. Eur. Ceram. Soc., Vol. 29, No. 9, pp. 1695-1701, 2009.

3. Špela Kunej, Srečo D. Škapin, Danilo Suvorov, "Phase relations in the pyrochlore-rich part of the Bi_2O_3-TiO_2-Nd_2O_3 system", J. Am. Ceram. Soc., Vol. 92, No. 10, pp. 2373-2377, 2009.
4. Manca Logar, Boštjan Jančar, Aleksander Rečnik, Danilo Suvorov, "Controlled synthesis of pure and doped ZnS nanoparticles in weak polyion assemblies : growth characteristics and fluorescence properties", Nanotechnology (Bristol), Vol. 20, No. 27, pp. 275601-1-275601-11, 2009.
5. Ni Qin, Marjeta Maček, Anton Meden, Danilo Suvorov, "Structural investigation of $K_xBa_{(1-x)}Ga_{(2-x)}Ge_{(2+x)}O_8$ solid solutions using the X-ray Rietveld method", J. Solid State Chem., Vol. 182, No. 7, pp. 1666-1672, 2009.

Awards and appointments

1. Ines Bračko, Urban Došler, Mojca Otoničar, Tina Šetinc, Asja Veber, Vojka Žunič: Award for efficient presentation of research achievements, Ljubljana, Jožef Stefan International Postgraduate School, Presentation of young researchers of Advanced Materials Department

Organization of conferences, congress and meetings

1. 3rd Slovenia- Korea Workshop on Advanced Materials, Ljubljana, Slovenia, 11–14 May 2009.
2. Materials Science & Technology 2009 Conference and Exhibition, International Symposium on Dielectric Materials and Electronic Devices, Pittsburgh, USA, 25– 29 October 2009 (co-organizers).

INTERNATIONAL PROJECTS

1. Development of Wear Resistant Coatings based on Complex Metallic Alloys for Functional Applications
   appliCMA
   7. FP, 214407
   EC; Susanne Fuchs, Austrian Research Centers GmbH - ARC, Functional Materials, Seibersdorf, Austria
   Dr. Srečo D. Škapin, Dr. Miha Čekada, Prof. Janez Dolinšek, Dr. Kristoffer Krnel
2. Controlled Production of High Tech Multifunctional Products and their Recycling
   SAPHIR, 6. FP
   NMP2-CT-2006-026666
   EC; Laurence Demoor, Christophe Goepfert, Compagne Industrielle des Lasers Cilas SA, Orleans, France
   Prof. Danilo Suvorov
3. Functional Nanostructured Ceramic Materials
   BI-AR/09-11-001
   Prof. Noemí Elisabeth Walsöe de Reca, CINSO (Centro de Investigaciones en Sólidos), CITEFA-CONICET, Buenos Aires, Argentine
   Prof. Danilo Suvorov
4. High K Dielectrics for Mobile Phone Base Stations
   Agreement IJS/EPCOS
   Dr. Christian Hoffmann, Pavol Dudesek, EPCOS OHG Ceramic Components Division, Deutschlandsberg, Austria
   Prof. Danilo Suvorov
5. LTCC Materials for High Frequency Applications
   Agreement IJS/EPCOS
   Pavol Dudesek, EPCOS OHG Ceramic Components Division, Deutschlandsberg, Austria
   Prof. Danilo Suvorov
6. Relaxor-based Tunable Materials
   T080038
   Dr. Christian Hoffmann, Dr. Andrea Testino, EPCOS OHG Ceramic Components Division, Deutschlandsberg, Austria
   Prof. Danilo Suvorov, Dr. Boštjan Jančar
7. LTCC Materials for High Frequency Applications
   T080033
   Pavol Dudesek, EPCOS OHG Ceramic Components Division, Deutschlandsberg, Austria
   Prof. Danilo Suvorov, Dr. Marjeta Maček Kržmanc
8. Biomimetic Preparation of Inorganic Nanomaterials
   BI-HR/09-10-037
   Dr. Ivan Sondi, Ruđer Bošković Institute, Zavod za raziskovanje morja in okolja, Zagreb, Croatia
   Dr. Srečo Davor Škapin
9. Ultra-low Dielectric Constant LTCC Material
   BI-CN/09-11-013
   Dr. Xing Hu, South China University of Technology, Guangzhou, China
   Dr. Srečo Davor Skapin
10. Synthesis of Piezoelectric Thin Films and Magnetoelectic Composites by a Layer-by-layer Self Assembly
    BI-KR/09-11-001
    Dr. Jae-Ho Jeon, Korea Institute of Materials Science, Changwon, Korea
    Prof. Danilo Suvorov
11. Designing of Functional Materials on Molecular and Nano Level
    Dizajniranje funkcionalnih materiala na molekularnom i nano nivou
    BI-RS/08-09-027
    Prof. Dragan Uskoković, Institut tehničkih nauka Srpske akademije nauka i umetnosti, Belgrade, Serbia
    Prof. Danilo Suvorov
12. Electric-field Tunable Ferroelectric Materials Based on $Na_{0,5}Bi_{0,5}TiO_3$
    BI-UA/09-10-007
    Prof. Anatolii Belous, SPE "Oxid" of V.I. Vernadskii Institute of General & Inorganic Chemistry NAS of Ukraine - Solid State Chemistry Department, Kiev, Ukraine
    Prof. Danilo Suvorov
13. Materials World Network: Improved Lanthanide-based Filters for Mobile Telekommunications
    BI-US/08-10-005
    Prof. Rick Ubic, Boise State University, Boise, Idaho, USA
    Prof. Danilo Suvorov

R & D GRANTS AND CONTRACTS

1. Self-cleaning antibacterial fotocatalitic coatings in whitewear production
   Prof. Danilo Suvorov
2. Functionalization of the surface of organic pigments for durable, efficient and colour-stable paints
   Dr. Srečo Davor Škapin
3. Physics and chemistry of porous aluminium for Al panels, capable of highly efficient energy absorbtion
   Prof. Danilo Suvorov
4. Multifunctional composites based on Al-Mg-Ti intermetallic compounds, reinforced with ceramic particles
   Dr. Srečo Davor Škapin

RESEARCH PROGRAM

1. Contemporary inorganic materials and nanotechnologies
   Prof. Danilo Suvorov

NEW CONTRACT

1. Co-financing L2-2185: Self-cleaning antibacterial fotocatalitic coatings in whitewear production
   Gorenje Household Appliances, d. d.
   Prof. Danilo Suvorov

VISITORS FROM ABROAD

1. Prof. Taras Kolodiazhnyi, National Institute for Materials Science, Tskukuba, Japan, 17 February 2009.
2. Dr. Ivan Sondi, Ruđer Bošković Institute, Zagreb, Croatia, 19 February 2009
3. Prof. Dragan Uskoković, Institute of Technical Sciences of SASA, Belgrade, Serbia, 22-26 April 2009.
4. Dr. Christian Hoffmann, EPCOS OHG, Deutschlandsberg, Austria, 22 April 2009.
5. Prof. K. Byrappa, University of Mysore, Mysore, India, 30 May to 3 June 2009.
6. Dr. Noemi Elisabeth Walsöe de Recca, Centro de Investigaciones en Solidos, CITEFA-CONICET, Buenos Aires, Argentina, 30 June to 22 July 2009.
7. Prof. Masahiro Yoshimura, Tokyo Institute of Technology, Yokohama, Japan, 23-26 August 2009.
8. Aleksander Babak B. Sc., NPP "Tomilinsky elektronny zavod", Tomilin, Russia, 21 August 2009.
9. Anton Konda B. Sc., Keko oprema, Žužemberk, Slovenia, 21 August 2009.
10. Dr. Christian Hoffmann, EPCOS OHG, Deutschlandsberg, Austria, 4 September 2009.
11. Dr. Pavol Dudešek, EPCOS OHG, Deutschlandsberg, Austria, 4 September 2009.
12. Dr. Hyo-Tae Kim, Korea Institute of Ceramic Engineering and Technology, Seoul, Korea, 22-24 October 2009.
13. Dr. Kyung Hoe Kim, Korea Institute of Ceramic Engineering and Technology, Seoul, Korea, 22-24 October 2009.
14. Dr. Yukio Sakabe, Murata, Kyoto, Japan, 11-18 October 2009.
15. Silva Gabriella Nobre Meneah, University of Sao Paolo, Sao Paolo, Brazil, 18-25 November 2009.
16. Monyse Nobre Meneah, University of Sao Paolo, Sao Paolo, Brazil, 18-25 November 2009.
17. Prof. Anatolii Belous, V. I. Vernadsky Institute of General and Inorganic Chemistry, Kiev, Ukraine, 10-15 November 2009.
18. Dr. Oleg Ovchar, V. I. Vernadsky Institute of General and Inorganic Chemistry, Kiev, Ukraine, 10- 29 November 2009.

Visiting researchers:

1. Marija Vukomanović, M.Sc., Institute of Technical Sciences of SASA, Belgrade, Serbia, 4 May 2009 to 31 December 2009.
2. Dr. Jyoti Prosad Guha, University of Rolla, Rolla, USA, 27 May to 31 August 2009.
3. Dr. Smilja Marković, Institute of Technical Sciences of SASA, Belgrade, Serbia, 2 November to 18 December 2009.

STAFF

Researchers
1. Asst. Prof. Boštjan Jančar
2. Dr. Marjeta Maček Kržmanc
3. **Prof. Danilo Suvorov, Head**
4. Dr. Srečo Davor Škapin

Postdoctoral associates
5. Dr. Jakob König
6. Dr. Uroš Kunaver*
7. Dr. Špela Kunej
8. Dr. Manca Logar
9. Dr. Matjaž Spreitzer
10. Dr. Marko Udovič*

Postgraduates
11. Ines Bračko, B. Sc.
12. Urban Došler, B. Sc.
13. Mojca Otoničar, B. Sc.
14. Tina Šetinc, B. Sc.
15. Asja Veber, B. Sc.
16. Vojka Žunič, B. Sc.
17. Dr. Jana Bezjak**

Technical and administrative staff
18. Maja Šimaga Saje, M. Sc.
19. Silvo Zupančič

Note:
* part-time JSI member
** young researcher financed by industry

BIBLIOGRAPHY

ORIGINAL ARTICLES

1. Anatolii Belous, Boštjan Jančar, Matjaž Spreitzer, (7 authors), "The effect of chemical composition on the structure and dielectric properties of the columbites $A^{2+}Nb_2O_6$", *J. Electrochem. Soc.*, vol. 156, no. 12, pp. G206-G212, 2009.
2. Anatolii Belous, et al. (10 authors), "Low-loss perovskite niobates $Ba(M^{2+}_{1/3}Nb_{2/3})O_3$: composition, structure, and microwave dielectric properties", In: *MMA 2008, The 5th International Conference on Microwave Materials and Their Applications, November 1-4, 2008, Hangzhou, China*, (Ferroelectrics, vol. 376, no. 1, 2009), New York, Gordon and Breach, 2009, vol. 387, no. 1, pp. 36-45, 2009.
3. Jana Bezjak, Boštjan Jančar, Philippe Boullay, Aleksander Rečnik, Danilo Suvorov, "Hexagonal perovskite-type phases in the BaO-rich part of the $BaO – WO_3 – Nb_2O_5$ system", *J. Am. Ceram. Soc.*, issue 12, vol. 92, pp. 3022-3032, 2009.
4. Jana Bezjak, Aleksander Rečnik, Boštjan Jančar, Philippe Boullay, Ivana Radosavljević Evans, Danilo Suvorov, "High-temperature transmission electron microscopy and X-ray powder diffraction studies of polymorphic phase transitions in $Ba_4Nb_2O_9$", *J. Am. Ceram. Soc.*, vol. 92, no. 8, pp. 1806-1812, 2009.
5. Xing Hu, Srečo D. Škapin, Danilo Suvorov, "Subsolidus phase relations in the $Bi_4Ti_3O_{12} – Ag/Ag_2O – TiO_2$ system", *J. Ceram. Soc. Jpn. (Print)*, vol. 117, no. 1364, pp. 494-498, 2009.
6. Marta Kasunič, Anton Meden, Srečo D. Škapin, Danilo Suvorov, Amalija Golobič, "Order-disorder of oxygen anions and vacancies in solid solutions of La_2TiO_5 and $La_4Ga_2O_9$", *Acta crystallogr., B Struct. sci.*, vol. B65, no. 5, pp. 558-566, 2009.
7. Varužan Kevorkijan, Srečo D. Škapin, "Fabrication and characterisation of Mg-B_4C composites", *Metalurgija*, vol. 15, br. 1, pp. 3-18, 2009.
8. Varužan Kevorkijan, Srečo D. Škapin, "Fabrication and characterization of TiAl/Ti_3Al-based intermetallic composites (IMCS) reinforced with ceramic particles", *Metalurgija*, vol. 15, br. 2, pp. 75-89, 2009.
9. Varužan Kevorkijan, Srečo D. Škapin, "Mg/B_4C composites with a high volume fraction of fine ceramic reinforcement", *Mater. manuf. process.*, vol. 24, iss. 12, pp. 1337-1340, Dec. 2009.
10. Varužan Kevorkijan, Srečo D. Škapin, "Preparation and testing of prototype $Mg_2Si – Mg – TiC$ and $Mg_2Si – TiC/TiB_2$ composites", *Mater. tehnol.*, vol. 43, no. 6, pp. 309-313, 2009.
11. Varužan Kevorkijan, Srečo D. Škapin, "Pressureless reactive sintering of TiAl-TiC and Ti3Al-TiC composites", *Mater. tehnol.*, vol. 43, no. 5, pp. 239-244, 2009.
12. Varužan Kevorkijan, Srečo D. Škapin, "Pressureless sintering and characterization of B_4C, TiC and TiB_2-particle-reinforced $TiAl_3$ matrix composites_", *Mater. tehnol.*, vol. 43, no. 3, pp. 123-128, 2009.
13. Jakob Koenig, Matjaž Spreitzer, Boštjan Jančar, Danilo Suvorov, Zoran Samardžija, Arkadije Popović, "The thermal decomposition of $K_{0.5}Bi_{0.5}TiO_3$ ceramics", *J. Eur. Ceram. Soc.*, pp. 1695-1701, 2009.
14. T. Kolodiazhny, Giuseppe Annino, Matjaž Spreitzer, T. Taniguchi, Robert Freer, F. Azough, A. Panariello, W. Fitzpatrick, "Development of $Al_2O_3 – TiO_2$ composite ceramics for high-power millimeter-wave applications", *Acta mater.*, vol. 57, no. 11, pp. 3402-3409, 2009.
15. Špela Kunej, Danilo Suvorov, "Dielectric properties of the $Bi_{(1.6-0.8x)}Y_xTi_2O_{(6.4+0.3x)}$ ($0.03 < x < 2$) pyrochlore solid solution", *J. Am. Ceram. Soc.*, vol. 92, no. 4, pp. 959-961, 2009.
16. Špela Kunej, Srečo D. Škapin, Danilo Suvorov, "Phase relations in the pyrochlore-rich part of the $Bi_2O_3 – TiO_2 – Nd_2O_3$ system", *J. Am. Ceram. Soc.*, vol. 92, no. 10, pp. 2373-2377, 2009.
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properties", *Nanotechnology (Bristol)*, vol. 20, no. 27, pp. 275601-1-275601-11, 2009.

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