Faculty of Technology
University of Novi Sad

Conference for Young Scientists in Ceramics

10th Students' Meeting
and
3rd ESR COST MP0904 Workshop

Book of Abstracts

SM 2013
COST SIMUFER

Novi Sad, Serbia, November 6-9, 2013

Conference for Young Scientists in Ceramics

CONFERENCE for YOUNG SCIENTISTS in CERAMICS

The Tenth Students' Meeting, SM-2013
The Third ESR Workshop, COST MP0904

PROGRAMME
and
BOOK OF ABSTRACTS

November 6-9, 2013
Novi Sad, Serbia

Programme and Book of Abstracts of The Conference for Young Scientists in Ceramics (The Tenth Students' Meeting - SM-2013, and The Third ESR Workshop, COST MP0904) publishes abstracts from the field of ceramics, which are presented at traditional international Conference for Young Scientists in Ceramics.

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Preface

The Conference for Young Scientists in Ceramics is organized by the Department of Materials Engineering, Faculty of Technology, University of Novi Sad, Serbia (November 6-9, 2013). This year it consists of two events - The Tenth Students' Meeting, SM-2013, "Processing and Application of Ceramics" and The Third Early Stage Researchers Workshop of the COST Action MP0904 "Single- and multiphase ferroics and multiferroics with restricted geometries".

The first Students' Meeting was held in 1998 as a national meeting for Serbian PhD students and this year tenth meeting will be the seventh international in a row. For several years now, the Meeting has a well earned reputation as an excellent opportunity for the promotion of the work in the field of ceramics done by early stage researchers, being MSc and PhD students or young doctors. Additionally, the young scientists will be in the position to attend sessions covering major general topics of broad interest which will be presented by experienced scientists through the invited lectures. In that way, young researchers will have a chance to participate in the active discussions with their senior colleagues who are all well known scientists in their area of expertise. We strongly hope that the overall activities during this event will create for the young researchers a fruitful platform for finding new topics, ideas and approaches for their scientific research and an excellent opportunity for establishing connections and finding proposals for collaborations.

General idea behind the Conference was and will continue to be the building of the closely intertwined European scientific network by offering the platform for young scientists to meet, discuss and exchange ideas in the ever growing field of ceramics. It is our deepest belief that this approach will be beneficial for both young researchers and the European science as a whole. Therefore, we strongly appreciate that the European Ceramic Society identified the efforts and the enthusiasm we have put into this idea of creating the bridge between young researchers and we truly hope that the European Ceramic Society will support this initiative in the future. Special thanks to the JECS Trust Fund and COST MP0904 for strong financial support of the Meeting. The Conference was also recognized by the Serbian Ministry of education, science and technological development as well as by the Provincial Secretary of science and technological development and we would like to thank them for their endorsement too.

A total number of 122 presentations given by young researchers and 1 plenary lecture and 14 invited talks coming from 26 countries with multidisciplinary profiles will be presented during the conference. It should be emphasised that presented topics cover research subjects of the highest scientific interest: experimental, theoretical and applicative aspects of synthesis, processing, advanced nano/microscale and functional characterisation of various types of structures and ceramic materials.

We wish to express our thanks to the members of the local organizing committee in Novi Sad for their effort and time during preparation of the Meeting, and especially to thank our endorsers and sponsors for making this event possible.

Editors

LIST OF SPONSORS

The European Ceramic Society

The JECS Trust Fund

COST MP0904, SIMUFER

Ministry of Education and Science,
Republic of Serbia

Provincial Secretariat for Science and
Technological Development

LIST OF ENDORSERS

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University of Novi Sad

Tourist organization of Vojvodina

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WEDNESDAY, NOVEMBER 6, 2013.

09.00 – 11.00 h – Registration (Conference desk)

11.00 – 11.30 h – Oppening (Amphitheater)

11.30 – 12.15 h – IM1 Invited lecture (Amphitheater)
Paula Maria Vilarinho, Portugal, Unveiling the relationships between piezoelectrics and the human body

12.15 – 13.30 h – Welcome Party (Ceremonial Hall)

13.30 – 15.15 h – Section 1

Synthesis of ceramic powders - 1 (Blue Hall)

13.30 – 13.45 h	**A1 – S. Lorenz, et al,, Germany** Antimony doping of zinc oxide – Where is the dopant located?
13.45 – 14.00 h	**A2 – A. Kocjan, et al., Slovenia** From AlN to high surface area aluminium (hydrous)oxide powders
14.00 – 14.15 h	**A3 – N. Tasić, et al., Serbia** Hydrothermally assisted sol-gel synthesis of nano-anatase TiO_2 for application in dye-sensitized solar cells
14.15 – 14.30 h	**A4 – P. Fazakas, et al., Hungary** Synthesis of TiB_2 nanosized powder in radiofrequency thermal plasma
14.30 – 14.45 h	**A5 – S. Ilić et al., Serbia** Preparation of mullite and Fe-doped mullite powder precursors by sol-gel combustion process
14.45 – 15.00 h	**A6 – A. Kusior, et al., Poland** Less common nanostructures - TiO_2 nanoflowers
15.00 – 15.15 h	**A7 – M.I. Bozdog, et al., Romania** Study of the formation of $(ZnCo)Fe_2O_4$ system using two low temperature synthesis methods

Ceramic processing - 1 (Class Room, R10)

13.30 – 13.45 h	**C1 – M. Karpe, et al., Latvia** Synthesis of nanoporous TiO_2-ZrO_2-SiO_2 ceramics using sol-gel technology
13.45 – 14.00 h	**A8 – B. Wójtowicz, et al., Poland** Influence of HPMC addition on hydrothermal crystallization of zirconium oxide
14.00 – 14.15 h	**C2 – K. Jach, et al., Poland** New application of ceramic foams for composites preparation
14.15 – 14.30 h	**C3 – A. Marzec, et al., Poland** Pro-ecological methods of synthesis of the metallic nanoparticles for composite applications
14.30 – 14.45 h	**C4 – A. Miazga, et al., Poland** Ceramic matrix composites with gradient concentration of metal particle obtained through gelcasting
14.45 – 15.00 h	**A9 – J. Roleček, et al., Czech Republic** Design of nuclear ceramic materials with enhanced thermal conductivity
15.00 – 15.15 h	**C10 – A. Egesz, et al., Hungary** Qualification and investigation of ceramic injection molding raw materials

15.15 – 16.00 h – IA1 Invited lecture (Amphitheater)

Ákos Kukovecz, Hungary, Sol-gel derived porous nanocomposite materials

16.00 – 16.15 h – Coffe Break

16.15 – 17.00 h – IA2 Invited lecture (Amphitheater)

Carmen Baudin, Spain, Toughness of Al_2O_3/SiC nanocomposites

17.00 – 18.45 h – Section 2

Ionic conductors - 1 (Blue Hall)

17.00 – 17.15 h	**IA11 M. Botros, et al., Germany** LLZO solid electrolyte for lithium ion batteries
17.15 – 17.30 h	**A12 – O. Tokariev, et al., Germany** Study of storage materials for high-temperature rechargeable oxide batteries (ROB)
17.30 – 17.45 h	**A13 – C. Loho, et al., Germany** Laser-assisted chemical vapor deposition of multinary oxides for thin-film battery application
17.45 – 18.00 h	**A14 – M. Prekajski, et al., Serbia**

Thermal stability and electrical properties of $Ce_{1-x}Bi_xO_{2-\delta}$ (x = 0.1– 0.5) solid solution

18.00 – 18.15 h **A15 – P. Gdaniec, et al., Poland**
YSZ thin films for solid oxide fuel cells deposited using spray pyrolysis

18.15 – 18.30 h **A16** – **T. Miruszewski, et al., Poland**
The ionic conductivity of polycrystalline donor and acceptor doped perovskite ceramics measured by limiting current technique

18.30 – 18.45 h **A17** – **M. Lapinski, et al., Poland**
Structure investigations of lithium titanate spinel oxide ceramics prepared by sol-gel method

Ceramic processing - 2 (Class Room, R10)

17.00 – 17.15 h **A18** – **A. Szudarska, et al., Poland**
The influence of glycerol monoacrylate on rheological properties of ceramic suspensions

17.15 – 17.30 h **A19** – **A. Wnuk, et al., Poland**
Morphology and composition of self-organized titanium dioxide nanotubes formed in ethylene glycol based solution

17.30 – 17.45 h **A20** – **V.M. Candelario, et al., Spain**
Carbon nanotubes prevent the coagulation at high shear rates of aqueous suspensions of equiaxed ceramic nanoparticles

17.45 – 18.00 h **A21 – A. Labuz, et al., Poland**
Preparation conditions and densification behaviour of calcium oxide stabilized zirconia nanopowder

Optics - 1 (Class Room, R10)

18.00 – 18.15 h **A22** – **B. Buchholcz, et al., Hungary**
Photocatalytic activity of the different stoichiometry antimony-oxychloride decorated titanate nanotubes

18.15 – 18.30 h **A23** – **A. Kompch, et al., Germany**
Synthesis and dispersion of lanthanide doped Gd_2O_3 nanoparticles and their optical characterization

18.30 – 18.45 h **A24** – **A. Sidorowicz, et al., Poland**
Influence of thulium oxide powder morphology on properties of transparent Tm:YAG ceramics

THURSDAY, NOVEMBER 7, 2013.

09.00 – 10.30 h – Section 3

Electroceramics - 1 (Blue Hall)

09.00 – 09.15 h	**A25 – Đ. Tripković, et al., Serbia** Characterization of $BaTiO_3$ films fabricated by ink-jet printing process
09.15 – 09.30 h	**C5 – O. Hanzel, et al., Slovakia** Electrically conductive Alumina-MWCNT composites
09.30 – 09.45 h	**A26 – B. Fraygola, et al., Brazil** Electric control of magnetic phase and colossal magnetoelectric effect in $Pb(Fe,W,Ti)O_3$ based multiferroics ceramics
09.45 – 10.00 h	**A27 – R.E. Stanculescu, et al., Romania** Investigation of the role of porosity on the functional properties of $Ba_{1-x}Sr_xTiO_3$ ceramics produced by using graphite forming agent
10.00 – 10.15 h	**A28 – G. Cadafalch Gazguez, et al., The Netherlands** Ceramic nanostructures: The electrospinning advantage
10.15 – 10.30 h	**A29 – A. Benes, et al., Germany** Ultrathin highly proton(-conducting) oxides for water electrolysis at Intermediate temperatures

Optics - 2 (Class Room, R10)

09.00 – 09.15 h	**A30 – A. Wajlerá, et al., Poland** Freeze granulation for fabrication of transparent yttrium aluminate ceramics
09.15 – 09.30 h	**A31 – Z. Dudas, et al., Hungary/Romania** Rare-earth co-dopant effect upon the structure of sol-gel derived inorganic luminophores
09.30 – 09.45 h	**C6 – V. Havasi, Hungary** Synthesis and characterization of strontium-aluminate phosphors and CdSe quantum dot based composites
09.45 – 10.00 h	**A32 – E. Đurđić, et al., Serbia** Raman spectra of $BaTiO_3/NiFe_2O_4$ multilayer thin films

Sintering (Class Room, R10)

10.00 – 10.15 h	**A33 – E. Horváth, et al., Switzerland** Pressureless sintering of titanate nanowires: Surface vs. bulk diffusion
10.15 – 10.30 h	**C7 – V. Pouchly, et al., Czech Republic** Kinetic study of sintering behavior of layered ceramic composites

10.30 - 10.45 h – Coffe Break

10.45 – 11.45 h – Section 4

Structural Ceramics - 1 (Blue Hall)

10.45 – 11.00 h	**C8 – C. Krautgasser et al., Austria** Mechanical strength degradation of glass-ceramic composites for microelectronic devices
11.00 – 11.15 h	**A34 – A. Samodurova, et al., Slovenia** The effect of silica sol infiltration on the low temperature degradation and mechanical properties of 3Y-TZP ceramics
11.15 – 11.30 h	**C9 – R. Bystricky, et al., Slovakia** Model experiments in GPS and thermodynamical analysis of Si_3N_4-Y_2O_3-SiO_2-C system
11.30 – 11.45 h	**C10 – E. Bódis, et al., Hungary** Graphene reinforced SiC ceramics sintered by spark plasma sintering

Electroceramics - 2 (Class Room, R10)

10.45 – 11.00 h	**A35 – M. Brychevsky, et al., Ukraine** EB-PVD 1Ce10ScSZ films for SOFC application
11.00 – 11.15 h	**A36 – A. Benel, et al., Germany** Nanoparticulate-based $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ cathodes for micro-solid oxide fuel cell applications
11.15 – 11.30 h	**A37 – A. Mielewczyk-Gryń, et al., Poland** Properties of perovskite structure doped stannates
11.30 – 11.45 h	**C11 – A. Lazar, et al., Slovenia** Synthesis and characterization of electrically conductive zirconia based composites

11.45 – 12.30 h – PL Plenary lecture (Amphitheater)

Horst Hahn, Germany, From tunable properties of nanostructures to printed device

12.30 – 13.15 h – IM2 Invited lecture (Amphitheater)

Liliana Mitoseriu, Romania, Organic-inorganic combinations of materilas for flexible electronics: from material design to applications

13.15 – 14.35 h – Lunch (Ceremonial Hall)

14.35 – 14.45 h – Oppening COST ESR Workshop (Amphitheater)

14.45 – 15.30 h – IM3 Invited lecture (Amphitheater)

Marlies van Bael, Ann Hardy, Belgium, Addressing challenges in the solution based deposition of oxide films

15.30 – 16.30 h – Section 5

Ferroelectrics, Multiferroics, Thermoelectrics - 1 (Blue Hall)

15.30 – 15.45 h	**M1 – C. Padurariu, Romania** Combining antiferroelectric-ferroelectric materials in composites in searching for new properties
15.45 – 16.00 h	**M2 – I. Bakaimi, et al., Greece** Magnetoelectric coupling in the 2D antiferromagnet: β-$NaMnO_2$
16.00 – 16.15 h	**M3 – C.G. Floare, et al., Romania** First-principles modelling of $SrTiO_3$ based oxides for thermoelectric applications
16.15 – 16.30 h	**M4 – J. Lesseur, et al., France** Using 3D-imaging by X-ray microtomography to characterise functional ceramics internal structure

Bioceramics - 1 (Class Room, R10)

15.30 – 15.45 h	**IA3 Invited lecture – T. Moritz, M. Ahlhelm, Germany** Network between Germany and states from the Danube region for cooperation in the field of ceramic bone replacing structures with increased mechanical properties by freeze casting (BONEFOAM)
15.45 – 16.00 h	**A38 – A. Putnins, et al., Latvia** Technology for creating porous calcium phosphate granules
16.00 – 16.15 h	**A39 – M. Lukić, et al., Serbia** Hydroxyapatite nanopowders: study of possibility for preparation of dense nanostructured bioceramics by pressureless sintering
16.15 – 16.30 h	**A40 – M. Domanická, et al., Slovakia** Preparation and characterization of porous silicon nitride for bioapplications

16.30 – 16.45 h – Coffe Break

16.45 – 17.30 h – IM4 Invited lecture (Amphitheater)

David Salamon, Czech Republic, Spark Plasma Sintering – how to design experiments

17.30 – 18.45 h – Section 6

Ferroelectrics, Multiferroics, Thermoelectrics - 2 (Blue Hall)

17.30 – 17.45 h	**M5 – L. Padurariu et al., Romania** Investigation of the role of porosity on the switching properties of Nb-PZT ceramics: Experiment and modeling
17.45 – 18.00 h	**M6 – A. Kassas, et al., France** Preparation and characterization of spherical TiO_2 micro-resonators by spray drying for THz application
18.00 – 18.15 h	**M7 – M. Plodinec, et al., Croatia** Phase transitions in Ba/Sr titanate and $BaTiO_3/TiO_2$ nanostructures studied by Raman spectroscopy
18.15 – 18.30 h	**M8** – **S. Kolev, et al., Bulgaria** Y-type hexaferrite $Ba_2Mg_2Fe_{12}O_{22}$ powders – obtaining and characteristics
18.30 – 18.45 h	**M9** – **N. Ilić, et al., Serbia** Autocombustion synthesis and caracterization of multiferroic bismuth ferrite ceramics

Bioceramics - 2 (Class Room, R10)

17.30 – 17.45 h	**C12 – M. Mirković, et al., Serbia** Structural modifications of bio-calcium phosphates
17.45 – 18.00 h	**A41** – **M. Sokolova, et al., Latvia** Scale-up and wet precipitation synthesis of β-tricalcium phosphate
18.00 – 18.15 h	**A42** – **D. Ivetić, et al., Serbia** Inorganic materials as supports for biomolecules: Immobilization of β-glucosidase onto mesoporous silica

Electroceramics - 3 (Class Room, R10)

18.15 – 18.30 h	**C13 – S. Simona-Luminita, et al., Romania** **Synthesis of Fe_2O_3/SiO_2 nanocomposites from Fe(III)-carboxylate precursors inside hybrid silica gels**
18.30 – 18.45 h	**A43** – **O.A. Kornienko, et al., Ukraine** Phase equilibria and properties of solid solutions in the system CeO_2-Eu_2O_3 at 1100-1500°C

20.00 h – Social Event

Restaurant “Fontana” *Meeting of Young Ceramist Network of the European Ceramic Society,* Invited talk “How to make excellent presentations and papers”

FRIDAY, NOVEMBER 8, 2013.

09.00 – 10.30 h – Section 7

Structural Ceramics - 2 (Blue Hall)

09.00 – 09.15 h	**C14 – E. Pawlikowska, Poland** Application of new ceramic-polymer composites for microwave electronic systems
09.15 – 09.30 h	**C15 – A. Dubeiel, et al., Poland** The influence of hBN addition on mechanical and elastic properties of Al_2O_3-TiN composite
09.30 – 09.45 h	**C16 – M. Vetrecin, et al., Slovakia** Machinable silicon nitride-based composites sintered with polymer derived ceramics as sintering additives
09.45 – 10.00 h	**C17 – I. Brodnikovska, et al., Ukraine** Relative density & dielectric response of AlN ceramics obtained with variation of modifying additives and sintering regime
10.00 – 10.15 h	**C18 – A. Sitnik et al., Poland** Alumina/zirconia composites with TiB_2, TiC inclusions and nanometric scale particles of nickel

Ferroelectrics, Multiferroics, Thermoelectrics - 3 (Blue Hall)

10.15 – 10.30 h	**M10 – L.E. Bibere, Romania** Viscoelastic behavior of new anionic clay – polymer hybrid materials

Ferroelectrics, Multiferroics, Thermoelectrics - 3 (Class Room, R10)

09.00 – 09.15 h	**M11 – M. Čebela, et al., Serbia** Characterization of $BiFeO_3$ nanopowder obtained by hydrothermal synthesis
09.15 – 09.30 h	**M12 – L. Kozielski, et al., Poland** Multiferroic PFN materials energy conversion characterization
09.30 – 09.45 h	**M13 – B. Mojić, et al., Serbia** Multiferroic Ba(Sr)TiO_3- $NiFe_2O_4$ composite ceramics from core-shell particles
09.45 – 10.00 h	**M14 – M. Pilch et al., Poland** Thermal treatment effects in $PbTiO_3$ crystals studied by XPS and electric conductivity tests
10.00 – 10.15 h	**M15 – M. Puscasu, et al., Romania** Self -assemblies of nanoparticles of Cr_2O_3-ZnTi LDHs and the derived mixed oxides as novel photocatalysts for phenol removal
10.15 – 10.30 h	**M16 – A. Dzunuzović, et al., Serbia** Synthesis and characterization of nickel zinc ferrites

10.30 – 10.45 h – Coffe Break

10.45 – 11.45 h – Section 8

Film deposition (Blue Hall)

10.45 – 11.00 h	**A44 – A. Escudeiro, et al., Portugal** Characterization of Zr co-sputtered DLC films
11.00 – 11.15 h	**C19 – A. Miletić, et al., Serbia** Characterization of nanostructured TiAlN/TiSiN coatings
11.15 – 11.30 h	**A45 – K. Leszczynska, et al., Poland** Attempts to deposit silicon-containing coatings on Ti-46Al-8(Ta/Nb) for hot corrosion protection
11.30 – 11.45 h	**A46 – N.K. Manninen, et al., Portugal** Silver segregation to surface in Ag-DLC thin films deposited by magnetron sputtering

Ferroelectrics, Multiferroics, Thermoelectrics - 4 (Class Room, R10)

10.45 – 11.00 h	**M17 – S. Balčiūnas, et al., Lithuania** Dielectric properties of nanograin BSPT caramics
11.00 – 11.15 h	**M18 – M. Balcerzak, et al., Poland** Dielectric response of $(Bi_{1-x}La_xFeO_3)_{0.5}(PbTiO_3)_{0.5}$ ceramics prepared from mechanically synthesized powders
11.15 – 11.30 h	**M19 – I.V. Ciuchi, et al., Romania** Temperature dependence of the main piezoelectric parameters in very soft, soft and hard piezoelectric ceramic disks
11.30 – 11.45 h	**M20 – Š. Svirskas, et al., Lithuania** Broadband dielectric spectroscopy of A-site substituted perovskite ceramics

11.45 – 12.30 h – IA4 Invited lecture (Amphitheater)

László Forró, Switzerland, TiO_2 nanowires: from basic science to applications

12.30 – 13.15 h – IA5 Invited lecture (Amphitheater)

Markus Winterer, Germany, Doping Nanoparticles - The Relevance of Local Structure

13.15 – 14.45 h – Lunch (Ceremonial Hall)

14.45 – 15.30 h – IA6 Invited lecture (Amphitheater)

Rodrigo Moreno, Spain, Colloidal processing of ceramics and composites

15.30 – 16.45 h – Section 9

Ferroelectrics, Multiferroics, Thermoelectrics - 5 (Blue Hall)

15.30 – 15.45 h	**M21 – A. Sakanas, et al., Lithuania** Characterization of the dielectric properties of barium titanate and nickel-zinc ferrite composite ceramics
15.45 – 16.00 h	**M22 – I. Rafalovskyi, et al., Czech Republic** IR and Raman studies of structural, magnetic and ferroelectric phase transitions in multiferroic $CaMn_7O_{12}$
16.00 – 16.15 h	**M23 – E. Palaimiene, et al., Lithuania** Dielectric properties of a new $Ba_{6-2x}Nd_{2x}Fe_{1+x}Nb_{9-x}O_{30}$ TTB system
16.15 – 16.30 h	**M24 – N. Pavlovic, et al., Belgium** Self-assembled $BaTiO_3$-$CoFe_2O_4$ and $BiFeO_3$-$CoFe_2O_4$ film composites: structural and magnetic studies
16.30 – 16.45 h	**M25 – D. Pérez-Mezcua, et al., Spain** Crystalline structure and compositional depth profile of solution derived lead-free $Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ (BNBT) thin films around the morphotropic phase boundary

Electroceramics - 4 (Class Room, R10)

15.30 – 15.45 h	**A47 – P. Galizia, et al., Italy** Thick dielectric films produced by electrophoretic deposition
15.45 – 16.00 h	**A48 – S. Pršić, et al., Serbia** Mechanochemically assisted solid-state synthesis of Cu substituted thermoelectric sodium cobaltite oxide
16.00 – 16.15 h	**A49 – A.C.M. Kuniyil, et al., Serbia** Synthesis and characterization of SnO_2 films
16.15 – 16.30 h	**A50 – G.V. Lisachuk, et al., Ukraine** Prospects for creation of radio absorbing ceramic materials
16.30 – 16.45 h	**A51 – M. Vuković, et al., Serbia** Low temperature sintering of high voltage ZnO varistor

16.45 – 17.00 h – Coffe Break

17.00 – 17.45 h – IM5 Invited lecture (Amphitheater)

Carmen Galassi, Italy, Processing and characterization of porous piezoelectric ceramic materials

17.45 – 18.45 h – Section 10

Catalysts (Blue Hall)

17.45 – 18.00 h	**A52 – V. Binas, Greece** The effect of copper on the performance of TiO_2 photocatalysts for the oxidation of dyes on ceramic coatings
18.00 – 18.15 h	**A53 – M. Bošnjak, et al., Serbia** Preparation, characterization and functional properties of CaO catalyst – influence of calcination temperature
18.15 – 18.30 h	**A54 – M. Efremova, et al., Russian Federation** The effect of magnetic field on the catalytic properties of chymotrypsin immobilized on magnetite nanoparticles
18.30 – 18.45 h	**A55** – **M.P. Nikolič, et al., Serbia** Synthesis and characterization of core/shell particles with different shell structures

Ionic Conductors - 2 (Class Room, R10)

17.45 – 18.00 h	**C20 – D. Brodnikovskyi, et al., Ukraine** Mechanical properties of porous (Ti-8.9 at % Si)-in situ composite material as a support substrate for SOFC application
18.00 – 18.15 h	**C21** – **S. Wachowski, et. al., Poland** Enhancing performance of Ni-$LaNbO_4$ cermet anode for protonic conductor fuel cell through CeO_2 infiltration

Glass-ceramics (Class Room, R10)

18.15 – 18.30 h	**C22 – A. Abdelghany, et al., Egypt** Preparation and characterization of some transparent nano-glass-ceramics from the system SrO-B_2O_3 together with SiO_2 and CaF_2 additives
18.30 – 18.45 h	**C23** – **J.D. Nikolić, et. al., Serbia** Synthesis of glass-ceramic in $Li_2O \cdot Al_2O_3 \cdot GeO_2 \cdot P_2O_5$ system

19.30 h – Social Event - Excursion

SATURDAY, NOVEMBER 9, 2013.

09.00 – 09.45 h – IM6 Invited lecture (Amphitheater)
Daniel I. Bilc, Philippe Ghosez, Romania/Belgium, First-principles accurate prediction of the electronic and structural properties of ferroelectric oxide bulks and nanostrustructures

09.45 – 10.30 h – IA7 Invited lecture (Amphitheater)
Goran Stojanovic, Serbia, Doping Nanoparticles - The Relevance of Local Structure

10.30 – 12.00 h – Section 11

Ferroelectrics, Multiferroics, Thermoelectrics - 6 (Blue Hall)

10.30 –10.45 h	**M26 – Š. Bagdzevičius, et al., Lithuania/Switzerland** PLD deposition and characterization of compressively-strained heteroepitaxial SrTiO$_3$ thin films
10.45 –11.00 h	**M27 – A. Faraz, et al., Irland** Temperature dependent local electromechanical investigations of atomic vapour deposition (AVD) grown Aurvillius phase Bi$_6$Ti$_3$Fe$_2$O$_{18}$ thin films
11.00 – 11.15 h	**M28 – A. Pérez-Rivero, et al., Spain** Improved properties of the lead free solid solution (Bi$_{0.5}$Na$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ prepared as multilayer composite thin films with BiFeO$_3$
11.15 – 11.30 h	**M29 – B. Bajac, et al., Serbia** Investigation of optimal processing parameters for multilayer BaTiO$_3$/NiFe$_2$O$_4$ thin films fabrication
10.30 – 11.45 h	**M30 – A. Neagu, et al., Romania** Dielectric properties of polymer-matrix nanocomposites
11.45 – 12.00 h	**M31 – R.E. Stanculescu, et al., Romania** Preparation and functional properties of PZT with ferrite magnetoelectric ceramic composites

Traditional ceramics -1 (Class Room, R10)

10.30 –10.45 h	**T1 – M. Grase, et al., Latvia** Submicron illite clay particles influence on geopolymer properties
10.45 –11.00 h	**T2 – L. Mahnicka Goremikina, et al., Latvia** Influence of doping agent on the mullitisation process in alumosilicate ceramics
11.00 – 11.15 h	**T3 – K. Gasek, et al., Poland** Effect of potassium and sodium feldspars on willemite crystalline glazes

11.15 – 11.30 h	**T4 – M. Omerašević, et al., Serbia** Thermal Induced phase transformation of Cs-exchanged LTA framework zeolite
10.30 – 11.45 h	**T5 – E. Klosek-Wawrzyn, et al., Poland** Microstructure and mechanical behavior of sintered materials made of kaolin and calcite mixture
11.45 – 12.00 h	**T6 – L. Dabare, et al., Latvia** Influence of thermal treatment and combustive additives on properties of Latvian clay ceramics pellets

12.00 – 12.15 h – Coffe Break

12.15 – 13.00 h – IA8 Invited lecture (Amphitheater)

László A. Gömze, Norken L. Gömze, Ludmila N. Gömze, Hungary, Ceramic based hetero-modulus, hetero-viscous and hetero-plastic complex materials with extreme dynamic strength

13.00 – 14.00 h – Section 11

Synthesis of ceramic powders - 2 (Blue Hall)

13.00 –13.15 h	**A56 – S. Ognjenovic, et al., Germany** Aluminium nitride nanoparticles by chemical vapor synthesis
13.15 –13.30 h	**A57 – S. Lukić, et al., Serbia** Chemical vapour synthesis and characterization of Al_2O_3 nanopowder
13.30 – 13.45 h	**A58 – J. Luković, et al., Serbia** New synthesis method and characterization of porous nanometric tungsten carbide

Traditional ceramics -2 (Class Room, R10)

13.00 –13.15 h	**T7 – J. Pantić, et al., Serbia** Chrome doped sphene pigments prepared via precursor mechanochemical activation
13.15 –13.30 h	**T8 – W. Panna, Poland** Identification methods of nanoparticles selected by sedimentation from raw siliceous clays

Polymer based composites (Class Room, R10)

13.30 –13.45 h	**C24 – M. Serkis, et al., Czech Republic** Waterborne polyurethane dispersions and films modified by colloidal silica
13.45 –14.00 h	**C25 – M. Danowska, et al., Poland** Polyurethane foams modified by silicates

14.00 – 14.15 h – Closing

The Tenth Students' Meeting, SM-2013
PROCESSING AND APPLICATION OF CERAMICS

The Tenth Students' Meeting, SM-2013
PROCESSING AND APPLICATION OF CERAMICS

Organizer

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INVITED TALKS
SM-2013

PL

FROM TUNABLE PROPERTIES OF NANOSTRUCTURES TO PRINTED DEVICES

Horst Hahn
Institute for Nanotechnology, Karlsruhe Institute of Technology (KIT), Germany

The properties of materials are determined by their microstructure, i.e. grain size, type and concentration of alloying elements and defects. Consequently, properties can only be changed by modifying the microstructure, for example by grain growth during annealing at elevated temperatures. Such a behavior, that fixes the properties irreversibly to the microstructure, is advantageous for many applications of materials, where long-term stability of the properties, i.e. mechanical strength for structural applications, is required. In contrast, the reversible change of properties offers completely new ways towards applications, in particular if the entire portfolio of available materials can be considered.

Semiconductors represent the most prominent example for reversible tuning of electrical conductivity. Their properties can be reversibly tuned by the application of an external electric field, as a consequence of the electrical charges at the interfaces between a dielectric layer and the semiconductor. For systems with metallic conductivity, tuning of properties cannot be observed unless the dimensions of the structures are in the nanometer regime, sometimes in the range of a few monolayers. The reason is the small spatial dimension of the space charge region due to the effective screening of the interfacial charges by the conduction electrons. Consequently, the reversible changes of properties (electric conductivity, magnetization) are typically in the order of a few percent for metallic systems.

Tuning of physical properties will be shown for several nanostructures in the form of thin films, nanoparticulate and nanoporous structures and nanowires. Tuning can be either achieved using dielectric/ferroelectric gating, well known from semiconductor physics, or by electrolyte gating using liquid or solid electrolytes. Examples of different gating mechanisms and reversible properties will be given: tunable electrical conductivity of Au- and ITO-films using electrolyte gating, tunable magnetic properties using ferroelectric gating of epitaxial LSMO-thin films and using electrolyte gating of porous LSMO nanostructures. As a novel extension of these concepts, an example of intercalation-driven reversible changes of magnetization of bulk iron oxide will be presented. As an example for applications based on tunable properties, it will be shown that printed electronics, i.e., field-effect transistors, can be fabricated completely at room temperature and exhibit superior electrical performance if compared to the organic counterparts.

Finally, the concepts discovered for tuning properties of nanostructures can be employed in applications as well. As an example, we developed field-effect transistors based on inorganic nanoparticles as the channel material and solid electrolyte for the gating. All active components were printed on flexible substrates and all processing steps were performed at room temperature. The performance of such printed FETs will be presented.

IA1

SOL-GEL DERIVED POROUS NANOCOMPOSITE MATERIALS

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The sol-gel method is a versatile technique for the preparation of porous solids and composites based on e.g. silica, alumina and titania matrices. By controlling the hydrolysis of the respective alkoxide precursors, it is possible to synthesize monoliths, hollow inverse opal structures, nanotubes and foams. Moreover, it is also possible to add modifiers to the sol and thus introduce additional functionalities into the material.

The MTA-SZTE "Lendület" Porous Nanocomposites Research Group (http://www.porousnanocomposites.com) develops new functional porous nanocomposite materials and studies the fundamental physical chemistry of their interaction with liquids and gases. In this talk I will first introduce the basics of the sol-gel method, then present a few case studies from our recent work where porous nanocomposites of different properties were prepared and characterized.

IA2

TOUGHNESS OF Al_2O_3/SiC NANOCOMPOSITES

Carmen Baudin
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Bulk ceramic nanocomposites are defined by the grain size of at least one of the constituent microstructural phases being smaller than 100 nm or finer. Since the seminal work by Niihara, the recognition of the appealing mechanical, physical and tribological properties of such materiales has generated considerable recent research activity. Moreover, different structures incorporating not only particulate second phases, but also carbon nanotubes and graphene, have been developed. In addition to processing, major challenge in this research field is the understanding of the basic properties of the materials. New developments can only be envisaged on the basis of well understanding intrinsic properties. In this sense, one of the most important properties is toughness, for which inconsistent results, most of them provided by indentation methods, have been reported.

Even though indentation methods could be useful for comparative purposes when insufficient volume of material is available, they are not adequate for the basic understanding of material behavior. The equations used at present are based on expressions for the stresses which have no experimental verification and contain unknown factors usually supplied by calibration.

Controlled fracture tests are required for the accurate determination of the toughness parameters of materials in order to assure the full conversion of the supplied energy into crack surface energy. The scarce toughness data obtained in stable fracture tests is due to the fact that, in general, the attainment of stability in displacement controlled tests requires complicate loading arrangements and specimen and crack geometries. In order to perform in a routine way stable fracture tests of ceramics, a new experimental setup to perform three point bending tests controlled by the crack mouth opening displacement (CMOD) was developed. The set up combines an electromechanical universal testing machine with a high precision optical micrometer. The CMOD was proposed as control variable because from the three parameters involved in the test, load, displacement and CMOD; this latter is the only one that continuously increases as fracture proceeds. This method constitutes an accurate and reliable determination of fracture toughness (K_{IC}) of ceramics nanocomposites. K_{IC} values are calculated from the maximum loads, K_{ICP} and from the total fracture energy determined in stable tests, $K_{IC\gamma}$. Results for fully dense alumina-matrix nanocomposites with 2, 5 and 10 vol.% SiC are analysed and compared with those for a reference fully dense alumina material with grain size similar to that of the nanocomposite matrix in order to detect toughness reinforcement.

IA3

NETWORK BETWEEN GERMANY AND STATES FROM THE DANUBE REGION FOR COOPERATION IN THE FIELD OF CERAMIC BONE REPLACING STRUCTURES WITH INCREASED MECHANICAL PROPERTIES BY FREEZE CASTING (BONEFOAM)

Tassilo Moritz, Matthias Ahlhelm
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The presentation of the project BONEFOAM shall act as a door opener and an invitation to industrial and RTD partners from states in the Danube region to create a scientific network with German partners in the field of bioactive ceramic bone scaffolds. The general goals of the network are:

- to develop bioresorbable materials with enhanced mechanical properties
- to apply novel techniques like freeze foaming for attaining personalized bone structures
- to test and to validate the developed components, and
- to get ready the materials and technologies for the market

A major point of collaboration in the network shall be the application for funding on European level. Within the next two years the partners will have to form a consortia for initiating an EC funded project.

A core group has been established at the early beginning of the project BONEFOAM, consisting of the Fraunhofer IKTS as a German research partner supporting the applied research of small and medium sized companies in Germany and Europe, the University of Novi Sad as an RTD partner and the Hungarian start-up company Innovation and Technology Management (ITM). Within the next month this core group shall attract further partners from the Danube region. For that purpose workshops and round-table-discussions initiated by the core group members will be used for getting potential partners together.

Especially smaller companies without considerable research capacity can benefit from the network and the resulting project activities.

IA4

TiO_2 NANOWIRES: FROM BASIC SCIENCE TO APPLICATIONS

László Forró

Laboratory of Physics of Complex Matter, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Titanium dioxide (TiO_2) is one of the most versatile functional materials. From its three polymorphs (anatase, brookite, rutile) the anatase phase is the most popular one. It can be synthesized at different length scales: bulk single crystals, thin films, single crystalline nanotubes/nanowires and nanoparticles. The single crystal studies address the fundamental properties of the material while the lower dimensional forms offer possibilities for various applications such as photovoltaics, spintronics, thermoelectrics, bioengineering etc.

This presentation will start by reporting some key measurements on the bulk material (transport coefficients, ARPES, STM) which are important for understanding the nature of the charge carriers at any length scales. The emphasis will be given to the synthesis and application of single crystalline anatase nanowires. The method of synthesis, beyond the high structural quality, allows the doping and manipulation of nanowires in order to have active nano-sized materials. A broad range of applications, including photovoltaic, fuel cells, sensors and purification membranes will be illustrated. For example, nanowires fused into a 3D fibrous network are used in a photovoltaic cell with solid electrolyte. This architecture possesses a high roughness factor, significant light scattering and up to several orders of magnitude faster electron transport which plays an important role in high conversion efficiency.

Acknowledgement: The contributions of Endre Horvath, Arnaud Magrez, Lenke Horvath, Jacim Jacimovic, Marco Grioni, Simon Moser, Osor Barisic and Michael Graetzel are gratefully acknowledged.

IA5

DOPING NANOPARTICLES – THE RELEVANCE OF LOCAL STRUCTURE

Markus Winterer

*Nanoparticle Process Technology (NPPT), Institute for Combustion and Gas Dynamics,
University of Duisburg - Essen, Germany*

Dopants are often required to generate functional materials. They are providing charge carriers in semiconductors, for example. However, the dopant atoms have to be positioned on specific sites in the lattice to fulfill the desired function. This local structure can be investigated using spectroscopic methods such as NMR or EXAFS. We present new results on Al doped ZnO and Ag doped CdSe and describe the detailed analysis of EXAFS spectra using Reverse Monte Carlo (RMC) simulations.

IA6

COLLOIDAL PROCESSING OF CERAMICS AND COMPOSITES

Rodrigo Moreno

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Colloidal processing has demonstrated to be a suitable method to produce nanostructured ceramics and composites since colloidal forces allow us to maintain the nanoparticles dispersed during handling and shaping. In the present talk the main issues concerning the stability of ceramic powders in water are described, focusing on the mechanisms of stabilization and the basic concepts of rheology of concentrated suspensions. The relationships between suspension parameters and microstructure and properties of the final materials are illustrated with different examples that demonstrate the feasibility of colloidal processing on the design and manufacture of ceramics and ceramic based composites.

One of the most important technological needings refers to the manufacture of nanodevices, in which colloidal suspensions are used. Nanopowders are difficult to stabilize because the particle size lies in the same order than the forces acting over the system. Some commercial suspensions are available but they usually have very low solids loadings, insufficient for conventional shaping. One easy procedure to concentrate those commercial suspensions is to use them as a dispersing medium for other powders, thus allowing a significant increase of the solids loading. In addition to the homogeneous dispersion of powders, the stability of mixtures is also discussed. Homogeneous mixtures of powders can be obtained by controlling the zeta potentials to have a co-dispersion if particles are similar in size and/or shape, or heterocoagulation, when particles have very different sizes and/or shapes. One clear example is the preparation of ceramics reinforced with a carbonaceous phase, such as carbon nanotubes or graphene. Colloidal processing can be also used in the manufacture of ceramic-metal composites, providing a simple route to produce complex shaped parts and tailored microstructures. As a conclusion, the suitable combination of different shaping methods allows manufacturing of complex 3-D bodies as well as single or multilayer coatings, self-sustaining films and laminates of any monolithic ceramic or composite.

IA7

PRINTED ELECTRONICS: FROM MATERIALS TO APPLICATIONS

Goran Stojanović

Department of Microelectronics, Faculty of Technical Sciences,
University of Novi Sad, Serbia

This invited talk deals with the emerging field of printed electronics which offers the possibility to broaden the horizon of classical electronics, due to new properties of devices (flexibility, lightweight, disposability and ultra-low cost fabrication) and a wide range of novel applications. It will be described a new electronics technology using solution processable organic, inorganic and hybrid materials to build functional devices on mechanically flexible substrates such as foils, papers, cardboards, etc. More precisely this lecture will present more recent results of the Laboratory for Nano and Printed electronics, within the Faculty of Technical Sciences, university of Novi Sad, Serbia, in this area. Developed prototypes and demonstrator will be presented such as: active shelf (a demonstrator - a counter of explicit number of products on the shelf based on flexible/printed electronics), TAG&FIND system (for searching lost things through wireless communication), SLALOM (an arcade game which consists of five ink-jet printed inductors acting as sensitive elements detecting the presence of a steel ball), PROVOD (a software package for fast and accurate inductance calculations printed/flexible inductors), etc.

IA8

CERAMIC BASED HETERO-MODULUS, HETERO-VISCOUS AND HETERO-PLASTIC COMPLEX MATERIALS WITH EXTREME DYNAMIC STRENGTH

László A. Gömze[1], Norken L. Gömze[2], Ludmila N. Gömze[2]
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Keywords: composites, mechanical properties, nanostructure, strength

It is obvious that ceramic materials with different mineralogical and crystalline composition have different chemical and physical properties including module of elasticity and melting temperature. Examining the material structures and behaviors of different ceramic bodies and CMCs under high speed collisions in several years the authors have understood the advantages of hetero-modulus and hetero-viscous material systems to absorb and dissipate the kinetic energy during high speed collisions and successfully developed a new family of hetero-modulus and hetero-viscous alumina matrix composite materials with extreme mechanical properties including dynamic strength. These reinforced with Si_2ON_2, Si_3N_4, SiAlON and AlN submicron and nanoparticles new corundum-matrix composites have excellent dynamic strength during collisions with high density metallic bodies with speeds about 1000 m/sec or more. At the same time in the alumina matrix composites can be observed a phase transformation of submicron and nanoparticles of alpha and beta silicone-nitride crystals into cubic c-Si_3N_4 diamond particles can be observed, when the high speed collision processes are taken place in vacuum or oxygen-free atmosphere.

Using the rheological principles and the energy engorgement by fractures, heating and melting of components the authors successfully developed several new hetero-modulus, hetero-viscous and hetero-plastic complex materials. These materials generally are based on ceramic matrixes and components having different melting temperatures and modules of elasticity from low values like carbon and light metals (Mg, Al, Ti, Si) up to very high values like boride, nitride and carbide ceramics.

Analytical methods applied in this research were scanning electron microscopy, X-ray diffractions and energy dispersive spectrometry. Digital image analysis was applied to microscopy results to enhance the results of transformations.

ADVANCED CERAMICS

A1

ANTIMONY DOPING OF ZINC OXIDE – WHERE IS THE DOPANT LOCATION?

S. Lorenz, A. Kompch, M. Winterer

Nanoparticle Process Technology (NPPT), Institute for Combustion and Gas Dynamics, University of Duisburg – Essen, Germany

Antimony doped zinc oxide (Sb:ZnO) nanoparticles are synthesized from the gas phase by chemical vapor synthesis (CVS). The crystal structure of the particles is investigated by X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) analysis. Crystal phases and cell parameters are determined by rietveld refinement. EXAFS spectra of the Zn-K and Sb-K absorption edge are analysed by Reverse Monte Carlo (RMC) [1] analysis using different doping models, e.g. antimony substituting for oxygen (Sb_O), antimony substituting for zinc (Sb_{Zn}) and a large size mismatch defect complex (Sb_{Zn}-$2V_{Zn}$). The radial partial pair distribution functions are extracted. The results support the existence of the predicted Sb_{Zn}-$2V_{Zn}$ defect complex [2], which can be used to explain the experimentally found p-type conductivity of Sb:ZnO [3].

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A2

FROM AlN TO HIGH-SURFACE-AREA ALUMINUM (HYDROUS)OXIDE POWDERS

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The tendency for aluminum nitride (AlN) powder to hydrolyze, which can lead to a complete degradation of the material, is unique in metal nitrides. This hydrolysis is generally considered as a nuisance, because it prevents aqueous powder processing. However, our recent in-depth studies of the solid reaction products of such hydrolysis, along with its reaction kinetics, opened up numerous possibilities for the exploitation of this hydrolysis, such as the processing of high-performance porous alumina ceramics and the preparation of nanostructured alumina coatings, that are applicable as templates for self-cleaning, super-hydrophobic coatings or in dentistry as adhesive coatings for cementing, the recently very popular, yttria-stabilized tetragonal zirconia (3Y-TZP).

In the present paper it will be shown that the hydrolysis of AlN powder can be exploited for the preparation of high-surface-area aluminum (hydrous)oxide-based powders. It is a nanostructured, yet micron-sized, transient alumina powder with surface areas exceeding 270 m^2/g and pore volumes of more than 0.5 cm^3/g. It is composed of bundles of aggregated lamellas (the single lamellae is a two-dimensional iso-crystal composed of 10-nanometer-sized crystallites). In addition to a small crystallite size they possess 1–2-nanometer-sized pores, being on the border of micro-meso porosity, which additionally contribute to the final specific surface area. By increasing the annealing temperature the specific surface area of the powder is gradually decreased, while the mean pore size is increased (and its distribution broadened), but the pore volume remains unchanged. Accordingly, the transient γ-alumina powder is transformed into δ–alumina and θ-alumina at 900 and 1000 °C, respectively, before proceeding to a complete transformation into the most thermodynamically stable, α-alumina phase.

It will also be shown that by consolidation of the as-prepared powders with a Spark Plasma Sintering (SPS) system, porous ceramic monoliths with a high pore-area/volume, exhibiting hierarchical heterogeneities, can be obtained. By manipulating the consolidating pressure and sintering conditions the ratio between meso- and macro-porosity can be controlled. On the other hand, we were able to exploit these powders as carrier powders in the preparation of the γ-Al_2O_3/TiO_2 composite, where nano-titania particles embedded into γ-Al_2O_3 lamellas significantly improved its photocatalytic activity.

A3

HYDROTHERMALLY ASSISTED SOL-GEL SYNTHESIS OF NANO-ANATASE TiO_2 FOR APPLICATION IN DYE-SENSITIZED SOLAR CELLS

N. Tasić[1], Z. Marinković Stanojević[1], Z. Branković[1], S. Savić[1], A. Dapčević[2], M. Žunić[3], G. Branković[1]

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[2]Faculty of Technology and Metallurgy, University of Belgrade, Serbia
[3]Instituto de Química - UNESP, Araraquara SP, Brazil

We have combined sol-gel synthetic route with hydrothermal synthesis under autogenous pressure to obtain stable TiO_2 precursor gels. The gels were mixed with organic functional additives into pastes, and deposited onto fluorine-doped tin oxide (FTO) conductive substrates (12–14 Ω/sq) using tape-casting film applicator. As deposited films were carefully dried at 60–100 °C, and calcined at 400 °C, resulting in porous crack-free structures. The porous films were produced in different thicknesses (2–18 μm) and used as photoactive electrodes in dye-sensitized solar cells (DSSCs). Also, we have introduced a compact passivating TiO_2 layer (100–300 nm in thickness), which prevents the direct contact between the conductive oxide substrate and electrolyte, thus, increasing the current density of the operating cell. The layer was produced by spin-coating deposition of TiO_2 sols, prepared by chemical procedure starting from Ti(IV) isopropoxide and triethanolamine (TEA) as complexing agent. Thermal properties of TiO_2 precursor pastes were characterized by TG/DSC; the morphology of the porous films was investigated by FE-SEM, while the surface of passivating layers was analyzed by AFM. The presence of anatase TiO_2 in the passivating and the porous layers was confirmed by XRD analysis. The band gap of the porous layer (3.30 eV) was calculated according to diffuse reflectance UV/VIS measurements, while the photovoltaic performance of fabricated DSSCs was investigated by measuring current density – voltage (*J*-*V*) curves.

A4

SYNTHESIS OF TiB_2 NANOSIZED POWDER IN RADIOFREQUENCY THERMAL PLASMA

P. Fazekas, S. Klébert, A.M. Keszler, E. Bódis, E. Drotár, I. Bertóti, I. Sajó, Z. Károly, J. Szépvölgyi

Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary

Metal borides (like TiB_2) are ceramic materials with attractive physical and chemical properties such as high strength, high melting point, high hardness, good thermal conductivity, partly high electrical conductivity and also high chemical inertness. This combination of properties makes them promising candidates for high technology applications including wear resistant parts, composite materials, metal melting crucibles, electrode materials.

Different methods are known to prepare metal boride powders, however just a few methods have been published for nanopowder synthesis such as self-propagating high temperature synthesis (SHS), vapour-phase synthesis and carbothermal reduction processes.

In this work the formation of TiB_2 nanopowder in radiofrequency (RF) thermal plasma was investigated from different starting materials. Parameters which influence the powder synthesis such as the plasma input power, the feed rate of powders, the quality and quantity of plasma gases were studied. The morphology of samples was characterized by scanning electron microscopy (SEM), while the phase composition by X-ray diffraction (XRD). Surface chemical composition was determined by X-ray photoelectron spectroscopy (XPS).

It was found, that in thermal plasma conditions nanosized powders were produced from micrometer-sized starting materials. However in some cases the particles are agglomerated in a great extent. XPS results show that the surface of the powders was oxidized significantly.

A5

PREPARATION OF MULLITE AND Fe-DOPED MULLITE POWDER PRECURSORS BY SOL-GEL COMBUSTION PROCESS

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[1]*Vinca Institute of Nuclear Science, University of Belgrade, Serbia*
[2]*Faculty of Technology and Metallurgy, University of Belgrade, Serbia*

Powders of pure and Fe-doped 3:2 mullite ($3Al_2O_3 \cdot 2SiO_2$) were prepared by sol-gel combustion process using ethanol-water solutions of TEOS, Al(III) nitrate, Fe(III) nitrate and urea. The prepared solutions were heated at 60 °C in order to evaporate solvents and obtained gels were further heated on a hot plate to initiate combustion process. Afterwards, obtained ashes were treated at 800 °C for 4 h to remove retained organic substances. Compositions up to 15 wt.% of Fe_2O_3 were investigated. XRD analysis confirmed that powders were amorphous, which confirms the thermodynamic predictions that the direct formation of mullite has not occurred during the combustion synthesis. The TGA/DSC analysis showed decrease of crystallization temperature of Fe-doped mullite as the amount of iron incorporated in mullite increases. The mullitization reaction is a two-step process including formation of transitional spinel alumina phase below 1000 °C, which reacts with silica to mullite at temperatures about 1200 °C. Micro-structures and compositions of powder particles were examined by SEM/EDS. The SEM micrographs revealed agglomerated powder particles which consist of smaller grains.

A6

LESS COMMON NANOSTRUCTURES – TiO_2 NANOFLOWERS

A. Kusior, M. Radecka
AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Cracow, Poland

The development of nanotechnology has led to the emergence of a huge number of scientific papers devoted to the production of nanostructures in the form nanotubes, nanowires and other nanoforms. There has also been growing interest in the transformation of the same nanostructures, in particular, examined the effect of changing their shape on the photocatalytic properties [1–3].

The aim of this study was to modify the process of preparation, which consists of changing the way substrate and its crystallization, as well as finding a correlation between the parameters of the reaction and the structure of the obtained materials. TiO_2

nanomaterials are obtained in the oxidation process. Titanium foil (99.7%) was reacted in a solution of 30% H_2O_2 at 80 °C.

In the next stage of the process the material were annealed in a protective atmosphere of Ar at 450 °C and 600 °C. A key factor in the number and size of snanostructures is the time of synthesis, which was varied from 15 minutes to 5 hour. The influence of temperature and reaction time on the properties of TiO_2 was also analyzed.

Acknowledgement: This work was supported by the project DOCTUS

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A7

STUDY OF THE FORMATION OF (ZnCo)Fe_2O_4 SYSTEM USING TWO LOW TEMPERATURE SYNTHESIS METHODS

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This paper presents a study regarding the cobalt-zinc ferrite obtained in the $Co_xZn_{1-x}Fe_2O_4$ system, by two different synthesis methods: co-precipitation synthesis method when the pure ferrite is obtained at 80 °C and the thermal carboxylate complex decomposition at 350 °C, with the pure cobalt-zinc ferrite formation.

The magnetic properties of the resulting product depend on the cobalt-zinc ratio and the obtaining method used. The final product has nanometric size and has a tendency to agglomerate, thus influencing the magnetic properties of the synthesized products.

The spinel system $Co_xZn_{1-x}Fe_2O_4$ can be applied in different areas like electrical devices, sensors, ferrofluids, disk recording and medical applications such as the cancer treatment by hyperthermia, MRI contrast agent, drug delivery and cell separation.

The obtained powders were investigated by X-ray diffraction (XRD), FTIR spectrometry and scanning electron microscopy (SEM).

A8

INFLUENCE OF HPMC ADDITION ON HYDROTHERMAL CRYSTALLIZATION OF ZIRCONIUM OXIDE

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The environment of hydrothermal crystallization of zirconia has been modified by an addition of HPMC (hydroxypropyl methylcellulose) and sodium fluoride. Effects of HPMC concentration, crystallization time and temperature on the chemical composition, phase composition and morphology of the resultant crystals were investigated using SEM/EDS, HR-TEM, XRD, XRF and FTIR/Raman spectroscopy methods. As a blank sample, powders crystallized from the zirconyl nitrate in the NaF saturated solution have been used.

As a result, two types of structures have been observed: large plates over 1 µm in size and of hexagonal geometry agglomerated in highly oriented stacks and a population of crystals with complicated 3D geometry. Both types of structures were agglomerated in hollow spheres of several tens of micrometers in diameter.

On the basis of the size and morphology of the obtained crystals and their agglomerates, the non-classical crystallization mechanism has been proposed.

A9

DESIGN OF NUCLEAR CERAMIC MATERIALS WITH ENHANCED THERMAL CONDUCTIVITY

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Despite the availability of numerous types of nuclear fuels commercial reactors in the world are powered by uranium dioxide (UO_2). This kind of the fuel is chosen for several reasons such as high melting point and oxidation resistance; however the thermal conductivity of this ceramic material is very low. Enhanced thermal conductivity of the nuclear fuel will increase safety of a reactor during normal operation and short-term accidents.

Direct application of the UO_2 in a laboratory experiments requires high administration cost, so we propose in the first stage to substitute UO_2 by CeO_2. High density, low thermal conductivity and similar sintering behaviour are common properties of the both oxides. Aim of this work is to build a suitable model for improvement of thermal conductivity by addition of highly conductive phase (SiC). Both aspects influence the additive on the thermal conductivity and behaviour in the nuclear reactor is discussed by experimental and theoretical approach. Our preliminary results shows that densification of both UO_2 and CeO_2 with addition of highly conductive phases is very similar and requires analogous approach.

A10

QUALIFICATION AND INVESTIGATION OF CERAMIC INJECTION MOLDING RAW MATERIALS

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Keywords: alumina powder, paraffin wax, ceramic injection molding, laser granulometry, scanning electron microscopy, thermal analyisi, rheology analysis.

The ceramic arc tube parts - in the illuminant industry - are made of high purity alumina powder. By producing ceramic parts, one of the most critical step is to optimizing the injection molding process, determining and controlling the influential machine paramteres, which have an effect on the quality of end product. [1]

There are used two different major components for producing injection molding raw material (feedstock): high purity alumina powder as the main component, and an organic paraffin wax as a binder material. It is expressly important to know the material, physical and chemical properties of these components, since mainly these have affect on the homogenity of feedstock, and therefore on the quality of end product. [2]

In this research, both of the main components and the moldable raw material was investigated by visual, physical, chemical and thermal methods. As most important and main statement, the researchers found that the dynamic viscosity of raw material depends more on the applied temperature, than on the deformation speed gradient. In addition, it was found, that the grain size distribution of alumina powder and the amount of binder material have a huge affect on the dynamic viscosity of molding material.

Applied analitycal methods were laser granulometry, sieve analysis, scanning electron microscopy, differential thermal analysis, specific surface area analyisis and rheology analysis.

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A11

LLZO SOLID ELEKTROLYTE FOR LITHIUM ION BATTERIES

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Solid electrolytes have gained a lot of attention in the last few years because of their higher energy density, high chemical stability and safety for Li-Ion batteries.

In this work we report on synthesis and characterization of nanocrystalline $Li_{7-3x}La_3Zr_2Al_xO_{12}$ solid electrolyte. The material is synthesized by nebulized spray pyrolysis (NSP). The as-synthesized powders were consolidated into pellets and sintered at 1000 °C. The structure of powders and sintered ceramics was characterized by X-ray diffraction (XRD). Furthermore the surface area and the microstructure were determined by nitrogen adsorption using the BET method and secondary electron microscopy (SEM). The sintered pellets were prepared for impedance spectroscopy (IS) and cyclic voltammetry (CV) measurements to study the conductivity for Li-Ions and the reversibility of the reactions at the electrolyte-electrode interface, respectively.

Although the achieved percentage of the theoretical density did not exceed 55 %, the conductivity of the nanocrystalline materials is in the same order of magnitude as reported for microcrystalline $Li_{7-3x}La_3Zr_2Al_xO_{12}$, which gives the nanocrystalline material more room for improvement towards higher conductivities.

A12

STUDY OF STORAGE MATERIALS FOR HIGH-TEMPERATURE RECHARGEABLE OXIDE BATTERIES (ROB)

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The work focuses on the research of porous storage material of a novel high-temperature rechargeable oxide battery (ROB). The ROB consist of regenerative solid oxide cell (SOC) and hydrogen/water vapor storage redox unit with embedded Fe/FeO porous redox material which has to meet the requirements, such as good kinetic properties, high oxygen storage capacity and high lifetime.

Because of long-term redox reactions at 800 °C the structure of the storage material can degrade, and thus makes the storage material incapable to store enough oxygen for continuous redox reactions. Due to that the Fe/FeO porous storage material has to be supported by e.g. inert and reactive oxides. To some extent the inert and stable mixed oxides show some resistance against structural degradation however, they could not completely provide a significant long-term oxygen storage capacity. In contrast to the stable oxides, reactive mixed oxides seem to be promising candidates which are capable to suppress a structural degradation after several redox cycles and improve the kinetic activity of Fe/MeO based storage material.

A13

LASER-ASSISTED CHEMICAL VAPOR DEPOSITION OF MULTINARY OXIDES FOR THIN-FILM BATTERY APPLICATION

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The research on thin-film batteries is driven by an increasing demand for micro-sized power sources, because of the progressive miniaturization of electronic components over the last decades. Especially an all-solid-state thin-film battery is desirable, since its excellent safety properties and easy integration in microelectronics, e.g. in RFID tags, are outstanding advantages.

In this presentation we report on a newly established technique to deposit functional thin-films for battery application. This CO_2-laser assisted chemical vapor deposition (LACVD) makes use of solid precursors, which evaporate instantaneously by absorption of infrared laser radiation. The deposition of the thin-films then takes place on a diode laser heated substrate.

By tuning the process parameters several structural features, such as the degree of crystallinity, density and thickness of the films can be adjusted. Thin-films of multinary oxides acting as electrode or solid-state electrolyte were deposited onto different substrates and electrochemically characterized. Further investigations comprise X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy as well as X-ray photoelectron spectroscopy (XPS).

A14

THERMAL STABILITY AND ELECTRICAL PROPERTIES OF $Ce_{1-x}Bi_xO_{2-\delta}$ (x = 0.1–0.5) SOLID SOLUTION

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Thermal stability of solid solution $Ce_{1-x}Bi_xO_{2-\delta}$ (x = 0.1 – 0.5), which were previously synthesized at room temperature using simple and fast Self Propagating Room Temperature procedure (SPRT), was investigated at various temperatures up to 1400 °C by applying differential thermal and thermogravimetric analysis (DTA/TG). Thermally treated powders were characterized by X-ray powder diffraction (XRPD), scanning electron microscopy (SEM) and Infrared (IR) spectroscopy. It was found that the sample with 10 mol% of Bi^{3+} stays stable and monophased even at temperature as high as 1400 °C. On the other side, samples with higher concentration of bismuth are unstable at high temperature. Namely, Bi leaves the structure of ceria and forms β-Bi_2O_3 as a second phase which will start to evaporate at temperatures higher than 1100 °C. Sintering of the obtained powders was performed by both conventional and microwave sintering. It appeared that the microwave sintering was more convenient to obtain dense samples. The ionic conductivity measured by impedance spectroscopy showed that the solid solutions with lower Bi^{3+} content exhibited primarily the grain boundary conductivity, whereas the sample with composition $Ce_{0.5}Bi_{0.5}O_{2-\delta}$ depicted the bulk conductivity. In both cases conductivity increased dramatically with increasing temperature as well as with Bi concentration.

A15

YSZ THIN FILMS FOR SOLID OXIDE FUEL CELLS DEPOSITED USING SPRAY PYROLYSIS

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Spray pyrolysis is a versatile coating technique applied in many fields of research or technology. It has already been used in solid oxide fuel cells, photovoltaic technology, sensors or electronic devices. It has a potential to produce thin (0.1–10 μm) and gas-tight ceramic layers on porous substrates. Moreover it does not need high temperature sintering stage thus it could prevent high temperature diffusion between the layers of different compounds.

Solid oxide fuel cell (SOFC) is one of the most promising technology for generating electricity because it provides high energy conversion efficiency, fuel flexibility and low pollution emission. The main part of SOFC is a solid electrolyte, such as most commonly used yttria stabilized zirconia (YSZ). In order to improve the fuel cell performance the electrolyte thickness should be decreased. Spray pyrolysis has been applied to fabricate electrolyte thin layer on porous anode substrate. Influences of deposition temperature and precursor type have been investigated. The morphology, structure and electrical properties were studied by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM) and impedance spectroscopy (IS). The substrate temperature was optimized for obtaining smooth, dense and homogeneous nanocrystalline films. The influence of thermal annealing on structural properties of films was studied.

A16

THE IONIC CONDUCTIVITY OF POLYSRYSTALLINE DONOR AND ACCEPTOR DOPED PEROVSKITE CERAMICS MEASURED BY LIMITING CURRENT TECHNIQUE

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Mixed Ionic-Electronic Conductor (MIEC) materials are widely used as electrodes in fuel cells or gas sensors. The phenomena of mixed conductivity in these materials are interesting due to its complex matter. Measurements of ionic conductivity in MIEC ceramics with high electronic and low ionic conductivity are difficult by conventional impedance spectroscopy. Therefore, in order to determine the ionic conductivity of these materials, the usage of DC blocking electrode method is required. Such configuration, which is called Hebb-Wagner method [1,2], was applied to measure the ionic conductivity in doped strontium titanate and lanthanum manganite.

The samples: $La_{0.7}Sr_{0.3}MnO_3$ (LSM), $Y_{0.07}Sr_{0.93-x}TiO_3$ (YS_xTO) (x= -0.05; 0; 0.05); and blocking electrode YSZ were prepared via conventional solid state reaction (SSR). The measurements of modified Hebb-Wagner system $(-)Pt|LSM/YS_xTO|Pt|YSZ|Pt(+)$ have been done by 2 point DC method. Current-voltage $I(U)$ plots for different temperatures were obtained. The ionic conductivity of investigated LSM/YS_xTO samples was calculated by two computational models based on diffusion process. The nonlinear current-voltage characteristics $I(U)$ were obtained for each sample.

The values of ionic conductivity of LSM sample calculated by computational model based on limiting current measurements are in good agreement with theoretical value. The computational model, shown by Li *et al.* [3], was proved to be inaccurate, because it disregards many important phenomena which occur during a 2 point DC measurement. The results of YS_xTO sample measurements show a value of ionic conductivity σ_{ion}~10^{-5} S/cm, and it strongly depends on nonstoichiometry level on

strontium site. The results of ionic conductivity measurements of LSM sample have shown that the modified Hebb-Wagner method with computational model based on limiting current is proper. The obtained ionic conductivity is in agreement with a theoretical value. Based on this computational model, the ionic conductivity of YS_xTO samples was also calculated.

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A17

STRUCTURE INVESTIGATION OF LITHIUM TITANATE SPINEL OXIDE CERAMICS PREPARED BY SOL-GEL METHOD

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Lithium titanate ($Li_{1+x}Ti_{2-x}O_4$ for $0 \le x \le 1/3$) is a II type spinel oxide superconductor with relatively high (~13 K for $x = 0$) zero resistance transition temperature T_c. Above T_c lithium titanate show metallic behavior and can be used e.g. as electrodes for rechargeable lithium-ion batteries.

One of the best methods of preparation of $LiTi_2O_4$ is the sol-gel method, which is cheap, simple and reproducible. For starting solution preparation, lithium acetate, butoxytitanium and ethanol were used as the reagents. The solution was left for seven days to evaporate the organic solvents and then was dried at 100 °C for 20 hours. The next step was calcination at 550 °C for 10, 20 and 50 hours in an argon atmosphere.

In this work correlation between annealing time and structure of lithium titanate ceramics is discussed. The structure of prepared samples was investigated by X-ray diffraction. The results of XRD measurements showed the two-phase system with a significant majority of lithium titanate spinel. Samples contained a bit of Ti_3O_5 and TiO_2 rutile which could testify to incomplete transformation into a crystalline phase due to lithium or oxygen deficiency. Strong influence of production parameters on lithium titanate – titanium oxide quantity relation was observed. Morphology of prepared samples was investigated by scanning electron microscope, while phase transitions and thermal stability was confirmed by differential scanning calorimetry method.

A18

THE INFLUENCE OF GLYCEROL MONOACRYLATE ON REOLOGICAL PROPERTIES OF CERAMIC SUSPENSIONS

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One of the basic studies for the work concerning the fabrication of advanced ceramic materials and composites by colloidal processing is the research on the rheological properties of ceramic suspensions. Shear-thinning behaviour is often observed for the ceramic non-newtonian liquids and the decrease of viscosity with increase of shear rate is favourable for casting of ceramic powders. On the contrary, shear-thickening behaviour of ceramic suspensions is very problematic in many industries; the ability of fluids to put the resistance to the operative force is a serious hindrance for mixing and flow, causing equipment overload. However, shear-thickening fluids, where instantaneous peak of viscosity with increasing shear rate occurs, can be very useful for some unique application in the technology of ceramics and composites, eg resistant textiles like sport cloths or *liquid armours.*

Glycerol monoacrylate, designed as the monomer for the gelcasting process of the ceramic powders, has been recently synthesised and widely investigated due to a very interesting influence on the rheological properties of the ceramic suspensions, based on alumina or silica powder. Not only it is able to polymerise *in situ* in the suspensions, but also it can contribute to the mechanism of a dilatancy effect. It results from the presence of many hydroxyl groups, creation of hydrogen bonds and thus highly strong macromolecular network. Therefore, glycerol monoacrylate can be a very useful additive for designing shear-thickening fluids of unique rheological properties.

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A19

MORPHOLOGY AND COMPOSITION OF SELF-ORGANIZED TITANIUM DIOXIDE NANOTUBES FORMED IN ETHYLENE GLYCOL BASED SOLUTION

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TiO_2 is one of the most studied compounds in materials science. The nanotubes oxide are one-dimensional (1D) nanostructures provide unique electronic properties, such as high electron mobility or quantum confinement effects, a very high specific

surface area. Titanium dioxide is known to be a very useful non-toxic, environmentally friendly, corrosion-resistant material. The key functional features are exceptional biocompatibility and even more the almost unique ionic and electronic properties of this oxide. Titania in all its crystal forms is a wide-bandgap semiconductor ($Eg \approx 3$ eV) with suitable band-edge positions that enable its use in solar cells and for photocatalytic reactions. Photogenerated electron–hole pairs can be used for splitting water into oxygen and hydrogen or can be used for the remediation of hazardous wastes, such as contaminated ground waters, or the control of toxic air contaminants. Synthesis of 1D TiO_2 nanostructures may be achieved by various routes including sol–gel methods, template-assisted methods, hydro/solvothermal approaches, and by electrochemical means. In this work, vertically oriented self organized titanium dioxide were formation by anodization of Ti substrates in ethylene glycol based solution. Growth of nanotubes has been carried out at the potential drop of 20 V, 30 V and 40 V. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) have been performed in order to investigate the crystallographic structure, morphology and contact angle of TiO_2 nanotubes were observed. As-prepared nanotubes have been found amorphous but subsequent annealing at 450 °C in argon atmosphere for 2 h transformed them into the anatase phase. SEM images show that TiO_2 nanotubes obtained in electrolytes containing glycerol are ordered and uniform. Surface morphology, average diameter and length of nanotubes are affected by the parameters of the process of electrochemical anodization.

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A20

CARBON NANOTUBES PREVENT THE COAGULATION AT HIGH SHEAR RATES OF AQUEOUS SUSPENSIONS OF EQUIAXED CERAMIC NANOPARTICLES

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Keywords: SiC, aqueous colloidal processing, CNTs, dispersion

Equiaxed ceramic nanoparticles and their mixtures are expected to exhibit shear-thinning behaviour when dispersed colloidally in aqueous media, whereas shear-thickening is the expectation for large aspect ratio phases such as, for example, carbon nanotubes (CNTs). Here, contrary experimental evidence is presented demonstrating the occurrence of severe coagulation at high shear rates in colloidally-stable, semi-concentrated, aqueous suspensions of equiaxed SiC nanoparticles (major phase) mixed with equiaxed $Y_3Al_5O_{12}$ nanoparticles (liquid-phase sintering additive), and how CNT addition prevents this coagulation if sufficient sonication is applied. It is also shown that although shear-thinning is the natural behaviour of the ceramic suspension up to moderate shear rates, coagulation is eventually a phenomenon inherent to the aqueous colloidal processing of these suspensions, with the critical shear rate for increasing and the rheopexy decreasing the better is the initial dispersion state achieved with the sonication. It is also shown that the critical shear rate for coagulation depends on the exact condition of shear rate increase, and that the re-sheared suspensions coagulate more significantly and at lower shear rates than the fresh suspensions. The mechanisms by which this coagulation occurs and is impeded by the CNTs are discussed, together with broader implications of these phenomena for the environmentally-friendly processing of nanostructured ceramics and ceramic composites.

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A21

PREPARATION CONDITIONS AND DENSIFICATION BEHAVIOUR OF CALCIUM OXIDE STABILIZED ZIRCONIA NANOPOWDER

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Preparation of calcium oxide stabilized zirconia nanopowders via the co-precipitation route makes some difficulties due to losses of calcium species during the water washing stage. This work describes an attempt to prepare the nanopowder from the $CaO\text{-}ZrO_2$ system by using a method with no the water washing stage. Therefore, a physical mixture of zirconia gel and crystalline calcium hydroxide was used as the precursor of fully calcium oxide stabilized zirconia nanopowder. The mixture was hydrothermally treated at 195 °C for 4 h. X-ray diffraction analysis (XRD), transmission electron microscopy observations (TEM), laser diffraction (DLS) and nitrogen adsorption (BET) methods were used to characterise the phase composition and properties of nanopowder. The densification behaviour of calcia-zirconia nanopowder was investigated by determination of compaction and dilatometric curves. Mercury porosimetry was used to determine pore size distributions of green compacts. The relative density of sintered polycrystals was measured by the Archimedes' method and the microstructure was characterized on the basis of SEM observations. Calcium oxide stabilized zirconia nanopowder of cubic symmetry and crystallite size of 8.5 nm was successfully prepared and consolidated to dense polycrystals. Advantages and disadvantages of the applied method for calcia-zirconia nanopowder preparation are discussed.

A22

PHOTOCATALYTIC ACTIVITY OF THE DIFFERENT STOICHIOMETRY ANTIMONY-OXYCHLORIDE DECORATED TITANATE NANOTUBE

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Since the discovery of the carbon nanotubes many researchers reported the synthesis and characterization of other one dimensional tubular nanostructures. Nowadays, one of the most important challenges in material science is to find new applications. Titanate nanotubes have promising properties such as the layered tubular structure, the large specific surface area and pore volume and high stability with photocatalytic activity, to name a few.

There are many ways to enhance the photocatalytic activity of these materials. After calcination the trititanate tend to form anatase and lower band gap energies are obtained. Another method is the sensibilization of the nanotubular titanate with semiconductor nanoparticles, for example with CdS or CdSe.

In this study $H_2Ti_3O_7$ nanotubes were synthesized via hydrothermal method in revolving autoclave followed by hydrochloric acid washing. Antimony-oxychloride nanoparticles were obtained by solvothermal synthesis at different pH values to regulate the stoichiometry. In order to prepare the nanocomposites the titanate nanotubes were added to the solution of SbOCl precursor in ethylene-glycol:water mixture and were kept at 120 °C for 12 h in a Teflon-lined stainless steel autoclave. The antimony-oxychloride decorated titanate nanotubes were examined by TEM, SEM, XRD, XPS and Raman spectroscopy. To study the photocatalytic activity of the as prepared materials we tested the degradation of methyl orange under UV and visible light.

A23

SYNTHESIS AND DISPERSION OF LANTHANIDE DOPED Gd_2O_3 NANOPARTICLES AND THEIR OPTICAL CHARACTERIZATION

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Nanoparticles of gadolinium oxide (Gd_2O_3) as well as europium and terbium doped Gd_2O_3 are produced by chemical vapor synthesis. Solid precursors of gadolinium acetylacetonate, terbium acetylacetonate and europium tetramethyl-heptandionate are evaporated inside a vacuum vessel by a CO_2-laser beam [1] and transported by carrier gas towards the hot-zone in a inductively heated tube furnace to form Gd_2O_3, Eu:Gd_2O_3 and Tb:Gd_2O_3. The as-synthesized powders are investigated using X-ray diffraction and Rietveld refinement for their structure. Dispersions made from these particles are analyzed by dynamic light scattering to obtain the size of the stabilized particle agglomerates, which are then used in a spectrofluorometer. Fluorescence is best for Tb:Gd_2O_3 dispersions.

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A24

INFLUENCE OF THULIUM OXIDE POWDER MORPHOLOGY ON PROPERTIES OF TRANSPARENT Tm:YAG CERAMICS

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Lasers based on thulium doped yttrium aluminum garnet ceramics can be very useful in medicine, remote sensing and in military technologies due to emitting in safe for the eyes wavelength of 2 µm. Radiation in this range is combined with the $_{3}F^{4}$-$_{3}H^{6}$ transition of thulium. Tm:YAG also benefits from a long fluorescence lifetime, which is attractive for high-energy Q-switched operation. Tm:YAG ceramics can be obtained by several techniques, but one of the most commonly used ways for fabrication of this material is reaction sintering. In this method, for a high transmission of the finally sintered material the crucial role play particle size, shape, degree of agglomeration and the sinterability of the powders used.

In this study thulium oxide powder has been prepared by thulium nitrate precipitation with different molar concentration (0.1M, 0.15M, 0.25M) using ammonium hydrogen carbonate as a precipitating agent. The aim of this work was investigation of relation between precipitation parameters (pH, precipitation temperature) and the properties of thulium oxide nanopowders obtained after precursors calcination. Tm_2O_3 powders and precursors were characterized by DTA-TG, XRD, SEM, BET techniques and were compared with commercially available powders. The mixtures for reaction sintering of Tm:YAG, containing the powders produced and commercially available, were prepared and consolidated. Finally, Tm:YAG ceramics obtained by reactive sintering (1830 °C/6 h) using different powders Tm_2O_3 have been compared in respect to microstructure and transmittance. For the resulting Tm:YAG ceramics were measured emission spectra and fluorescence dynamics.

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A25

CHARACTERIZATION OF $BaTiO_3$ FILMS FABRICATED BY INK-JET PRINTING PROCESS

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Ink-jet printing represents a novel technique for fabrication ceramic thick films, which have broad application in microelectronics. This technique is suitable for fast and precise printing of complex forms and potentially offers lower cost film fabrication. By ink-jet printing droplets of prepared sol (ink) are deposited at predetermined locations on a substrate. Performances of final product mainly depend of ink properties - consequently one of the aims of this research was to prepare different barium titanate ($BaTiO_3$) sols suitable for use in ink-jet printing. As precursors for $BaTiO_3$ sols barium-carbonate and tetrabutyl-orthotitanate were used, with glacial acetic acid as solvent. In addition, formamide was added to precursor sols in different concentrations to improve stability of sols. Viscosity, surface tension and particle size distribution measurements were used for characterization of the precursor sols. The prepared sols were printed on previously cleaned glass and silicon substrates using a commercial ink printing device. Structure and morphology of deposited films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy.

A26

ELECRTIC CONTROL OF MAGNETIC PHASE AND COLOSSAL MAGNETOELECTRIC EFFECT IN Pb(Fe,W,Ti)O_3 BASED MULTIFERROIC CERAMICS

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A wide variety of experimental results and theoretical investigations in recent years have strongly demonstrated that several transition metal oxides and other multiferroic materials have dominant states that are not spatially homogeneous. This phenomenon causes interesting effects, such as colossal magnetoresistance and ferroelectric polarization due magnetoelectric effect. Coupling and controlling different degrees of freedom in such materials opens unprecedented ways to achieve new functionalities. In "simple" ferroelectric perovskites one may well consider several kinds of competitions between different symmetries, different polar states, different distortions as oxygen tilting, or different dynamics. Thus all the ingredients, and additionally competing phases and quenched disorder, are present in relaxors. Simultaneously, in perovskites with magnetic ions, the competition between different orders and the presence of distortions play a fundamental role in the determination of them proprieties. Join both, multiferroic are certainly not simple materials. The many active degrees of freedom - spin, charge, lattice, and orbital - interact leading to an intrinsic complexity. To understand this physics, it is important to incorporate several techniques and phenomenological approaches, and the effects of lattice distortions appear as an important (and fundamental) factor of study. In lead iron tungstate, a complex perovskite ($Pb(Fe_{2/3}W_{1/3})O_3$) independent phases may appear due to segregation at the nanoscale, giving rise to two different types of classic disordered states: on one hand, the ionic charge disorder originates quenched electric random fields which provoke relaxor ferroelectric behaviour (Tm~180 K). On the other hand, owing to the occupation of the B sublattice with magnetic Fe^{3+} ions, a dilute antiferromagnet with a high Neel temperature TN ~340 K is accomplished. At high temperature, at T*, together with a local phase transition that gives rise to the appearance of static polar nanoclusters associated with an order disorder transitions of the Pb^{+2} cations, a colossal elastic response was observed, accompanied by a giant peak in the dielectric constant. Simultaneously, an increase in dielectric constant at the magnetic ordering temperature was observed (6%), understood in terms of spin phonon coupling, that on the other hand, couples to the electric polarization. This increase is even more remarkable when an electric field is applied (25%, for 600 kV/mm), giving a colossal magnetoelectric effect and controlling not only the magnetic proprieties but as well the temperature where the magnetic order is established with an applied electric field. The results were explained according to the thermodynamic model.

A27

INVESTIGATION OF THE ROLE OF POROSITY ON THE FUNCTIONAL PROPERTIES OF $Ba_{1-x}Sr_xTiO_3$ CERAMICS PRODUCED BY USING GRAPHITE FORMING AGENT

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The tailored porosity exposes special properties and characteristics of some materials, which might be completely different than their conventional dense equivalents. By introducing a controlled porosity into the ceramic systems, some properties can be improved and make the material proper foe being used for high-frequency ultrasonic transducers or for tunable applications [1].

$Ba_{1-x}Sr_xTiO_3$ ceramics with various porosities have been prepared using graphite as pore former agent. The compositions BST 30, BST 35 and BST 40, corresponding to x=0.30; 0.35 and 0.40, respectively, were obtained after calcination of mixed precursors at 950 °C for 4 h, after they were ball-milled for 48 h and by planetary milling for 2 h with 400 rot/min. Samples containing 0 %, 10 %, 20 %, and 35 % amount of graphite (400 µm particle size) were obtained by linear pressing at 50 MPa. After sintering at 1450 °C for 2 h, ceramics with various porosity degrees close to the nominal expected one, were produced. We noticed that the increasing of the amount of graphite increases the graded porosity and conducts to a low mechanical quality factor. Graphite was burned out through the sintering process and this resulted in a modification of morphology, microstructure and pore density of the ceramic product. Microstructural, morphological and dielectric investigations have been performed and data were compared with other literature studies [2]. The role of porosity on the functional properties was discussed.

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A28

CERAMIC NANOSTRUCTURES: THE ELECTROSPINNING ADVANTAGE

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The formation of special nano-sized structures normally requires the use of expensive equipment and/or techniques, such as cleanroom or ultra-high vacuum. On the contrary to these methodologies, the proposed approach allows the formation of nanostructure by means of the combination of two inexpensive alternatives: sol-gel and electrospinning techniques. The proposed methodology, in fact, yields a simple and versatile method for creating nano-sized ceramic structures with full control.

Electrospinning is a well-known electrodeposition technique for fabrication of matrixes of polymeric fibres which are currently used in different fields of technology, such as biological cell growth, advanced batteries and water treatment systems. Recently the research was extended to the applicability of the deposition technique into ceramic applications.

In this study, we show three different types of ceramic structures created with such a combination of techniques: nanochannels, nanofibres and nanotubes.

Nanochannels

This technique consists of using the electrospun fibres as templates which are infiltrated with Yttrium Stabilized Zirconia (YSZ) sol-gel precursor. This results in YSZ with nanochannel-shaped porosity with diameter of ~220 nm in diameter. Moreover, the deposition of nickel catalyst is controlled by the presence of nickel precursors in the fibres. Therefore, we ensure a high porosity with large surface area and placement of the catalyst on its most active site.

As a result, the state-of-the-art technique of using pore formers is improved by increasing the surface area and controlling the catalyst deposition. This makes the present architecture promising for Solid Oxide Fuel Cell (SOFC) anodes. Fig. 1a shows the templated nanochannels covered with NiO nanoparticles.

Nanofibres

In this case, a mixture of YSZ sol-gel precursor and polymer was electrospun. Ceramic nanofibres were formed after annealing the green matrix. These had an average diameter of ~560 nm with a length up to several μm.

Subsequently, the samples were infiltrated with nickel precursor such that the YSZ fibers were covered with NiO nanoparticles as shown on Fig. 1b. Such a configuration is interesting for SOFC anodes.

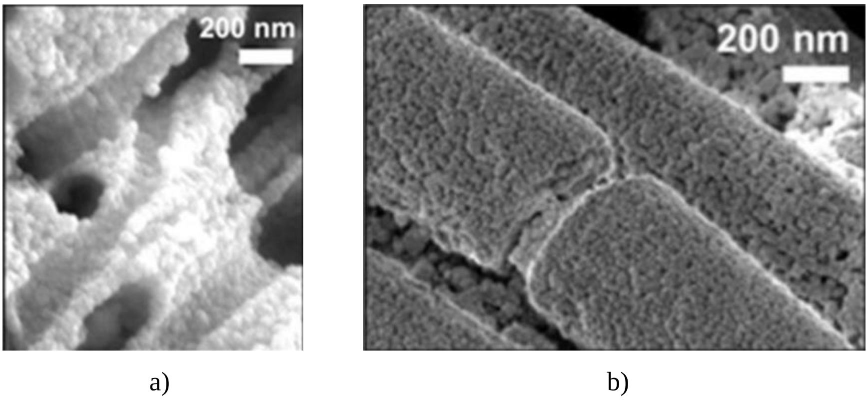

Figure 1. Templated YSZ nanochannels covered with NiO nanoparticles (a), YSZ nanofibers covered with NiO nanoparticles (b)

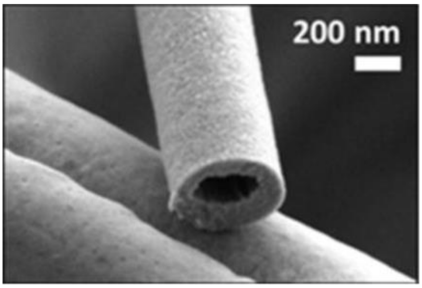

Figure 2. YSZ nanotubes

Nanotubes

The electrospinning setup can be modified in order to spin two concentric fibres, i.e. coaxial electrospinning. If the inner fibre is a polymer immiscible with the outer precursor-polymer mix then ceramic nanotubes can be formed after annealing of the green matrix. The resulting nanostructure, presented in Fig. 2, has an average inner diameter of ~230 nm and an average outer diameter of ~530 nm. The porosity and morphology of the fibres can furthermore be tuned by selected heat treatments. This configuration can provide a superior architecture for support of a heterogeneous catalysis due to its large surface area.

Summarizing, we presented a method capable of making different nanostructured materials in a low cost and facile manner.

A29

ULTRATHIN HIGHLY PROTON(-CONDUCTING) OXIDES FOR WATER ELECTROLYSIS AT INTERMEDIATE TEMPERATURES

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A current major challenge is the development of sustainable and clean energy sources as well as the storage of the produced energy. Solid oxide fuel cells (SOFC) are considered to be a promising technology for power generation due to their high efficiencies and fuel flexibility. If an SOFC is run in reverse mode it is called solid oxide electrolysis cell (SOEC) and hydrogen is produced. In this way energy can be converted from electrical to chemical energy and thus be stored efficiently. Y-doped $BaZrO_3$ (BZY) has found increased use as a proton conducting electrolyte in SOFCs since it offers advantages in terms of high bulk conductivity at lowered temperatures (350–600 °C) and since it shows good chemical stability, especially towards CO_2. By doping with Y oxygen vacancies are created allowing for the incorporation of water into the crystal lattice (resulting in the formation of mobile protons). For the SOEC process the use of proton conducting electrolytes is advantageous since hydrogen is produced at the cathode side of the cell and is therefore not diluted with water (as opposed to oxygen conducting electrolytes), avoiding secondary purification. The challenge of the current work is to produce ultrathin dense films of BZY to reduce the ohmic resistance and thus to lower the operation temperature for the SOEC application. For this purpose thin films of BZY were produced by chemical vapor deposition and compared to materials made via solid state reactions. The stoichiometry of the samples was verified by X-ray photoelectron spectroscopy (XPS) and the formation of single phase products confirmed by X-ray diffraction (XRD). In addition electrochemical impedance measurements were carried out to investigate the materials' conductivity.

A30

FREEZE GRANULATION FOR FABRICATION OF TRANSPARENT YTTRIUM ALUMINATE CERAMICS

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In the last years a considerable increase in the number of devices equipped with lasers applied in various areas of everyday life and industry is observed. Therefore, an intensive research works are ongoing for preparation of new materials for the use in laser

technologies. Particular interest is paid to polycrystalline materials produced by ceramic technology. They are known to be more advantageous than single-crystals because of shorter manufacturing time, a wider size and shape range, and a higher dopant level incorporated into matrix. However, numerous studies show that full elimination of porosity to reach laser-quality of ceramics only seems to be a simple process. It is well known, that for fabrication of transparent ceramics all preparation steps are of great importance. The most crucial seems to be shaping. If the green sample has wide, bimodal pore size distribution, elimination of porosity during sintering is very difficult. It is desired to fabricate green samples with the smallest possible porosity volume, pore size less than the size of the primary particles, and particularly a monomodal distribution of the porosity. Such is believed to be available when a freeze granulation and following freeze drying of properly composed slurries are used. This method offers the possibility to eliminate the capillary forces in the granulation process, resulting in soft spherical granules with improved flowability, disintegrating into primary particles during compression molding.

This paper presents the results of application of freeze granulation for the production of transparent yttrium-aluminum garnet ceramics. Aqueous suspensions of alumina and yttria powders were composed basing on nanometric or submicronic grain size powders commercially available or prepared by precipitation. The relations between the suspension composition (solid content, amount of plasticizer and dispersant), granulate properties (bulk density, morphology) and final properties of ceramics (microstructure, optical transmission) were studied.

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A31

RARE-EARTH CO-DOPANT EFFECT UPON THE STRUCTURE OF SOL-GEL DERIVED INORGANIC LUMINOPHORES

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In the last decades rare-earths gained more and more attention due to their essential role in fabrication of permanent magnets, lamp phosphors, catalysts, rechargeable batteries, information displays, electroluminescent and optoelectronic devices and more recently, radiation detectors in medical imaging systems [1–4]. The sol-gel technique is one of the most used methods in synthesis of materials with controlled composition, morphology and texture [5,6]. Combining the opportunities and advantages offered by sol-gel method and the rare earths elements both crystalline and amorphous materials properties could be improved. In present work it will be presented information about the influence of Eu^{3+}, Ce^{3+} and Tb^{3+} (co-)dopants upon amorphous silica and willemite structure, morphology and luminescent properties. The obtained crystalline materials were characterized by using X-ray diffraction and neutron diffraction; thermal stability by thermal analysis; textural properties by N_2 adsorption/desorption; morphology by electron microscopy techniques; chemical composition by FT-IR; luminescent properties by UV-visible and photoluminescence spectroscopy.

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A32

RAMAN SPECTRA OF $BaTiO_3/NiFe_2O_4$ MULTILAYER THIN FILMS

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$BaTiO_3/NiFe_2O_4$ multilayer thin films were obtained by spin coating deposition technique of precursor sols at 3000 rpm for 30 sec, using single crystal silicon (400) as substrates. Precursor sols were obtained by sol-gel synthesis. Titanate sol was prepared by using $BaCO_3$ and titan-butoxide as precursors, with glacial acetic acid as a solvent. For ferrite sol, $Ni(NO_3)_3\times6H_2O$ and $Fe(NO)_3\times9H_2O$ were used as precursors with 2-methoxyethanol as solvent. Each layer was annealed at 500 °C for 5 minutes, while final thermal treatment was at 900 °C for 30 minutes. Structure changes were investigated by Raman spectroscopy. Raman measurements were carried out in backscattering geometry using the DPSS (Diode Pumped Solid State) green laser, as excitation source, emitting 532 nm with maximum power 10 mW coupled with 50LDX objective and 5 cm^{-1} spectral resolution. The spectral range for taken measurements of

DXR Raman Microscope (Thermo Scientific Fisher) is 50–3500 cm^{-1}, CCD camera was used as a detector. The aim of this work is to analyze accurately the vibration spectra of multilayer of 500 nm thickness with a special regard to the comparison with the vibrational spectra of the starting compounds $BaTiO_3$ and $NiFe_2O_4$ in nano-powdered forms. Our results indicate that $BaTiO_3/NiFe_2O_4$ multilayer thin films exhibits some of the characteristic lattice modes of the ferroelectric phase of $BaTiO_3$ with tetragonal symmetry $4E$(TO+LO) $+3A_1$(TO+LO)$+B_1$(TO+LO) [1] and all Raman active mode of cubic spinel structure ($A_{1g}+E_g+3T_g$) of $NiFe_2O_4$ [2].

Acknowledgements This work was supported by the Ministry of Education and Sciences of the Republic of Serbia (Project no. III 45021).

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A33

PRESSURELESS SINTERING OF TITANATE NANOWIRES: SURFACE vs. BULK DIFFUSION

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Much has been learned on the coarsening behavior of nano TiO_2, mainly because of recent studies almost exclusively addressed to the coarsening of nearly spherical, isotropic nanoparticles. Indeed, the degree of the particle anisotropy can induce a severe shape-dependent variation in properties of matter which raises the question how the coarsening of anisotropic particles proceeds at the interfaces and in the bulk ($\leq$ 100 nm from the interface). In order to understand the sintering behavior of elongated titanate based 3D coatings we have studied the temperature dependent structural and geometrical evolution of its building "bricks", the individual titanate nanowires. In this talk the phase transformation kinetics and the external morphology of porous films, as well as individual titanate nanowires on SiO_2 surface will be discussed based on the interpretation of AFM, SEM and XRD data. The elongated titanates were coarsened at temperatures far below the melting temperature of TiO_2. Two temperature dependent geometrical transformation regimes were identified. In regime I (the titanate to anatase recrystallization from room temperature to 873 K) significant shrinkage of the height of the nanowire was observed. In regime II, (sintering temperature: 873–1273 K) altering titanium oxide diffusion mechanism was observed on the surface as compared to the bulk. The temperature dependent surface area evolution of titanium oxide nanowires on SiO_2 appreciably differs from the classical Ostwald ripening surface diffusion model.

A34

THE EFFECT OF SILICA SOL INFILTRATION ON THE LOW TEMPERATURE DEGRADATION AND MECHANICAL PROPERTIES OF 3Y-TZP CERAMICS

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Yttria partially stabilized tetragonal zirconia (3Y-TZP) is becoming increasingly popular as an alternative material in restorative dentistry. One of the issues concerning tetragonal zirconia is its sensitivity to low temperature degradation (LTD) process, i.e. ageing. [1]. LTD is a slow transformation of metastable tetragonal to a more stable monoclinic phase in the presence of moisture at tempeartures lower than 400 °C [1]. The transformation initiates on the surface and proceeds into the bulk of the ceramic, which may result in microcracking, grain pull out, and finally surface roughening, which normally leads to strength degradation depending on the transformed layer thickness.

LTD resistance of 3Y-TZP can be improved by doping with other oxides. In fact, commercial 3Y-TZP powders, such as E-types or TZ-PX-242A (Tosoh, Japan) contain 0.25 and 0.05 wt.% of alumina, which lowers the sintering temperature and improves the aging properties of the material. Though, the mechanism behind the suppressed ageing is not yet clear. It was also reported that the addition of a small amount of silica to 3Y-TZP decreases the internal stress by the presence of rounded grains, which improves the LTD resistance of t-zirconia [2].

The systematic study evaluating the effect of costabilization of t-zirconia with alumina and silica was not performed yet.

In the present work, the effect of silica and/or alumina on the ageing resistance and mechanical properties of 3Y-TZP ceramics was evaluated in order to obtain deeper understanding between their distinctive or combined contribution to the ageing resistance. Specimens were prepeared from commercialy available powders, containig different amounts of alumina (0, 0.05 and 0.25 wt.%). Additionly, silica-doped specimens were prepared by the infiltration of silica sol into the pre-sintered porous 3Y-TZP disks. After final sintering ceramic one parallel set of specimens were subjected to *in vitro* accelerated ageing at 134 °C in deionized water for various times. Finally, all the specimens were verified for density, phase composition, mean grain size, flexural strength, Vickers hardness and indentation toughness.

Sintered ceramics were nearly dense (> 98 % T.D.). The results of transmission electron microscopy and energy dispersive X-ray spectroscopy analyses revealed that silica was mainly present as an amorphous phase located at triple grain junctions. The presence of silica in alumina-free 3Y-TZP greatly increases the resistance to LTD. The addition of small amounts of silica to alumina-containig 3Y-TZP futher improves the ageing properties of 3Y-TZP without affecting flexural strength, Vickers hardness and indentation toughness. Also it was found, that 0.25 wt.% of alumina has the same effect on LTD of tetragonal zirconia as ~ 0.25 wt.% of silica. The results show that each dopant has its own mechanism behind the LTD suppression and when combined they add up the resistance.

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A35

EB-PVD 1Ce10ScSZ FILMS FOR SOFC APPLICATION

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Now requirements to properties of materials often cannot be performed using known materials. One way to improve the properties is the structural optimization current materials. In many studies reported about growth of different properties of materials during transition to nanoscale condition [1].

Electron beam physical vapor deposition technology is well developed for the deposition of thermal barrier coatings based on zirconium dioxide [2]. Therefore, its application to form electrolyte film is very promising. Moreover, formed structure has natural textured condition, and can be controlled by changing of technological parameters of deposition.

In work is carried out study of mechanical properties of thick 10Sc1CeSZ films (6–60 μm) deposited on porous anode substrate at different temperatures of deposition and annealed at different temperatures. Also it was studied influence of technological parameters and the quality of the substrate surface to form the structure of deposited films.

The study thin film structures with SEM and TEM has shown column and lamination structure of deposited films and good adhesion film to components of the anode substrate.

It was found that the elastic modulus changes over the film thickness. The area bordering anode has the highest value of modulus especially for low annealing temperatures. Depending on the annealing temperature the modulus takes values of 120–140 GPa instead of 100–120 GPa near the surface. Such the distribution of modulus might resulted from features of solidification of films deposited from the vapour phase with electron beam and distribution of chemical composition along the thickness of film.

It was shown that nanoscale EB-PVD film had an order of magnitude higher total electric conductivity than films made with screen printing method.

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A36

NANOPARTICULATE-BASED $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ CATHODES FOR MICRO-SOLID OXIDE FUEL CELL APPLICATION

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In this work, nanocrystalline $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) powder with ultrafine microstructure and high specific surface area (60 m^2/g) was synthesized via salt-assisted spray pyrolysis method. The XRD results show the formation of a nanocrystalline single phase perovskite structure. LSC nanoparticles with a low degree of agglomeration were stabilized in water-based dispersion and the particle size distribution measured at pH=10 shows the medium particle diameter of 44 nm. Nanoparticulate cathode thin films of LSC and LSC-GDC (Gadolinium doped ceria) with thicknesses between 150 and 500 nm were prepared via single step spin coating on yttria stabilized zirconia (YSZ) substrates. Gadolinium doped ceria (GDC) film was applied to YSZ substrate to avoid the chemical reaction between cathode and electrolyte. The performance of the thin film cathodes was evaluated by high temperature impedance spectroscopy on symmetrical samples. LSC cathode thin films (250 nm) with 30 wt.% GDC content exhibit the lowest area specific resistance (ASR) values of 0.32, 0.78 and 2.04 $\Omega\cdot cm^2$ in ambient air at 650, 600 and 550 °C, respectively. The future work will focus on detailed chemical and microstructural analysis of the nanoparticulate LSC and LSC-GDC thin film cathodes to gain more understanding on the electrochemical processes within the functional layers. The synthesis method will be modified to obtain LSC nanoparticles with smaller grain size, which can improve the electrochemical performance of the LSC electrodes. Furthermore, long-term stability and degradation of the material will be investigated.

A37

PROPERTIES OF PEROVSKITE STRUCTURE DOPED STANNATES

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Alkaline-earth stannates, $ASnO_3$, is a group of perovskite oxides. One of the most interesting members of this group is barium stannate. Undoped $BaSnO_3$ is a wide-gap semiconductor with a bandgap larger than 3.1 eV. The presence of oxygen vacancies compensated by reducing a fraction of Sn^{4+} into Sn^{2+} renders it an n-type semiconductor. Its electrical properties can be supplementary modified by A- and/or Sn- cation substitution with iso- and non-isovalent elements. Dominant charge carriers concentration in doped stannates is a complex function of dopant type and concentration, oxygen and hydrogen partial pressure and temperature. As a result, they may conduct electrons, holes, oxygen ions or protons. What makes a picture more multifarious and remarkable, doping influences also the charge carriers mobility because of alteration of lattice structure, defect energies, electronic disorder, microstructure etc.

A38

TECHNOLOGY FOR CREATING POROUS CALCIUM PHOSPHATE GRANULES

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Calcium phosphate (CaP) ceramic materials such as hydroxyapatite (HA) and *β*-tricalcium phosphate (*β*-TCP) have been widely used as bone substitution material. CaP are similar to the mineral phase of human hard tissues, therefore these materials possess excellent biomaterial properties. CaP ceramics mostly are applied in orthopedics as block implants, granules or coating, either dense or porous.

Biomaterials with porous structure have certain advantages compared to dense. Porous network improves tissue attachment to the implanted body. Pores provide a mechanical interlock leading to a firm fixation of the implanted material. Bone tissue easily grows into the implant and increases implanted CaP materials strength. Best tissue adhesion is achieved when pores are in sizes 50–100 μm or according to some researchers even 250–500 μm to improve osteoblast colonization. Other requirements for porous implant bodies include pore interconnectivity for osteoblast cell penetration and surface roughness for cell adhesion.

Granular implant materials are easier to handle than solid bodies. Extra fine tuning of implant shape isn't necessary, because granules can easily accommodate practically any embodiment. Multiple methods for producing porous CaP granules are known.

Porosity is induced either by using foaming agents or burning out polymer filler. Results for porous CaP granule fabrication using lyophilisation and templating method will be presented. Our aim is to present convenient method for producing CaP granules.

A39

HYDROXYAPATITE NANOPOWDERS: STUDY OF POSSIBILITY FOR PREPARATION OF DENSE NANOSTRUCTURED BIOCERMICS BY PRESSURELESS SINTERING

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Preparation of hydroxyapatite bioceramic materials, widely used as implant materials for bone tissue reconstruction, in the form of fully dense nanostructured ceramics attracts great attention because of improved mechanical, biological and optical properties ascribed to such microstructural design. One of the first premise for preparation of nanostructured sintered materials should be synthesis of nanopowders, but a lot of studies indicated that this is far from enough for low-temperaure densification yielding to fully dense nanostructured materials. Overcoming the gap in understanding of sintering behavior of hydroxyapatite nanopowders is important for broadening of their application spectra.

In this study, different stoichiometric hydroxyapatite nanopowders were prepared by chemical precipitation and hydrothermal processing. Extensive caharacterization of prepared powders have been done by different instrumental techniques describing structural, chemical and morphological ascpects of materials. Densification behavior was monitored by heating microscopy, while pressureless, conventional and two-step sintering, techniques have been used to densify green bodies.

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PREPARATION AND CHARACTERIZATION OF POROUS SILICON NITRIDE FOR BIOAPPLICATIONS

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The aim of present work is preparation and characterization of porous silicon nitride with properties similar to the human trabecular bone.

The pore structure of highly porous trabecular bone is formed by interconnected large pores of approximately 300–1000 µm. The similar structure of ceramics was attained by the replica method using polyurethane sponge which was initially impregnated with ceramic suspension. Porous ceramics have been prepared in two ways, namely as air-sintered silicon nitride (ASSN, porosity 65 vol.%) and sintered reaction-bonded silicon nitride (SRBSN, porosity 73 vol.%). Also the multiple infiltration was tested in order to improve strength.

The prepared porous ceramics were characterized using same methods as for bone samples – density measurement, SEM, XRD analysis, XRD-microtomography and Hg porosimetry. Also the mechanical properties as hardness (H), elastic modulus (E) and compressive strength (σ) of prepared materials have been measured and the obtained values were compared with the values of bone samples. The results show that the mechanical properties of air-sintered silicon nitride (H = 0.46 ± 0.07 GPa; E = 11.4 ± 0.9 GPa; σ = 3.2 ± 1.8 MPa) are very close to the values measured for bone (H = 0.51 ± 0.03 GPa; E = 11.2 ± 0.9 GPa; σ = 4.7 ± 1.6 MPa) contrary to reaction bonded silicon nitride ceramics (H = 6.3 ± 2.3 GPa; E = 92.1 ± 21.3 GPa; σ = 5.95± 0.4 MPa).

Both types of the materials fulfilled the microstructural requirements for tissue replacement, moreover their non-cytotoxicity was proved by measuring yellow tetrazolium MTT proliferation assay using human fibroblast cell line. These preliminary results are promising and the prepared porous ceramics can be a potential biomaterials for bone replacement.

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SCALE-UP AND WET PRECIPITATION SYNTHESIS OF β-TRICALCIUM PHOSPHATE

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β-Tricalcium phosphate (β-TCP) is calcium phosphate (CaP), which is one of the most used implant materials in the reconstructive surgery to repair damaged hard tissues. CaP has excellent properties due to bioactivity of hydroxyapatite and bioresorbability of β-TCP. Apatitic tricalcium phosphate (ATCP) $Ca_9(HPO_4)(PO4)_5(OH)$ is a calcium orthophosphate that transforms into β-tricalcium phosphate $Ca_3(PO_4)_2$ by heating above 750 °C.

In the last twenty years the main interest is devoted to the CaP synthesis. The progressive requirement for calcium phosphate bioceramics promotes scale–up laboratory synthesis. In this study β-TCP was prepared by wet chemical precipitation method from calcium oxide (*Fluka, Germany*) and ortophosphoric acid (*Sigma-Aldrich, Germany*) solution. Product composition depends on many factors during the synthesis procedure, such as quality and concentration of reagents, addition rate of phosphoric acid, temperature, synthesis ending pH and mixing conditions. The precipitation process is the most reported method for preparing CaP powder. Process is simple, low cost and suitable for industrial production.

X-ray diffractometry (XRD) was used to analyze phase composition of obtained bioceramic samples. Fourier-transform infrared spectroscopy (FT-IR) was used to determine the various functional groups in the sintered calcium phosphate samples. Scanning electron microscopy (SEM) was used to characterize the morphology of products.

Mixing has significant impact on the phase composition of the calcium phosphate product by wet precipitation synthesis method. With improved mixing it is possible to obtain up to 75 % more product mass in the same volume by using increased concentration $Ca(OH)_2$ suspension in laboratory scale reactor (LSR). By using a developed method it is possible to obtain 0.1 kg of pure apatitic tricalcium phosphate powder in laboratory scale reactor (LSR) (molar concentration of calcium hydroxide suspension is 0.5 mol/l and phosphoric acid - 2.00 mol/l) compared with previous laboratory reactor parameters - 28 g ATCP.

By using a developed method it is possible to obtain 0.5 kg of pure ATCP powder in pilot scale reactor (PSR) (molar concentration of calcium hydroxide suspension is 0.50 mol/l and phosphoric acid - 2.00 mol/l) compared with laboratory reactor - 0.1 kg ATCP. It was investigated that mixing has noticeable influence on phase composition of precipitation product. Other key factors for successful realization of laboratory scale *β*-TCP synthesis are molar concentration of calcium hydroxide suspension and addition rate of ortophosphoric acid.

A42

INORGANIC MATERIALS AS SUPPORTS FOR BIOMOLECULES: IMMOBILIZATION OF β-GLUCOSIDASE ONTO MESOPOROUS SILICA

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Inorganic materials have attracted many researchers' attenion because of their unique properties: highly ordered structure, uniform pore size and high thermal stability. Mesoporous materials are potential candidates that could be used as carriers for biomolecules in many areas such as catalysis, sensors, medicine and drug delivery. Even more, characterisctics of biocatalysts such as activity, stability and reusability can be improved by their immobilization on solid supports reflecting in higher catalysts productivity. Thus, current trends in biotechnology have promoted the usage of immobilized enzymes for a wide range of applications.

Considering that enzymatic modification of cellulose is a field of great interest, immobilization of cellulolytic enzymes complex might be beneficial. Among this complex, immobilization of β-glucosidase could be of special interest due to its limiting role in hydrolysis by preventing product inhibiton. Thus, the aim of this work was to investigate conditions and mechanisms of immobilization of new commercial β-glucosidase onto mesoporous silica support using physical adsorption and covalent binding.

Several silica supports with different characteristics in respect of pore size, total pore volume and specific surface area were screened for immobilization of β-glucosidase. Conditions suitable for physical adsorption were investigated along with influence of salt and detergent addition, which indicated mechanism of β-glucosidase adsorption onto mesoporous silica. Covalent binding of β-glucosidase onto silica support was conducted via glutaraldehyde which was previously bonded to silanized silica support. Covalently bonded β-glucosidase had higher yield of immobilized enzyme as well as higher activity and substrate affinity in comparison to the one physically adsorbed. In addition, covalent binding did not considerably changed pH and temperature stability of obtained biocatalyst which retained more than 70% of its activity after 10 cycles of reuse.

A43

PHASE EQUILIBRIA AND PROPERTIES OF SOLID SOLUTIONS IN THE SYSTEM CeO_2-Eu_2O_3 AT 1100-1500 °C

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Systems with ceria and europium oxide are perspective for the development of laser and other optoelectronic components, ceramics for the thermal barrier coatings and intermediate temperature solid oxide fuel cells. Doped ceria is a candidate material for application in controlling air-to-fuel ratio in automobile exhaust. This system can be widely used in atomic power engineering for creation of the safe disposal techniques for the nuclear waste and development of advanced and new generation of reactors.

The objective of this work is to investigate the phase relations in the binary system CeO_2-Eu_2O_3 at 1100–1500 °C in air in the whole concentration range. Powders of $CeO(NO_3)_2$ and Eu_2O_3 (99.99 %) were used as raw materials. The samples were prepared in steps of 1 and 5 mol % from nitrate solutions with their subsequent evaporation and decomposition at 1000 °C for 2 h. Thermal treatments were carried out in the furnaces with heating elements based on H23U5T (1100 °C for 15960 h) and $MoSi_2$ (1500 °C for 170 h) in air. The phase compositions were investigated by X-ray diffraction, microstructural phase and electron microprobe X-ray analyses.

The study of solid state reaction of CeO_2 (fluorite-type, F) and Eu_2O_3 (monoclinic modification of rare-earth oxides, type, B) at temperature 1500 °C showed that three types of solid solutions based on monoclinic modification of B-Eu_2O_3, cubic modifications of F-CeO_2 and C-Eu_2O_3 in the CeO_2-Eu_2O_3 system. These solid solution regimes were separated from end to end with the two-phase fields: (C + B) and (C + F). The boundaries of the homogeneity fields for the solid solutions based on F-CeO_2, B- and C-Eu_2O_3, as well as lattice parameters of the unit cells for solid solutions F-CeO_2, B- and C-Eu_2O_3 were determined.

The refined solubility of Eu_2O_3 in F- modification of CeO_2 is about 25 mol% at 1500 °C (170 h). The lattice parameter of the unit cell varies from a = 0.5409 nm in pure CeO_2 to a = 0.5423 nm in the sample containing 25 mol% Eu_2O_3. The solubility of CeO_2 in cubic C-modification europium oxide attain ~50 mol% CeO_2 (1500 °C). The lattice parameters of the unit cell C phase varies from a = 1.0868 nm in pure Eu_2O_3 to a = 1.0860 nm for the solid solution of boundary composition. The solubility of CeO_2 in monoclinic B- modification europium oxide is about ~1 mol% CeO_2 at 1500 °C. The lattice parameters of the unit cell B phase varies from a = 1.4042, b = 0.3638, c = 08746 nm, $\beta = 100°7'$ in pure Eu_2O_3 to a = 1.6388, b = 0.3626, c = 0.8644 nm, $\beta = 97°1'$ (1500 °C) for the solid solution of boundary composition. It has been found that the boundaries of the B- phase homogeneity field became narrower but the extension field for the solid solutions based on C-Eu_2O_3 became wider when temperature decreased of to 1100 °C.

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CHARACTERIZATION OF Zr CO-SPUTTERED DLC FILMS

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Diamond-like carbon has been widely studied in the past years for the automobile, electrical and biomedical field. However, it is well known that typically DLC presents high internal stress which significantly limits the adhesion of the coating to metallic substrates, especially under highly corrosive environment. In fact, it has been found that the main problem of DLC coatings is that the interface between substrate and functional coating can suffer a corrosion process by the penetration of body liquid through imperfections or pinholes that may exist on coatings surface. The use of transition metal (Zr, Ti, Cr, etc.) co-sputtered amorphous carbon (a-C) films has been widely studied as one possible solution for such problems due to its peculiar structure based on carbibe nanograins embedded into the amorphous carbon matrix capable to create a catalysis effect on the formation of the DLC film.

In this study Zr-DLC coatings were deposited by dc unbalanced magnetron co-sputtering. Two different atmospheres were used for the production of non-hydrogenated films (Ar) and hydrogenated films (Ar/CH_4). The Zr content was varied [0 to 9 at.%] with the increase of the number of pellets embedded in the erosion area of the graphite target. To improve adhesion between film and substrate a functional gradient Ti based layer was deposited (~450 nm).

The coating structure was characterized using XRD, XPS and Raman spectroscopy. It was found that increasing Zr content the films could be characterized as nanocomposite with ZrC nano-crystalline phase embedded into the amorphous carbon matrix. Pure DLC films show a very low adhesion; however, doping with Zr led to much higher critical load values obtained by scratch test and better qualitative adhesion estimated from Rockwell indents.

A45

ATTEMPTS TO DEPOSIT SILICON-CONTAINING COATINGS ON Ti-46Al-8(Ta/Nb) FOR HOT CORROSION PROTECTION

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Advanced alloys based on intermetallic phases γ-TiAl and α_2-Ti_3Al draw scientific interest as lightweight structural materials with potential applications in aircraft and automotive industry. Compared with the state-of-the-art nickel- or iron-based alloys, their density is almost twice lower. Moreover, they are characterized by good oxidation resistance up to 700–800 °C. Potential applications may, however, be limited by insufficient resistance to hot salt corrosion. A coating containing silicon is expected to protect the alloy against harmful effects of salt deposits, due to the formation of SiO_2 which is stable in the molten salt environment.

In this work we tried to undertake the problem of hot corrosion prevention by depositing layers based on titanium silicides in a pack cementation process. Alloy samples were embedded in powder pack consisting of Al_2O_3 and Si in a mass ratio of 3:1 with halide activator. There were several attempts of pack cementation process with varying type and concentration of activator and deposition time. Temperature was always 850 °C and argon was used as inert gas. Post-deposition examination of samples included scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDS/EDAX). Some samples were contaminated with NaCl and Na_2SO_4 and oxidized in thermal cycling conditions. Thermogravimetric method was used to evaluate protective properties of the coatings.

In the initial trials the coatings were porous, brittle and non-adherent to the substrate. Apparently, titanium silicide layers were formed at the cost of titanium diffusing outward from the alloy, which gave rise to interfacial porosity. In the next series of experiments, a titanium-containing interlayer was deposited to prevent loss of this element from the alloy. The applied procedure helped reduce porosity and increased

coating adhesion. Oxidation studies gave promising results. Further improvements of coating deposition are possible and the investigations are underway. The best coatings will be tested for hot corrosion resistance.

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A46

SILVER SEGREGATION TO SURFACE IN Ag-DLC THIN FILMS DEPOSITED BY MAGNETRON SPUTTERING

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Keywords: Ag-DLC thin films, surface segregation, XRD, SEM, GDOES, XPS

Diamond like carbon coatings combine high wear resistance with low friction coefficient; furthermore carbon based coatings are biocompatible, which has prompted their use in different biomedical devices, such as hip joints, knee joints, heart valves, coronary artery systems and ureteral stents. Silver is claimed to be an effective antibacterial agent, able to avoid microbial colonization, thus enhancing the biomaterials lifetime. Several reports state that silver clusters are able to diffuse in carbon-based coatings even at room temperature, which leads to a non-uniform Ag distribution across the coating thickness. The aim of this work was to evaluate the stability of Ag doped DLC coatings with time. The coatings were produced by magnetron sputtering and the evolution of the in-depth Ag distribution was studied along time using glow discharge optical emission spectroscopy (GDOES). Three different Ag-DLC thin films (16 at.% of Ag) were analyzed: two films with different thicknesses (250 nm and 1200 nm) and a 250 nm (Ag-DLC) film covered with a 90 nm carbon barrier layer. For comparison purposes, a silver thin film covered with a similar carbon barrier layer was also studied. The evolution of the Ag particle size/ distribution with time was analyzed by X-ray diffraction (XRD) and SEM. X-ray photoelectron spectroscopy (XPS) was performed on Ag-DLC coating without carbon layer for understanding the binding state of Ag atoms.

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THICK DIELECTRIC FILMS PRODUCED BY ELECTROPHORETIC DEPOSITION

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Electrophoretic deposition (EPD) from colloidal suspensions was utilized for the preparation of lead zirconate titanate films (PZT) on PZT based substrates. The present process is developed as a convenient forming process for the development of devices based on thick ceramic films. The deposition parameters - using EPD - such as colloidal parameters, deposition voltage and deposition time and the post process parameters, such as drying velocity and sintering will be controlled. Conductive materials are customarily used as deposition substrates, but the possibility of depositing on semiconductors (SC) has recently been demonstrated in this laboratory [1]. This work wants to continue the research started by Baldisserri *et al*. that puts emphasis on the analysis of current transients during constant-voltage deposition as a diagnostic tool for the assessment of some crucial features of the EPD process [2,3]; the correlations between the above parameters and final microstructure, by checking the salient features like the film adhesion, compaction and functionality, will be investigated.

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A48

MECHANOCHEMICALLY ASSISTED SOLID-STATE SYNTHESIS OF Cu SUBSTITUTED THERMOELECTRIC SODIUM COBALTITE OXIDE

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In the last decade there has been an explosion of interest for materials with good thermoelectric properties. The ceramic sodium cobaltite became a promising candidate for potential thermoelectric applications, because of its large thermopower and relatively low resistivity. Polycrystalline samples of $NaCo_{2-x}Cu_xO_4$ (x=0, 0.01, 0.03, 0.05, 0.1) were prepared using mechanochemically assisted solid state reaction method. Bulk samples were prepared by pressing into disc-shaped pellets and subsequently subjected to a heat treatment at 880 °C in inert argon atmosphere. Changes in structural characteristics and particle morphology, caused by Cu substitution, were characterized using X-ray powder diffraction analysis and scanning electron microscopy, respectively. The results of ICP analysis showed that the compositions of the samples in the final products were very close to the nominal compositions. From the results obtained in this study, observed changes in microstructure were correlated with changes in the lattice parameters, indicating the influence of Cu ion incorporation in $Na_xCo_2O_4$ crystal lattice.

A49

SYNTHESIS AND CHARACTERIZATION OF SnO_2 FILMS

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Main goal of this research was to synthesis of tin oxide sol and deposit film of SnO_2 on α-alumina substrate, which is known to possess good sensing abilities on the detection of reduction gases such as H_2S, CO and CO_2. Tin oxide sols were synthesized by hydrolysis of $SNCl_2$ using 2-methoxy ethanol as a solvent system. The reaction carried out at room temperature and concentration of the precursor solution was set to 1 M cation concentration and all other processing parameters were remained unchanged. Tin oxide films were fabricated dip-coating as a chemical deposition technique on previously cleaned α-alumina substrates. Morphology and structure of the fabricated film were characterized by scanning electron microscopy, X-ray diffraction and EDX techniques. Inter-digitated capacitive (IDC) circuit was prepared on the deposited tin oxide films using ink-jet printing technique. Dielectric properties of the obtained tin oxide thin films were determined by impedance analyzer.

A50

PROSPECTS FOR CREATION OF RADIO ABSORBING CERAMIC MATERIALS

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Electromagnetic radiation in the range of radio frequency leads fatigue, disorders of the central nervous system, has an adverse impact on the technical condition of the electronic systems under conditions of exceeding the allowable values.

Currently, in order to reduce the impact of electromagnetic radiation reflecting, absorbing, and composite materials are used. The phenomenon of electromagnetic reflections when using conductive screens has an adverse effect associated with the formation of re-scattered waves, which affects shielded object, causing a change in its parameters. Based on the foregoing, at present, there's the task of materials scientists to create new materials and coatings which absorb electromagnetic radiation.

The authors of the work found the following based on literature search and patent research:

- radio absorbing ceramic (RAC) are mainly used to reduce the harmful effects of electromagnetic radiation on human beings and electronic devices, masking of radar detection of various objects (missiles , tanks , aircraft, surface ships, etc.), shielding radio receiver in order to reduce their impact on radio; for special equipment of cameras used for testing of radio-electronic equipment, protection of technical and biological objects by electromagnetic weapons , etc.;
- Recent developments in the field of RAC are aimed in order to increase the intensity of energy absorption of electromagnetic waves, widening the range of working height , weight and increase strength and stability in the conditions of high temperatures generated in flight by missiles and planes;
- Key areas of advanced technology for RAC creation were identified: deposition (magnetron, vacuum, innova -plasma, etc.), smearing a thin layer, and so on.

According to provided analysis, it is found that the promising direction of creating RAC materials is their application for the absorbing phase of ferromagnetics, ferroelectrics and ferrites.

Given the above, the development of new RAC materials is an actual problem of modern materials.

A51

LOW TEMPERATURE SINTERING OF HIGH VOLTAGE ZnO VARISTORS

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Nanosized varistor constituents: Mn- and Co-doped ZnO, α-Bi_2O_3 and Sb_2O_3 in the mass ratio 70:25:5 were used for preparation of high voltage varistors. The constituents were suspended in absolute ethanol, homogenized with an ultrasound probe and dried at 60 °C for 45 minutes. The obtained powder mixture was uniaxially pressed at 1.5 t/cm^2, then the pellets were sintered in a preheated furnace at 770 °C for 1 hour and slowly, furnace cooled. Obtained varistor samples were characterized by XRD and SEM, as well as by electrical measurements. XRD results revealed that sintered varistor consisted of ZnO, γ-Bi_2O_3 and a pyrochlore, $Bi_3Sb_3Zn_2O_{14}$, in the 68:17:15 ratio. The mean sintered samples density was 97 % of the theoretical value. A satisfactory density was obtained by sintering at low temperature for only 1 hour, due to the high reactivity

of varistor nanoconstituents. SEM micrographs showed fine grained microstructure with homogenous distribution of phases. Measured voltage-current characteristics confirmed the excellent electrical properties of the obtained varistors. Nonlinearity coefficients (α) in the current density ranges of 0.1–1 and 1–10 mA/cm^2 were calculated to be 71 and 51, respectively. The breakdown field (K_c) was established on 3150 V/mm and the leaking current (j_l) was 9,6 μA/cm^2.

A52

THE EFFECT OF COPPER ON THE PERFORMANCE OF TiO$_2$ PHOTOCATALYSTS FOR THE OXIDATION OF DYES ON CERAMIC COATINGS

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Functional ceramic coatings may contribute towards the resolution of a wide spread waste-water problem in textile industries which produce large volume of toxic and non-biodegradable dyes. Dyes effluents have caused serious environmental pollution problems worldwide. Various techniques have been developed to treat wastewater containing dye pollutants such as physical adsorption, biological methods, chemical methods and their combinations. The main disadvantage of these processes is the incomplete degradation of dyes. Of all tested the most promising has been proved to be that of photocatalysis. Titanium dioxide, is the most well-known photocatalyst, as an effective pollutant reducing agent but requires high-energy ultraviolet light (i.e. solar) to operate.

In this work we present an overview and recent advances on the synthesis and characterization of TiO$_2$ depolluting material doped with copper in different concentrations capable to absorb and activate under visible light irradiation. The crystal structure, particle size, morphology, and porosity were examined with an XRD-powder system, SEM, TEM and porosimetry respectfully. Surface morphology and elemental analysis of the samples were carried out using scanning electron microscopy (SEM) and an energy dispersive spectrometer (EDS). The microscopic nanostructures were observed by TEM. In this work, we report on the study the photo-catalytic activity on the degradation of dyes such as methylene blue (MB) and methyl orange (MO) in different pH on ceramic tiles. The photocatalytic activity of the copper doped TiO$_2$ on the degradation of MB has shown ~90% decolorization in 180min under visible light.

A53

PREPARATION, CHARACTERIZATION AND FUNCTIONAL PROPERTIES OF CaO CATALYST – INFLUENCE OF CALCINATION TEMPERATURE

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Recently there has been great interest in heterogenisation of transesterification reaction for biodiesel synthesis in order to reduce disadvantages of the homogeneous process. Heterogeneous transesterification is considered to be a green process, with no necessity for catalyst recovery and aqueous treatment steps resulting in waste water. Currently alkali and earth-alkali metals, having basic catalytic properties, are in the focus of the investigation. However, heterogeneously catalyzed transesterification generally requires more severe operating conditions, justifying further investigations on more active catalysts. High specific surface area, strong basic strength and high concentration of basic sites are characteristics of an active transesterification catalyst. In this work different pretreatment temperature influence on physico-chemical properties and catalyst activity was investigated. CaO catalyst was calcined at: 500, 700, 800, 900, 1000 and 1100 °C, following its characterisation by means of phase composition (X-ray diffraction), textural (low temperature nitrogen adsorption) and thermal properties (simultaneous thermogravimetric and differential thermal analysis), as well as strength and number of active basic sites (temperature programmed desorption of pre-adsorbed CO_2). Catalyst activity was tested by yield of methyl-esters formed in transesterification reaction and verified by gas-chromatography analysis. Reaction was performed in a glass laboratory batch reactor equipped with a magnetic stirrer and a cooler. Reaction parameters were kept constant during reaction as follow: methanol:oil = 6:1 molar ratio, catalyst loading 1 %mas, reaction time 2 h, reaction temperature 65 °C and rate of mixing 625 rpm. The results of catalytic activity are very well correlated with the catalyst acidic/basic properties, showing the importance of pretreatment conditions (optimal calcinations temperature).

A54

THE EFFECT OF MAGNETIC FIELD ON CATALYTIC PROPERTIES OF CHYMOTRYPSIN IMMOBILIZED ON MAGNETITE NANOPARTICLES

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At the present time, some attempts of the application of magnetic Fe_3O_4 nanoparticles as agents-intermediaries of localized control of biochemical reactions are known, in which radio frequency magnetic field can play a role of trigger which activates or interrupts/slows down an enzymatic reaction. The goal of this work was to investigate effects of magnetic field on catalytic properties of chymotrypsin immobilized on magnetite nanoparticles.

Nanoparticles of iron oxide Fe_3O_4 were coated with gold or functionalized with oleic acid, then different organic molecules (L-cysteine, lipoic, 3- mercaptopropionic acids, dodecanoic and PEG acid with HS-groups or copolymers PAA-PEG/PMA-PEG) were bound to these complexes, then the enzyme was attached.

To study the effect of magnetic field on catalytic properties, the reaction of hydrolysis of N-benzoyl-L-tyrosine-para-nitroanilide catalysed by chymotrypsin was used. In all samples (except containing dodecanoic and PEG acids) which were exposed to magnetic field the enzyme inactivation after each exposition was observed, even if the substrate was added after the expositions. That indicates the direct influence on immobilized chymotrypsin. The absence of any effect for the samples with dodecanoic and PEG acid with HS-groups can be explained by big length and flexibility of these molecules and weaker binding between nanoparticle and the enzyme molecule in this case.

Also the enzyme activity versus field intensity at the frequency of 50 Hz was studied. It can be mentioned that all series of activity-field intensity curves have maximum (corresponding to inactivation at the level of 30 ± 5%). The presence of maxima in these plots indicates the existence of competitive processes which appear as a result of magnetic field different intensity and influence the kinetics oppositely. The most probable reason for the observed effect is the change of active centers topology on the enzyme surface as a result of its deformation under applied forces.

Thereby, the effect of magnetic field on catalytic properties of chymotrypsin immobilized on magnetite nanoparticles, notably the slowdown of catalysed reaction, was found. From practical point of view it can give an instrument for drug delivery and remote dosage of their activity.

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A55

SYNTHESIS AND CHARACTERIZATION OF CORE/SHELL PARTICLES WITH DIFFERENT SHELL STRUCTURES

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Core/shell particles were synthesized by assembling of ferrite (Fe_3O_4, $NiFe_2O_4$, $ZnFe_2O_4$) and silica nanoparticles on the surface of monodispersed silica core particles (having size 0.4 mm) prepared by hydrolysis and condensation of tetraethylortosilicate. Optimal conditions for synthesis of silica core/Fe_3O_4 shell particles were found at pH 5.4. The obtained particles have superparamagnetic behavior above a blocking temperature of 25 K. Incorporation of nickel and zinc into ferrite structure could not be achieved at pH = 5.4, so the process was performed at higher pH in the presence of functionalized silica particles. Incorporation of nickel and zinc into ferrite structure was successful at pH above 7, however at higher pH the formation rate of ferrite particles becomes very fast and the self-aggregation dominates the competing formation of the ferrite shell. Because of that the self-aggregation was prevented by surface modification of nickel–ferrite and zinc-ferrite nanoparticles with citric acid before their deposition on the functionalized silica core. Silica core/shell particles were prepared by deposition of silica nanoparticles synthesized from highly basic sodium silicate solution, on the surface of silica core particles. Silica shell has mesoporous structure and large total pore size. Silica core/Fe_3O_4 shell particles were used as templates for deposition of silica nanoparticles which resulted in formation of external silica layer around magnetite shell. Mesoporous structure of the external silica layer can be used for enzyme immobilization while magnetic property of internal magnetic shell allows separation of immobilized biocatalyst from reaction mixture by an external magnetic field.

A56

ALUMINIUM NITRIDE NANOPARTICLES BY CHEMICAL VAPOR SYNTHESIS

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In addition to its use in optoelectronics for the production of ultraviolet Light Emitting Diodes (LED) and Laser Diodes (LD) and phosphors for white LEDs, aluminium nitride has been used for thermal management in the semiconductor industry thanks to its large thermal conduction coefficient and good dielectric properties. As with all materials used in the semiconductor industry, the purity of the final product should be high. Moreover, being a covalently-bonded non-oxide material, the sinterability of AlN is poor. Therefore, the idea of a bottom-up synthesis route that would produce chemically and phase pure nanoparticulate material with increased sinterability is very appealing. Thus, many synthesis routes are used to produce AlN nanoparticles with a varying degree of success. In this work aluminium nitride nanoparticles are synthesized by Chemical Vapor Synthesis (CVS) method which involves the reaction of precursors, triethylaluminium and ammonia, in the gas phase. The influence of processing parameters such as temperature, system pressure and flow rates on the characteristics of final powders are investigated, in particular, particle and crystallite size, degree of crystallinity, and phase composition are examined.

A57

CHEMICAL VAPOUR SYNTHESIS AND CHARACTERIZATION OF Al_2O_3 NANOPOWDER

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One of the methods to synthesize ceramic nanopowders is the chemical synthesis from the vapour phase (CVS), which has proved to be a very promising method for the synthesis of fine and unagglomerated oxide nanoparticles of high purity with narrow size distribution. CVS method is complex and demands a very meticulous and expert approach in all of its steps, from designing the CVS system itself, selecting adequate precursors and ways of transmuting to the vapor phase, to precise controlling all of its process parameters during the synthesis. The process is based on utilizing low values of pressure and high values of temperatures.

In laboratory for the new materials at Faculty of Technology, University in Novi Sad, a CVS system is constructed and tested for a process of synthesis of Al_2O_3 nanopowders. Alumina nanopowders were synthesized using liquid precursor aluminium-tri-sex-butoxide (ATSB) within this method for the first time in Serbia. Precursor vapours are transported by helium flow to the reaction zone where react with oxygen and particles are formed. Based on a thermoforetic effect particles are separated from a gas phase in a collector. Finally, synthesized alumina nanopowders were structurally characterized.

A58

NEW SYNTHESIS METHOD AND CHARACTERIZATION OF POROUS NANOMETRIC TUNGSTEN CARBIDE

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Porous nanometric tungsten carbide (WC) was prepared by applayng simple method. Activated carbon cloth is used as a new precursor for synthesis of this material. The effects of the carbon/tungsten ratio, temperature and duration of heat treatment on properties of the obtained powders were studied. WC powder was synthesized in excess carbon after eight hours heat treatment and at temperature 1000 °C Phase evolution was observed using X–ray diffraction (XRD) analysis. The specific surface area of powders was measured by Brunauer-Emmett-Teller (BET) method. The morphology and microstructure of the powder were examined by scanning electron microscopy (SEM) analysis.

CERAMIC COMPOSITES

C1

SYNTHESIS OF NANOPOROUS TiO_2-ZrO_2-SiO_2 CERAMICS USING SOL-GEL TECHNOLOGY

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Keywords: nanoporous ceramic materials, sol-gel technology, TiO_2-ZrO_2-SiO_2.

In this research we describe the synthesis, mechanical and structural properties of nanoporous TiO_2-ZrO_2-SiO_2 ceramic materials synthesized by sol-gel technology. More attention has been paid to the sol-gel synthesis of the binary TiO_2-SiO_2, ZrO_2-SiO_2 materials. TiO_2 and ZrO_2 incorporation into silica could lead to the development of materials for optical, electronic and catalytic applications [1].

The aim of the research was to prepare nanoporous TiO_2-ZrO_2-SiO_2 ceramic via sol-gel technology and determine structural, mechanical properties and porosity of ceramic. Nanoporous TiO_2-ZrO_2-SiO_2 ceramic was prepared from titanium, zirconium and silicon alkoxides by sol-gel technology. The nanoporous ceramic samples were prepared by sintering of sol-gel derived xerogel powder that was previously homogenized by milling to particle size between 91–354 nm.

The sol was synthesized using TEOS as the SiO_2 source, and alkoxides of zirconia and titania as source of TiO_2 and ZrO_2 oxides, propanol-2 as a solvent but 1 N HCl as a hydrolysis catalysts. Molar percentage $TiO_2/ZrO_2/SiO_2$ ratio was 10/20/70, 15/15/70 and 20/10/70. The xerogel was calcined at 500 °C and milled 1 h or 6 h for powder homogenization. Pressed samples were sintered at 800 °C or 1000 °C temperature. Phase analysis was performed by X-ray diffraction (XRD) analysis. Surface area was measured by BET nitrogen adsorption- desorption isotherms.

XRD analysis shows srilankite ($TiZrO_4$ and Ti_2ZrO_6) phases. The apparent density of the nanoporous ceramic samples sintered at 800 °C was in the range 1.42–1.51 g/m^3, but after sintering at 1000 °C increased to 1.84–1.87 g/m^3. After sintering of the samples at 1000 °C higher compressive strength was observed, but portion of opened porosity decreased.

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C2

NEW APPLICATION OF CERAMIC FOAMS FOR COMPOSITES PREPARATION

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Alumina/copper composites are popular materials, which possesses a good combination of features like high thermal conductivity, high absorption and dissipation of heat, high resistance to thermal fatigue and good frictional wear resistance. The properties of these composites depend on a number of factors including the content, shape and distribution of the ceramic phase and the method of their obtaining. As have been proved in the past, the fabrication alumina/copper composites with use of an alumina powder can lead to a composite with low density and non-uniform microstructure. It is a result of not complete alumina phase consolidation due to powder agglomeration and relatively low temperature of the composite fabrication, dictated by the melting point of copper.

The paper presents a new solution for fabrication of Cu-Al_2O_3 composites with dispersed reinforcement phase. Contrary to conventional approach, which relies on the alumina powder addition, in this work selected fraction of the sintered ceramics derived from the fragmentation of highly porous ceramic foams is used. High brittleness of the thin-walled ceramics allows for the easy fragmentation and isolation of fractions of fragments of average size less than 50 microns. The composites were prepared from a mixture of copper powder and the alumina in an amount up to 10 vol.% by hot pressing. The main aim of the presented investigations was to study the effects of volume content of ceramic phase and particle-size of copper powder on the microstructure and selected properties of copper - alumina composites.

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C3

PRO-ECOLOGICAL METHODS OF SYNTHESIS OF THE METALLIC NANOPARTICLES FOR COMPOSITE APPLICATIONS

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Nanotechnology is a modern, interdisciplinary science, which is beneficial in many industries. Metallic nanoparticles are potentially very important group of additives used for composite fabrication. Composites modified by nanoparticles exhibit significant properties improvement when compared to materials containing bigger additives.

As over the last decade a greater emphasis has been put on the biochemical syntheses of metal nanoparticles, which aim to completely eliminate or at least minimise the amount of produced waste and to implement sustainable processes, carried out according to the twelve fundamental principles of green chemistry. This paper presents the biochemical method for synthesising of metal nanoparticles in agreement with aforementioned principles.

The Spectrophotometric Analysis (UV-VIS) and the Dynamic Light Scattering (DLS) confirm, that the metal nanoparticles produced in this method are comparable to those produced with use of traditional methods. They are chemically stable, their size could be controlled and they have low tendency to agglomeration. The use of water environment and renewable materials such as the vegetable extract is highly beneficial. The combination of non-toxic solvent and renewable reagents presents a wide range of possibilities for the future development of biochemical syntheses of metal nanoparticles.

C4

CERAMIC MATRIX COMPOSITES WITH GRADIENT CONCENTRATION OF METAL PARTICLE OBTAINED THROUGH GELCASTING

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Application of ceramic materials is restricted due to their low fracture toughness. One of the ways to increase the mechanical properties of ceramics is insertion of metallic ductile phase, creating ceramic/metal composites. One group of such materials are functional gradient materials (FGM) which some properties (such as hardness) change as a function of distance from the surface of the material.

The main aim of this work is to present the possibility to fabricate Al_2O_3/Ni composite by gelcasting method. The gradient was carried out in two ways: by sedimentation under gravitation force and by an application of magnetic field.

The following materials were used: alumina powder (TM-DAR, Tamei Japan) of average particle size d = 0.21 µm and nickel powder (Sigma Aldrich) of average particle size d = 1.2 µm. The commercially available monomers 2-hydroxyethyl acrylate and N,N`-methylenebisacrylamide as a cross-linking were used. The activator was N,N,N`,N`,-tetramethylenediamine (TEMED) and the ammonium persulfate was added as an initiator of polymerization process.

Composite water-based slurries with 10 vol.% of nickel powder (with respect to total volume) were prepared. The solid content of alumina and nickel powder varied from 20 to 50 vol.%. The samples were sintered in reducing atmosphere at a temperature of 1400 °C. The chosen physical and mechanical parameters were examined. The microstructure of composites was characterized by scanning electron microscopy.

C5

ELECTRICALLY CONDUCTIVE ALUMINA-MWCNT COMPOSITES

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Alumina - carbon nanotubes composites were studied with respect to obtain the homogeneous distribution of nanotubes within the alumina matrix. Disaggregation and uniform dispersion of carbon nanotubes in alumina matrix are crucial requirements for improvement mechanical and also functional properties of these composites. New approach comprises functionalization MWCNTs by acid treatment, stabilization of

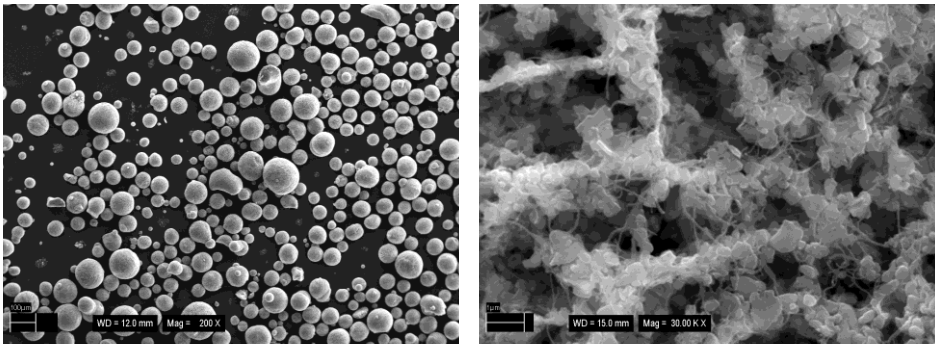

Figure 1. Granulated alumina/CNT composite powder and detail of granule surface with distribution of MWCNTs and alumina grains

alumina/MWCNT dispersion with subsequent freezing has been used, which resulted in formation of granulated powder. This freeze granulation process makes it possible to retain the homogeneity of the aqueous suspension in the ceramic green bodies and make easy next processing. On Fig. 1 from scanning electron microscope is clearly seen that on surface of granulated powder MWCNTs are individually isolated and homogeneously distributed.

The ceramic composites were prepared by hot pressing at 1550 °C using these granulated powders. Microstructural analysis as well as electrical and thermal conductivity measurements has been done.

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C6

SYNTHESIS AND CHARACTERIZATION OF STRONTIUM-ALUMINATE PHOSPHORS AND CdSe QUANTUM DOT BASED COMPOSITES

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The strontium-aluminate phosphors are researched extensively because of their long-lasting phosphorence, great resistance against photo-degradation and good thermostability. These phosphors exhibit a wide emission spectra with a 490 or 520 nm emission peak maxima depends on the actual chemical composition. The phosphorescence phenomena is based on the activator ions which was the frequently used Eu^{2+} while to the long-lasting phosphorescence the presence of some trapping sites in the crystal. are also required. These trapping sites, also known as co-activators were the well-tried Dy^{3+} and the Ho^{3+} was also used with good results.

After the successfully modification of the emission properties of the strontium-aluminate phosphors we tried to further fine-tune the emission with using of emission-tunable quantum dots (QDs). QDs are fluorescent semiconductor nanocrystals. They emission peaks are tubable with changing their size across the width of the band gap. This type of downconverter composite material with mixing the long-persistent phosphors with quantum dots could be used in LED technology to get different coloured phosphor converted (PC) LEDs or also in photovoltaics to enhance their performance in dark circumstances.

The composite samples were characterized by different spectroscopy (UV-Vis, PL), crystallography (XRD) and microscopy (SEM, TEM) methods.

C7

KINETIC STUDY OF SINTERING BEHAVIOR OF LAYERED CERAMIC COPMOSITES

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The layered Al_2O_3/ZrO_2 ceramic composites with layer thickness of about 50 μm were prepared by electrophoretic deposition. The sintering behaviour of layered ceramic composites was observed in longitudinal (parallel with layers) and transversal (perpendicular to layers) direction by high-temperature dilatometry. The differences in both directions was characterized by different sintering shrinkage behaviour and described by Master Sintering Curve model.

C8

MECHANICAL STRENGTH DEGRADATION OF GLASS-CERAMIC COMPOSITES FOR MICROELECTRONIC DEVICES

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Keywords: LTCC, mechanical strength, subcritical crack growth.

The aspiring technology of the last decades has been the printed circuit board (PCB) providing the backbone for all electronic components. Nowadays electronic parts are used in daily devices (e.g. the personal computer, a calculator or a mobile phone) as well as in many unusual products (e.g. an ultrasonic toothbrush or a "simple" socket-to-USB power supply unit). To date the main structural material for PCB has been a polymer compound strengthened with embedded glass fibres. However, the polymer limits the application field, unable to withstand high loaded environments (e.g. temperature, mechanical loading).

The **L**ow **T**emperature **C**o-fired **C**eramics (**LTCCs**) technology is aimed to **improve thermal and geometrical stability** with respect to conventional polymer-based PCB. LTCC are functional components which can be used as **electronic devices** in highly loaded environments. The **lifetime prediction** of LTCCs is associated with their mechanical strength and crack growth resistance during service. Therefore, the understanding of cracking in these components and the response to crack propagation must be assessed if a reliable design is pursued. A limiting factor for the lifetime of

glasses and ceramics is related to the **subcritical crack growth** phenomenon which may occur in glass–containing components subjected to tensile stresses, especially in environments with high moisture content. In this work, the **mechanical strength** of bulk LTCC specimens has been measured under **different environments** (i.e. water, air, silicon oil, argon) at **various temperatures** using a **biaxial strength test** (ball–on–three–balls test). Experimental findings show a **strong effect** of **environment** and **loading rates** on **strength**. Whereas **high strength** values are measured under **inert conditions**, **lower strength** is obtained in **water rich environments**.

C9

MODEL EXPERIMENTS IN GPS AND THERMODYNAMICAL ANALYSIS OF Si_3N_4-Y_2O_3-SiO_2-C SYSTEM

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The possibility of Si_3N_4/SiC composite preparation by gas pressure sintering was studied in this work. The main aim was to find out the conditions for *in situ* formation of SiC inclusions within Si_3N_4 microstructure via carbothermal reduction of SiO_2 during gas pressure sintering. Series of samples were prepared with 15 wt.% addition of sintering additives Y_2O_3 and SiO_2. Their molar ratio was 0.39 and 0.51 mol%. Some model experiments were done in the systems: SiO_2-C, Y_2O_3-SiO_2-C, Si_3N_4-Y_2O_3-SiO_2-C. The thermodynamical analysis of possible reactions was done. This analysis showed the importance of gas regime during the sintering process. Si_3N_4/SiC composite was successfully prepared at 1550 °C by introducing carbonmonoxide and nitrogen gas mixture into furnace. The formation of SiC was confirmed by XRD analysis. Carbonitride phase arise at 1650 °C in Si_3N_4/SiC composite, which hinder the densification process.

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C10

GRAPHENE REINFORCED SiC CERAMICS SINTERED BY SPARK PLASMA SINTERING

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Silicon carbide (SiC) ceramic has superior properties in terms of wear, corrosion and oxidation resistance as well as excellent thermal shock and high temperature mechanical behavior. From application point of view the two major problems with SiC are its difficulty to sinter as well as its poor fracture toughness.

In this work multilayer graphene, a recently discovered allotrop modification of carbon having extreme strength was added to SiC ceramics in 1 wt.% and 3 wt.% to improve toughness. Its effect on the overall mechanical behavior was also investigated. To overcome sintering difficulties we applied a spark plasma sintering, in which diffusion is enhanced by the microdischarges developing among the particles. Using different sintering additives liquid and solid phase sintering mechanism was also compared.

C11

SYNTHESIS AND CHARACTERIZATION OF ELECTRICALLY CONDUCTIVE ZIRCONIA BASED COMPOSITES

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Yttria partially stabilized tetragonal zirconia (Y-TZP) is a versatile oxide ceramic material with outstanding mechanical and chemical properties, utilizing in many various structural and biomedical applications. This is because it experiences transformation toughening. One of the drawbacks of this material is related to the high cost of the final machining. With this in mind the aim of our work was to prepare electrically conductive Y-TZP based ceramics by the addition of nanosized titanium nitride (TiN) particles, suitable for cheaper machining method such as electrical discharge machining (EDM). Since it is known the addition of secondary phase-particles commonly hinders densification, resulting in reduced strength, we tried to find a way to reach percolation threshold with minimum amount of electro-conductive phase as possible. In order to do so, we prepared the TiN nanoparticles on the surface of host ZrO_2 particles using *in situ* precipitation of titanium hydroxide ($Ti(OH)_4$) in an aqueous suspension of host particles.

A controlled heating program was used for the transformation of hydroxide to titanium oxide (TiO_2), which was subsequently converted to TiN by thermochemical process in ammonia gas. Spark plasma sintering (SPS) technique was used for densification of ZrO_2 – TiN composites. The influence of TiN content in composite on strength and electrical conductivity of the final product was studied. At this point we faced with some problems according to heterogeneity of composites which reflected in moderate biaxial flexural strength of composites. With elimination of heterogeneity percolation threshold could be lower and consequently higher strength of composites could be obtained. Anyway composite met the requirements for EDM (electrical conductivity above 0.01 S) already at 15 vol.% TiN in comparison to Salehi et al. who reported that comparable electrical conductivity was obtained at more than 30 vol.% TiN.

C12

STRUCTURAL MODIFICATIONS OF BIO-CALCIUM PHOSPHATES

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Calcium phosphate (CaP) minerals are the most abundant biomineral group in the human body. Biologic hydroxylapatite differ in stochiometry from the ideal formula. The main inorganic component of teeth and bones is poorly-ordered carbonate-rich hydroxylapatite (CO_3Ap). Moreover, they usually have Na, K, Mg, Sr, Cl, F and other trace amounts of different ions incorporated in their lattice. Due to their similarity synthesized CaP have excellent biocompatibility, therefore they are widely used as biomaterials for hard tissue repair as implants and bone scaffolds. In order to improve bioactivity of these minerals doping with Sr, Mg have proved to be biologically significant. Bio-hydroxylapatite $Ca_5(PO_4)_3OH$ and brushite $CaHPO_4 \times 2H_2O$ (DCPD) were synthesized by a simple precipitation method. Phase composition of the obtained powders was analyzed by X-ray powder diffraction (XRD), and the morphology and crystallite size and shape was recorded by scanning electron microscopy (SEM). In order to improve the properties of these biomaterials pressed powders were sintered at low temperatures in order to prevent the phase transitions and the alteration of their structures.

C13

SYNTHESIS OF Fe_2O_3/SiO_2 NANOCOMPOSITES FROM Fe(III) CARBOXYLATE PRECURSORS INSIDE HYBRID SILICA GELS

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The study reports the preparation of Fe_2O_3/SiO_2 nanocomposites by a new modified sol-gel method starting from iron nitrate, diols and tetraethyl ortosilicate (TEOS) for final composition of 50 % Fe_2O_3/50 % SiO_2. The methods is based on the formation of Fe(III) carboxylate precursors during the redox reaction between the NO_3^- ion and the diol (1,4-butanediol, 2,3-butanediol, 1,3-butanediol) at 140 °C within the silica gel. The thermal decomposition of this complex combination takes place at ~300 °C with the formation of γ-Fe_2O_3 within the pores of hybrid silica gels.

With the thermal treatment temperature increased to 600 °C the γ-Fe_2O_3 stabilize in the silica matrix obtaining nanocomposites γ-Fe_2O_3/SiO_2 with crystallites < 10 nm. The measured specific surface areas are in relationship with the nature of the diols and the synthesis method. The formation of the precursors inside the silica matrix were characterized by thermal analysis (TA), FT-IR spectroscopy, the crystalline phase was confirmed by X-ray diffraction (XRD) and specific surface areas were investigated with BET analysis.

C14

APPLICATION OF NEW CERAMIC-POLYMER COMPOSITES FOR MICROWAVE ELECTRONIC SYSTEMS

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In the last century, ferroelectric materials have become an integral part of electrical engineering. The rapid development of radio techniques creates the need to design new solutions and discovering new materials allow operation at higher frequency bands. More and more opportunities give working in a wide range of microwave spectrum. An example of a modern solutions are "smart" antenna systems.

The scientists dealing with these questions predict that significant progress will be achieved by using a new generation of ferroelectric materials. Moreover they suggest the possibility of producing these materials as thin film, which is expected to eliminate

previous drawbacks, such as exfoliation of elements in green state. They are therefore considered to be very attractive for applications in microwave band.

The aim of research was the selection of components for ceramic slurry which enabled to obtain thin films by tape-casting method. Ceramic powder showing ferroelectric properties used in the study was barium strontium titanate (BST) doped by appropriate amount of, for example: nickel oxide.

C15

THE INFLUENCE OF hBN ADDITION ON MECHANICAL AND ELASTIC PROPERTIES OF Al_2O_3-TiN COMPOSITE

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The possibility of lowering the friction coefficient of a composite consisting of alumina matrix and titanium nitride reinforcement by addition of hexagonal boron nitride was verified. Composites containing 10 vol.% of titanium nitride and varying amount of hexagonal boron nitride (5 vol.%, 2 vol.%, without an addition of hBN) were prepared by hot pressing out of commercial powders. The microstructure and phase composition of the composites were analyzed using SEM and XRD methods. Fracture toughness, bending strength, hardness and elastic properties of composites were examined. The influence of hBN addition on friction coefficient was checked.

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C16

MACHINABLE SILICON NITRIDE-BASED COMPOSITES SINTERED WITH POLYMER DERIVED CERAMICS AS SINTERING ADDITIVES

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Keywords: silicon nitride, machinability, SiAlOC, SiAlON

Conventional sintering additives (MgO, Al_2O_3, Y_2O_3) used for the preparation of Si_3N_4-based ceramic materials by pressureless sintering or hot-pressing were in this work replaced by SiAlOC polymer precursors. The green bodies were prepared by uniaxial pressing and/or cold isostatic pressing (CIP) from three kinds of powder compositions

with the addition of 23.3, 30 and 40 wt.% of SiAlOC to the Si_3N_4 matrix. The machinability tests showed that the green bodies before pyrolysis cannot be machined without crack formation. Therefore, the samples were pyrolysed in quartz tube furnace with a controlled flowing atmosphere of nitrogen. The machinability of CIP-ed and pyrolyzed samples in a lathe was much better compared to the uniaxially pressed samples. The machined samples were pressureless sintered at 1750 °C for 1 hour in nitrogen. The sintered samples were characterized in terms of shrinkage, phase composition and microstructure.

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C17

RELATIVE DENSITY AND DIELECTRIC RESPONSE OF AlN CERAMICS OBTAINED WITH VARIATION OF MODIFYING ADDITIVES AND SINTERING REGIME

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AlN-based ceramics is a prominent material for high temperature insulators and transcalent dielectric substrates for high-power integrated circuits, semiconductor structures, heat removal systems etc. But it's still not clear enough how different additives and point defects affect the structure of ceramic composites and improve its electrical properties. Thereby, the aim of our work was to establish influence of dopants (TiO_2, TiH_2, TiN and TiC up to 4 vol.%) and sintering regime on relative density and dielectric response of AlN ceramics.

Samples were prepared by hot-pressing with the time of isothermal soaking of 5-30 min at a temperature of 1700–1900 °C (30 MPa). Porosity of the samples was calculated from their density which was determined by hydrostatic weighing. Temperature and frequency dependences of dielectric properties (ε', tgδ) were measured at the temperatures 20–350 °C, in the low-frequency range (LF, 10^3–10^5 Hz) and at radio frequencies (RF, 10^4–10^7 Hz).

It was established, that the porosity, the dielectric permeability and the dielectric loss tangent of AlN-TiO_2 composites depends parabolically on the doping percentage with minimal values (0.1%; 9.7; $1.3\cdot10^{-3}$, respectively) at 0.5–2 vol.% TiO_2. TiH_2 addition leads to the formation of metallic nanofilms oriented perpendicularly to the pressing direction, thus increasing the strength and the thermal conductivity of AlN-TiH_2 composites. Temperature dependence of dielectric loss factor revealed that the deviation from the optimal temperature regime increases the leakage loss because of defects accumulation and conductive phase's formation. Frequency dependence of active impedance indicated the contribution of space-charge polarization at low frequencies (LF) (10^3–10^5 Hz) and hopping polarization at radio frequencies (RF) (up to 10^7 Hz). Effective thickness of conductive channel was determined from the frequency dispersion. Thus we established the micrometric defects (≈ 16 µm) response at LF. Nanofilms response was found at RF from the slope of the frequency dependence of impedance. In this way dielectric response was used to develop a technique for non-destructive monitoring of ceramic composites' microstructure evolution.

C18

ALUMINA/ZIRCONIA COMPOSITES WITH TiB_2, TiC INCLUSIONS AND NANOMETRIC SCALE PARTICLES OF NICKEL

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The development of $Al_2O_3/(ZrO_2\text{-}TiC)/Ni$ particulate nanocomposites exhibiting high hardness and wear resistance was a main motivation of the work presented. The study on the materials was focused on checking in practice the hardening effect of nickel nanoparticles dispersed in the ceramic matrix, which is related, among others, to Hall-Petch phenomena. Secondly, the work checks if the classical action of hard ceramic particles (ZrO_2-TiC) acts together, in a meaning of synergy, with the above mentioned reinforcing mechanism.

The materials of the following phase systems were examined: $Al_2O_3/(ZrO_2\text{-}TiC)/Ni$, and ZrO_2/TiC/Ni. Reference materials without nickel particles were also tested. The volumetric concentration of TiC was from a single per cent to ca. 20%, while a nickel content was 2.5 vol.%. The basic $Al_2O_3/(ZrO_2\text{-}TiC)$ system was manufactured by physical mixing of alumina powder and the ZrO_2/TiC composite powder. Nickel nanoparticles were derived from an oxalic precursor.

Phase compositions of the powders and sintered bodies together with crystallite sizes were measured by XRD. A particle-size analysis of the powders was determined by DLS. Apparent density of the composites was measured with the Archimedes method. The indentation method was used to determine the values of Vickers hardness and critical stress intensity factor. Wear resistance was tested according to the procedure being in agreement with the ATSM G65 standard. The microstructure was characterised by means of SEM/EDS.

The research showed the positive impact of the nano-Ni and ZrO_2-TiC particles on mechanical properties of the alumina matrix nanocomposites.

C19

CHARACTERIZATION OF NANOSTRUCTURED TiAlN/TiSiN COATINGS

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Ceramic thin films have been widely used to improve surface properties of mechanical components. Traditional transition metal nitrides, such as TiN, played an important role in first decades of protection of tool surfaces. Properties of TiN can be greatly enhanced by addition of Al which leads to formation of TiAlN films characterized by high hardness (≈ 32 GPa) and high oxidation resistance (up to 800 °C). Nowadays, nanocomposite and nanolayered coatings attract the greatest interest. The most studied TiSiN nanocomposite coating consists of TiN nanocrystals embedded in an amorphous Si_3N_4 matrix. This coating exhibits superhardness (> 40 GPa), high oxidation resistance (≈ 850 °C) and high thermal stability (up to 1100 °C). Nanolayered coatings are composed of few nanometers thick layers of two or more materials (e.g. TiN/SiN_x). Their properties depend mostly on thickness of individual layers, number and width of interfaces.

In this research TiAlN and TiSiN layers were deposited alternatively to form nanolayered TiAlN/TiSiN coating. Single-layer TiAlN and TiSiN coatings were prepared along with the nanoayered coating for its better understanding. Industrial magnetron sputtering unit with two TiAl and two TiSi targets was used for coating preparation. Conventional and high resolution TEM along with X-ray diffraction were used for microstructural analysis. Chemical and phase composition were assessed by X-ray photoelectron spectroscopy. Mechanical properties were determined by nanoindentation technique.

According to the results of XRD and XPS measurements TiSiN and TiSiN/TiAlN coatings are nanocomposites composed of crystalline and amorphous phases. The single-layer TiSiN coating is built of 5 nm large TiN crystals embedded in amorphous Si_3N_4 matrix, while the nanolayered TiAlN/TiSiN coating consists of nano-crystalline TiN and $Ti_{1-x}Al_xN$ phases along with amorphous Si_3N_4.

Nanolayered TiAlN/TiSiN coating exhibited high hardness of 39 GPa. This value is considerably higher from the 29.7 GPa which was estimated by applying the rule of mixture. Observed hardness enhancement can be attributed to hindering of dislocation motion due to grain size refinement along with blocking of grain boundary sliding by relatively sharp interfaces.

C20

MECHANICAL PROPERTIES OF POROUS (Ti-8.9 at.% Si)-IN SITU COMPOSITE MATERIAL AS A SUPPORT SUBSTRATE FOR SOFC APPLICATION

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The main requirements for the properties of the ceramic fuel cell support substrate are strength (≥100 MPa), heat resistance (operating temperature of 600–650 °C), high porosity (30–50 %), electrical conductivity (from 1.25×10^4 to 2.4×10^6 S/cm), matching the CTE and chemical compatibility with other components of solid oxide fuel cell (SOFC).

Recently, Fe-Cr-based alloys are used as a material for support element [1]. But in practices, these materials have the significant disadvantage because of Cr diffusion in other SOFC components. As a result degradation of SOFC properties is observed [2]. Decreasing fuel cell operating temperatures from 800 to 600 °C would allow replacing Fe-Cr alloys system by Ti-Si in situ composites.

The aim of this work is to study the influence of pressing pressure and sintering temperature of Ti–8.9-at.% Si material on its structure and strength. The Ti–8.9-at.% Si powder was manufactured with rotated electrode sputtering method. The powders with spherical particles were obtained with ion of sputtering of melt alloys by means of the mixture of inert gases Ar and He. The fraction size distribution of the powder was within the limits of -500+315 μm. The rectangular samples were pressed with pressures of 624 and 780 MPa and sintered in a vacuum 1.3×10^{-3} Pa at different temperatures: 1250, 1270, 1300 and 1400 °C .

It was found that pressure has no essential influence on pressing samples porosity (33–40%). Volume shrinkage of samples starts to grow with sintering temperature ≥1300 °C up to temperature of liquid phase arising (1340 °C). The strength of sintered samples increases from 135 to 200 MPa with decreasing porosity from 40 to 33 %. This material fulfills SOFC supporter requirements concerning the strength and porosity.

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C21

ENHANCING PERFORMANCE OF Ni-$LaNbO_4$ CERMET ANODE FOR PROTONIC CONDUCTOR FUEL CELL THROUGH CeO_2 INFILTRATION

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Lanthanum orthoniobate is a novel proton conductor, which is considered as a potential electrolyte for Protonic Conductor Fuel Cells (PCFC) due to its good mechanical and chemical stability and low manufacturing costs. However, there is still need for searching and developing proper anode and cathode materials for fuel cell based on $LaNbO_4$ electrolyte. Anode is particularly significant for PCFC performance thus it is very important to develop an mechanically compatible with electrolyte material with good and stable electric and catalytic properties.

Porous ceramic-metal - cermet-composites are materials based on combination of metal and electrolyte materials. Ni-$LaNbO_4$ cermet anodes have good electric and ionic conductivity, mechanical stability and have compatible thermal expansion coefficient with an electrolyte. Nickel is a cheap and good electric conductor with significant catalytic properties. Nevertheless, nickel during prolonged exposition to high temperatures tends to agglomerate, which is associated with decreasing in anode performance by triple-phase boundary shortening and leads, in the end, to failure of the fuel cell device.

Infiltration of Ni-$LaNbO_4$ anode with solution of cerium nitrate and further heat treatment causes formation of nanocrystalline cerium oxide inside the electrode. Cerium oxide nanocrystals prevents nickel agglomeration during prolonged performance in high temperatures hence it improves the stability of electrical properties of selected PCFC anode.

C22

PREPARATION AND CHARACTERIZATION OF SOME TRANSPARENT NANO-GLASS-CERAMICS FROM THE SYSTEM SrO-B_2O_3 TOGETHER WITH SiO_2 AND CaF_2 ADDITIVES

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Keywords: strontium borate glass, SiO_2, CaF, FTIR, XRD, nano- ceramics, gamma ray

Glasses from the strontium borate system of the basic composition 45%SrO–55%B_2O_3 together with samples doped with 2 or 5% of either SiO_2 or CaF_2, respectively, were prepared using the melt annealing technique. The prepared samples were characterized by means of Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). XRD diffraction patterns have indicated the amorphous nature of the parent glasses within the compositional range studied. Differential thermal analysis (DTA) studies were undertaken to measure the glass transition and crystallization temperatures and to get detailed information about the stability of the glass network together with identifying the detailed thermal properties of the prepared glasses. Thermal heat treatment regime was conducted for all the samples. All glasses are observed to be transformed to distinct glass-ceramic derivative containing crystalline strontium borate (SrB_6O_{10}) phase. The other heat treated samples containing either SiO_2 or CaF_2 show nano-behavior or transformation to nanoglass-ceramic formation on the examination by x-ray diffraction. FTIR spectra have indicated that the introduction of either SiO_2 or CaF_2 with the levels of 2% or 5% causes no changes in the main IR vibrational bands which contain vibrational modes due to tetrahedral and triangular borate groups.

Glass samples were subjected to successive gamma irradiation to doses of 2, 6 and to a final dose of 8 Mrad, and their FTIR spectra showed only minor changes in their intensities but the main IR bands remained the same in their positions and numbers. This IR spectral result indicates the stability of such strontium borate glass system containing heavy SrO to the effect of gamma irradiation.

C23

SYNTHESIS OF GLASS-CERAMIC IN $Li_2O·AL_2O_3·GeO_2·P_2O_5$ SYSTEM

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Key words: germanium phosphate glass, crystallization, kinetics, crystal growth

In this paper the results of synthesis of glass-ceramics from the system $Li_2O·AL_2O_3·GeO_2·P_2O_5$ are shown. The crystallization behavior of glass prepared from this system was studied in details. The crystallization properties were examined under non-isothermal and isothermal crystallization conditions. DTA, XRD and SEM methods were employed. It was detected that this glass crystallizes by the volume crystallization mechanism. The results showed that the glass crystallize by primary crystallization. As a primary phase the $LiGe_2(PO_4)_3$ is formed and the traces of GeO_2 as a secondary one is present. The crystallization process occurred at a high homogeneous nucleation rate and the spherical morphology of crystal growth. The kinetics of formation glass-ceramic is characterized with activation energy of 462 kJ/mol.

C24

WATERBORNE POLYURETHANE DISPERSIONS AND FILMS MODIFIED BY COLLOIDAL SILICA

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Four successive steps (prepolymerization, chain extension, neutralization and water dispersion by the phase inversion) were used for waterborne polyurethane dispersion (PUD) preparation. Polycarbonate diol (PC), hexamethylene diisocyanate (HDI), dimethylolpropionic acid (DMPA), butane-1,4-diol (chain extender), triethylamine (TEA; neutralization agent) and dibutyltin dilaurate (DBTDL, catalyst) were used for the polyurethane (PU) dispersion synthesis. The contents of the soft segment (PC), ionomer (DMPA and TEA) and chain extender (BD) were changed in order to optimize functional properties of PUDs and PUD-based films. Obtained dispersions were also modified by mixing with colloidal silica. The influence of abovementioned parameters on end-use properties of products (dispersions and films) will be presented. Fourier transform infrared spectroscopy was used for the kinetic studies of the reaction of isocyanate groups and for the control of the end of the chain extension reaction. Particle size distributions of prepared PUDs (30 to 100 nm in diameter) were measured by dynamic light scattering. Zeta potential measurements, i.e., values important for the stability of PUDs, ranged between –30 and –60 mV. Surface topography and roughness of films prepared from PUDs was studied using atomic force microscopy (AFM). Tensile tests of transparent thin films made from PUDs are characterized by very high flexibility, however inferior and only moderate values of tensile strengths, if compared with pertinent PU elastomers made from PC, HDI and BD in bulk. We concluded that the addition of silica has not impact on stability of PU dispersions; however it influences mechanical properties of obtained organic-inorganic nanocomposite films.

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C25

POLYURETHANE FOAMS MODIFIED BY SILICATES

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Nanocomposites are relatively new class of materials which includes more than one solid phase, where at least one phase has dimension of a nanometer range, typically in a range of 1–100 nm. The nanoparticles generally possess very high mechanical strength and high thermal stability, whereas polymer materials comparing to metals and ceramics are weak both thermally and mechanically. However, due to their higher surface energy nanoparticles tend to agglomerate and in most cases, it is very difficult to disperse them into a polymer matrix. Agglomerated nanoparticles act as structure defects and can have detrimental effect on polymer performances. Thus, it is imperative to disperse the nanoparticles into the polymer matrix, when they are in liquid stage so that interactions at the molecular level can be achieved to produce a material with the superior thermal and mechanical properties [1,2].

The nanofillers: natural montmoryllonite (MMT) - bentonite, natural MMT modified with a quaternary ammonium salt - Cloisite®30B and synthetic MMT - Laponite RD, have been used in rigid polyurethane foams (PUFs). The influence of fillers amounts on processing parameters, physical-mechanical properties (density, water absorption, brittleness and compression strength) and thermal properties (thermal stability, fire behaviours) of such foams has been analysed. The cream, rise and gel time for PUFs modified with nanofillers been observed during synthesis and has been elongated in comparison to unmodified foam.

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TRADITIONAL CERAMICS

T1

SUBMICRON ILLITE CLAY PARTICLE INFLUENCE ON GEOPOLYMER PROPERTIES

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Keywords: geopolymerization method, illite clays, structure and properties.

A variety of industrial minerals, such as kaolinite, feldspars, and etc., and industrial solid residues or wastes, such as fly ashes, metallurgical slags , mine wastes, etc., have been used as solid raw materials in the geopolymerization technology [1]. The use of clays as a raw material promises low cost and it is easily available material all over the world. In Latvian clays dominant clay mineral is illite. The aim of this study was to find out the Liepas red and gray clays aptitude for geopolymer production. The raw material in this study was obtained by the use of sedimentation method. Clay fraction and dust fraction, was subjected to the treatment with NaOH solution and afterwards treated at different temperatures. The effect of drying temperatures and aging time, which directly influence final compressive strength values of geopolymer specimens, were investigated and compared.

Temperatures in the range of 50–60 °C are widely accepted values used for successful geopolymer hydration [2].

Used methods and instruments in this research include Casagrande method, X-ray diffraction, Fourier transform infrared spectroscopy, Scanning electron microscopy, Brunauer Emmett Teller adsorption method and others. By the use of these methods it was confirmed that Liepas deposit homogenized gray and red clays are suitable for geopolymer method realization. Clay fractions, which are the most delicate particles of clay composition, after thermal activation and treatment with NaOH solution shows significant compressive strength. Also such sub-micrometer size particle distribution can contribute to the reactions of geopolymerization process.

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T2

INFLUENCE OF DOPING AGENT ON THE MULLITISATION PROCESS IN ALUMOSILICATE CERAMICS

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Keywords: mullite, kaolin, alumina, metal oxide, porosity, refractory ceramics

The ceramics for heat insulation, improvement of technological process of ceramics production, economy of energy and raw materials are actual nowadays. For example, the refractoriness of alumosilicate ceramics at temperature above 1580 °C can be achieved when mullite ($3Al_2O_3{\cdot}2SiO_2$) phase is the main crystalline phase of these materials. Mullite ceramics also display definite mechanical strength and excellent resistance to chemical corrosion. Therefore the dense mullite ceramics have been widely used as constructional materials as well as the high porosity mullite ceramics serve as heat insulators and filters in the thermal protection systems and technical equipments.

Different alumina and silica raw materials can be used for such ceramic production. The process of mullitisation, its initial temperature and dominance of mullite phase depends on these raw materials and some additives such as metal oxides. Therefore the aim of this work was to investigate the influence of MgO, WO_3 and ZrO_2 on the process of mullitisation of samples. The porous mullite materials were prepared by slip casting of suspension of raw materials where the aluminium paste was used as a pore former. The raw materials were kaolin (*MEKA, Germany* with SiO_2 - 56.2 wt.%, Al_2O_3 - 31.0 wt.%), pure silica (d_{50} = 6.94 µm), different alumina (*Nabalox, Germany*, α-Al_2O_3 (d_{50} = 4 µm) and γ-Al_2O_3 (d_{50} = 80 µm). The Al_2O_3 and SiO_2 were in 2.57:1 ratio and conformed to the mullite stechiometric composition ($3Al_2O_3{\cdot}2SiO_2$). The ratio of α- and γ-alumina was 1:3. The kaolin used 30 wt.%, additives - 1, 3, 5 and 7 wt.%. Porous mullite ceramic was obtained by slip casting of suspension of raw materials and H_2 elimination by chemical reaction of Al with water. The samples were sintered at the different temperatures (1300 °C, 1500 °C, 1650 °C and 1700 °C).

The Differential thermal analysis, X-ray diffraction analysis and scanning electron microscopy were used as the main methods respectively for analysis of mullitisation beginning, phase composition and microstructure of samples.

T3

EFFECT OF POTASSIUM AND SODIUM FELDSPARS ON WILLEMITE CRYSTALLINE GLAZES

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The one of the most decorative and mysterious glazes used in ceramic are crystalline willemite glazes. The unique effect crystalline coatings are realized by the diversity of shapes willemite crystals and the ability to dye them different colors. However, the process formation of zinc silicate crystals and their growth to appropriate, desired size is difficult from a technological point of view. Many factors such as kind of ceramic base, the thickness of the glaze layer and the firing condition, like a change a few minutes may lead to achieve other layer results than expected.

The willemite crystals form during the cooling-soaking firing cycle from melted glaze saturated with zinc oxide. They made up of small needle-like embedded in the glass matrix grow in all directions from the center nucleus. Depending on the temperature and the soaking time it is possible to obtain different morphology of willemite crystals. The promote forms of crystals are spherulites, which are the most developed crystalline forms.

In this paper the influence of the kind of feldspar on formation of the willemite crystal inside of glazes was tested. Feldspars are a group of aluminum-silicate materials commonly found in the Earth's crust. In the composition of glazes are two particularly important feldspars: albite $Na[AlSi_3O_8]$ and orthoclase $K[AlSi_3O_8]$, which are the fluxes. Due to formation of liquid phase with different feldspars the differences in parameters are observed. It is a reason why potash and sodium feldspars were selected for this study.

Two crystalline glazes compositions differ only in the kind of feldspar. Other parameters, such: ceramic body, thickness of glaze coatings and firing condition, were constant. The optical microscopy was used to determine the shape, color, numbers and sizes of the individual crystals in willemite glazes. The glaze surface topography and location of the crystals in glassy matrix were studied in 3D by using confocal optical microscope. The microstructure of crystalline glazes was analyzed with a scanning electron microscopy. X-ray analysis of glazes was possible to indicate the phase composition of samples.

T4

THERMAL INDUCED PHASE TRANSFORMATION OF Cs-EXCHANGED LTA FRAMEWORK ZEOLITE

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Cesium aluminosilicate phases are of great interest as possible hosts for ^{137}Cs immobilization in radioactive waste management. Cs^+ exchanged forms of two synthetic zeolites (4A and 3A) were prepared by standard procedure, and content of exchanged ions was determined by ion chromatography. Obtained samples were investigated by differential thermal gravimetry TG/(DTG) and SEM/EDS analysis. All samples were annealed in the range of 600–1500 °C. High temperature phase transformations of Cs^+ exchanged zeolites (LTA) were investigated. Based on data obtained by XRD analysis of the samples, it was concluded that above 1000 °C Cs-LTA (4A and 3A) frameworks recrystallized in a pollucite phase.

T5

MICROSTRUCTURE AND MECHANICAL BEHAVIOR OF SINTERED MATERIALS MADE OF KAOLIN AND CALCITE MIXTURE

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Microstructure of sintered ceramic materials is complex and depends on the initial composition of masses, forming and sintering process. Microstructure affects the properties of the final material.

In this work, we consider microstructure of sintered materials made of kaolin with addition of different quantity of pure calcite. Two different types of kaolin were used: first with higher content of quartz and smaller content of kaolinite and second with higher content of kaolinite and very small content of quartz. The kaolins had different grain size distribution and indicate different behavior during sintering as it was showed in our former works

We consider microstructure changes with increasing content of calcite and with increasing temperature. The following techniques were used: scanning electron

microscopy (SEM/BSEM), mercury intrusion porosimetry (MIP), XRD method and hydrostatic method for determining the density. In addition, a comparison between the microstructure of the sintered bodies and their physic-mechanical properties have been made.

T6

INFLUENCE OF THERMAL TREATMENT AND COMBUSTIVE ADDITIVES ON PROPERTIES OF LATVIAN CLAY CERAMICS PELLETS

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Clays are specific materials with a very wide range of applications. During thermal treatment they go through different complicated processes, which define afterwards the properties of ceramic materials. The knowledge of these processes and factors affecting them helps to design and produce materials with specific properties for concrete purposes.

Clays from 4 deposits were investigated – Planci, Progress, Laza and Liepa. Those are Devonian and Quaternary clays with different mineral compositions. As combustive additives are used saw dust and straw. Pellets are formed from plastic paste and sintered at 4 temperatures.

Main clay mineral in all of investigated clays is illite. During sintering, depending on the temperature, illite reforms in to anorthite in case of Progress and Laza and in spinel in case of Planci and Liepa. Formation of two different mineral types is caused by their composition's diversity. Progress and Laza are calcareous clays and contain calcite. In ceramic of these clays traces of calcium oxide are detected. Whereas Planci and Liepa are non-calcareous clays and the specific color of ceramic materials are given by hematite.

Investigated clay pellets show different pH levels of water after immersion. Calcareous clay pellets shown pH in range of 9.8–10.7 for the sintering temperature range 700–900 °C. This is caused by presence of calcium oxide, which forms calcium hydroxide in water. At higher sintering temperature all CaO is bounded in structure of anorthite. pH for non-calcareous clay pellets is in range of 6.2–7.5 for all sintering temperatures.

The porosity and specific surface area of pellets were determined using mercury porosimetry. Through all temperatures the porosity is mostly in range from 15 to 25 % for all investigated pellets. It can be observed a slight decrease at 1050 °C. On the contrary specific surface area is much higher at 700 °C and 800 °C and varies from 9.5 to 30 m^2/g. With higher temperatures specific surface area decreases sharply and it drops below 4 m^2/g at 1050 °C for all pellets. Such results are easily explainable with intensification of sintering process.

To estimate the possibility of using these pellets for environmental applications sorption properties were tested during 3 weeks using I_2, K_2Cr_2O7 and NH_4OH water solutions. Most promising results were obtained in case of iodine sorption. For most pellets the sorption capacity was 12.7 mg/g, although for pellets sintered at 1050 °C it was lower (8.2–11.2 mg/g). Sorption capacity of dichromate ions is in wider range (2.7–11.1 mg/g) and the highest is shown by pellets sintered at 800 °C. Determination of adsorbed ammonium ions was more difficult for calcareous clay pellets due to their alkalinity. For all pellets the sorption capacity is very low (0.002–0.333 mg/g).

T7

CHROME DOPED SPHENE PIGMENTS PREPARED VIA PRECURSOR MECHANOCHEMICAL ACTIVATION

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Keywords: Sphene; Mechanochemistry; Chromium; Pigments

Mechanical activation of precursors has been used for the preparation of Cr-doped sphene ceramic pigments ($CaTi_{1-y}Cr_ySiO_5$) using vibro-milling for homogenization and activation of precursors. Phase evolution in $CaTi_{1-y}Cr_ySiO_5$ composition with thermal treatment was investigated by X-ray powder diffraction (XRPD). Texture properties and particle size distribution were analyzed by scanning electron microscopy (SEM) and laser diffraction, respectively. UV/vis reflectance spectra are used to determinate the behavior of the chromium ion. The color efficiency of pigments was evaluated by colorimetric analysis (CIE L*a*b system). Photoluminescence measurements were also performed.

T8

IDENTIFICATION METHODS OF NANOPARTICLES SELECTED BY SEDIMENTATION FROM RAW SILICEOUS CLAYS

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One of the most important aspects of mineral processing technology is phases separation. It is possible to achieve on a laboratory scale by sedimentation methods. One of these methods is a separation of the ultracentrifuge. Two types of raw siliceous clays were used for the studies. They originated from Dylągówka (SE Poland, the Polish Carpathian Foredeep). These raw materials are characterized by a high content of calcium-magnesium smectite and opal. The components of this rock were subjected to separation in the ultracentrifuge at a velocity of 4500 rpm for 3 hours. Three samples from various sites were collected in order to identify the distribution of the particles in the sedimentation profile. Such specimens were tested using X-ray diffraction analysis and the analysis of particle size distribution, as well as the content of smectite were determined by sorption of methylene blue and copper triethylenetetramine (TETA Cu(II)). X-ray patterns of three samples show a variation of the first, low angle peak of smectite, indicating various smectite contents in these siliceous clays taken from different depths of the sedimentation vessel. The quantitative assessment of the content of smectites was performed by spectrophotometric sorption of methylene blue and TETA Cu(II). The results show difference in smectite contents: 47% for the sample originated from the highest part of the sedimentation vessel and 35% for the sample from its lowest level. These results confirm the different particle size distributions depending on the sampling site. The SEM studies of the fracture of the dried samples after sedimentation indicate that the upper portion of the sedimentation vessel is loosely fielded by clay minerals. On the contrary, there are highly compressed particles of opal and other grain surrounded by montmorillonite particles on the bottom part of vessels. These analyses show that the separation of the components of the siliceous clays from Dylągówka using ultracentrifuge methods lead to significant changes in the arrangement of the components of rock., The spectrophotometric analyses play a significant role in such researches due to its ability to identify the nanometric smectite. These methods are relatively easy and – first of all – cheap way to determine the percentage content of smectite in the test batch.

The Third Early Stage Researchers Workshop

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INVITED TALKS

FERROELECTRICS,
MULTIFERROICS
THERMOELECTRICS

IM1

UNVEILING THE RELATIONSHIPS BETWEEN PIEZOELECTRICS AND THE HUMAN BODY

Paula Maria Vilarinho

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This talk is about piezoelectricity and the human body. The main purpose of the talk is to unveil the relations between piezoelectricity and the biological activity, towards the discussion of the promising applications of electric field driven platforms for Tissue Engineering and Regenerative Medicine. The talk comprises concepts and practical applications that should be of interest to young researchers working in functional materials field and to the Electroceramics community as well.

Life expectancy is increasing and with it improvement of life quality is of utmost importance. Tissue Engineering and Regenerative Medicine, ultimately aiming at organs repair and regeneration, are consequently key technologies [1]. A leverage of the current success and practical applications achieved up to now with Tissue Engineering and Regenerative Medicine is expected. For that some barriers have to be overcome. Because electrical phenomena have a role in the body and it is associated with several biological phenomena, its exploitation within Tissue Engineering and Regenerative Medicine might be promising. Indeed there are many similarities between the nervous system and electrical circuits [2]. In the 50´s Fukada *et al* reported for the first time the piezoelectric activity of bone associated with collagen fibrils [3]. And very recently a ferroelectric activity was reported in aortic walls [4].

This talk reviews the most recent works carried out on the exploitation of electrical phenomena in particular piezoelectricity and piezoelectric materials for tissue growth. The talk will cover our most recent results on the evidences of protein adsorption process dependence on the surface polarization of piezoelectric, bioactive and biodegradable poly L-lactic acid (PLLA). I´ll show that the process of protein adsorption is highly favoured in poled areas of PLLA. In addition, poling PLLA at temperatures above glass transition allows obtaining polarization stable up to dozens days. This period is enough to trigger and maintain proteins adhesion and cells proliferation, if PLLA is used as a platform for tissue growth. The talk will also cover the current controversy on the piezoelectric activity of hydroxyapatite. Finally indications of bioactivity *in vitro* of ferroelectric niobates and tantalates will be presented and the apatite formation mechanism described. The talk concludes by summarising the evidences for the numerous possibilities to use piezoelectrics as "substrates" for tissue engineering, providing unique chances for breakthroughs in biomaterials developments.

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IM2

ORGANIC-INORGANIC COMBINATIONS OF MATERIALS FOR FLEXIBLE ELECTRONICS: FROM MATERIAL DESIGN TO APPLICATIONS

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The large scale electronics used in all the major technological applications but also in the everyday life devices (computers, mobile phones, sensors/actuators, GPS, etc.) is based on semiconductors and dielectric/ferroelectric materials, which are (multi)functional inorganic materials included in the category of electroceramic oxides. All the materials with superior performances used in the microelectronic industry both for passive and active components, like semiconductors, ferroelectrics, magnetic ordered materials, electrooptics, magnetoelectric, piezoelectric, etc. fall into the category of crystalline solids and they are *rigid materials*. On the contrary, the term “organic” reminds the idea of plastic materials that are largely regarded as flexible electrical insulators.

A new field of electronics emerged recently, together with the discovery of conducting and semiconducting organic materials in solid forms. However, the functional performances of such materials are still poor by comparison with ones of the crystalline structures. For example, the mobility of free careers in polymer semiconductors are 2-3 orders in magnitude lower than in crystalline semiconductors. The very few ferroelectric polymers (PVDF-based) have a much lower switchable polarization, permittivity and higher coercive field than the oxide crystalline ferroelectrics.

The new field of flexible electronics demands for new materials and structures to accomplish both demands of high functional performances and flexibility. The envisaged applications of flexible electronics are ranging from flexible displays, electronic textiles, sensory skins, active antennas, electromagnetic shielding, energy harvesting and biomedical real time monitoring/healing.

The lecture will revue the emerging research field of designing and developing alternative inorganic-organic composite materials and patterning techniques for macroelectronic systems, with a goal of increasing their performance, decreasing their cost (per unit area), and enabling them to be formed on low-cost, bendable substrates.

IM3

ADDRESSING CHALLENGES IN SOLUTION BASED DEPOSITION OF OXIDE FILMS

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In order to meet with the demand of increasing speed and improving performance, but also considering new technologies in various fields, functional oxides with nanostructured morphology become a necessity. Mostly, these materials are deposited on a solid support whereby strong control over the nanostructure, film thickness or nano-island formation, grain size, crystal structure or amorphicity, phase purity, morphology and texture is required. Handling questions related to composition-morphology-property relations at the nanoscale is crucial as these determine the functionality of the materials and their performance in devices.

In view of an increased awareness of sustainability, the composition of these materials as well as the ways to produce them need to be taken into account as well. Indeed, an important challenge, besides the search for better materials, is the deposition of well performing layers allowing high throughput production at a low prize. Solution based deposition is an appealing alternative to standard physical deposition methods that require a high vacuum or to ceramic methods that require high energy milling and thermal treatments. However, there are still many issues related to solution based methods which need to be solved before they can be really competitive with e.g. vacuum based methods.

In our group, syntheses of monometal oxides and multimetal oxides are studied by solution based methods such as sol(ution)-gel syntheses, thermal decomposition routes, hydro/solvothermal syntheses, co-precipitation methods etc. In this presentation our current focus on reducing toxic solvents, lowering thermal budgets, and an in depth study of the relation between the synthesis and application directed properties are exemplified by some recent examples.

Acknowledgments: The work is supported by the Flemish FWO and SIM (Strategic Materials Initiative). The COST action 'simufer' is acknowledged for financing travel and networking.

IM4

SPARK PLASMA SINTERING – HOW TO DESIGN EXPERIMENTS

David Salamon

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Spark plasma sintering (SPS) has attracted increasing attention over the last decade and the process is known of its rapid densification of metals and ceramics. The mechanism behind this rapid densification has been discussed during the last few decades and is yet uncertain. Technically, SPS is similar to conventional hot pressing, in which a sample is loaded inside a graphite die and a uniaxial pressure is applied during sintering. In a hot-pressing apparatus, furnace elements act as the heating source, where–as in SPS a pulsed direct current passes through the electrically conducting pressure die (sometimes also through the sample) thereby heating the sample. This enables very high heating rates (up to 1000 °C min^{-1}), allowing completion of the sintering cycle within a few minutes instead of hours, as required by a conventional hot press.

Very short time of the SPS experiments requires precise design of the experimental setup to achieve reproducible results within controlled conditions. This presentation will address several specific issues related to SPS, information in literature will be discussed from the experimental point of view. One of the most discussed topics is temperature profile during SPS experiments and control points for reproducible temperature profile will be provided. Generally, the recorded and displayed physical variables may provide relevant information for reproducible and controlled SPS experiment. Improved understanding of the experimental procedure is going to stimulate research and application of SPS technique.

IM5

PROCESSING AND CHARACTERIZATION OF POROUS PIEZOELECTRIC CERAMIC MATERIALS

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The talk reviews the processing of porous piezoelectric ceramics with interconnected porosity, in a wide range of pore volumes and pore size and distribution. The porosity can be introduced through dry or wet techniques. In the dry techniques a fugitive phase is added to the powder by mechanical mixing. Wet techniques involve the manipulation of suspensions and a better control of the final morphology and microstructure of the samples can be achieved by the colloidal approach. Several techniques for generation of porosity are surveyed including die pressing, slip casting, tape casting, direct consolidation, solid freeform fabrication. Porous materials can also be designed as isotropic or anisotropic structures or functionally graded materials (FGM). Examples of the processing results will be shown related to the production piezoelectric materials. In fact the pore size distribution and microstructural differences resulting from various processing parameters influence the physical properties, particularly the acoustic/piezoelectric response of piezoelectric materials. Dense PZT-type piezoceramics show low hydrostatic figure of merit (FOM) and the introduction of tailored porosity can considerably improve the performances of ultrasonic devices, such as hydrophones or medical diagnostic devices. In anisotropic, porous piezoelectric materials, the decoupling between transverse and longitudinal effects leads to an increase of the FOM while the transfer of acoustical energy to water or biological tissues is improved as a consequence of a lower acoustical impedance (Z). Functionally graded porous piezoceramics are of interest for ultrasonic applications as the gradual decrease of acoustical impedance improves the transfer of acoustic energy to water or biological tissues, assuring at the same time an high piezoelectric response.

IM6

FIRST-PRINCIPLES ACCURATE PREDICTATION OF THE ELECTRONIC AND STRUCTURAL PROPERTIES OF FERROELECTRIC OXIDE BULKS AND NANOSTRUCTURES

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We report a systematic comparison of various Density Functional Theory (DFT) and hybrid exchange-correlation functionals for the prediction of the electronic and structural properties of prototypical ferroelectric (FE) oxides. We find that some, although not all, usual DFT functionals predict the structure with acceptable accuracy, but always underestimate the electronic band gaps. Conversely, common hybrid functionals yield an improved description of the band gaps, but overestimate the volume and atomic distortions associated to ferroelectricity, giving rise to an unacceptably large *c/a* ratio for the tetragonal phases of $BaTiO_3$ and $PbTiO_3$. This *super-tetragonality* is found to be induced mainly by the exchange energy of the Generalized Gradient Approximation (GGA). We thus propose an alternative functional, B1-WC1, that mixes exact exchange with the recently proposed GGA of Wu and Cohen which, for solids, improves over the treatment of exchange of the most usual GGA's. B1-WC renders accurate description of both the structural and electronic properties of typical ferroelectric oxides. Because of the band gap problem of usual DFT functionals, the study of metal/FE interfaces can give rise to unrealistic situations with the Fermi energy located in the bottom of the conduction band instead being in the band gap. B1-WC allows us to provide improved first-principle description of Schottky barriers formed at

the interfaces between different ferroelectrics ($BaTiO_3$, $PbTiO_3$, $SrTiO_3$) with metal electrodes (Al, Ag, Au, Cu, Ir, Pt, $SrRuO_3$). The dependence of Schottky barriers on work functions and the main trends will be discussed.

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Book of Abstracts

FERROELECTRICS
MULTIFERROICS
THERMOELECTRICS

M1

COMBINING ANTIFERROELECTRIC-FERROELECTRIC MATERIALS IN COMPOSITES IN SEARCHING FOR NEW PROPERTIES

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The interest in improving tunability properties in various types of ceramics is related to the continuous growth of their use as tunable microwave devices. In order to fulfill technological requirements e.g. tg$\delta < 0.3\%$, $\varepsilon_r \sim 1000$, the combination of ferroelectric (FE) $BaTiO_3$ with antiferroelectric (AFE) PLZT phases in ceramic composite structures is proposed in the present work. While AFE materials are characterized by low dielectric permittivity with a field-induced transition to the ferroelectric state, the FE phase is described by a relatively high permittivity combined with low electric field strength dependence.

Di-phase composite powders AFE-FE with composition 50% $Pb_{1-x}La_xTi_{1-y}Zr_yO_3$ - 50% $BaTiO_3$ have been prepared by two different methods: (i) solid state reaction (PLZT_BT_SS) and (ii) core-shell method (PLZT_BT_CS). The samples were obtained using two different AFE phases: $Pb_{0.96}La_{0.04}Ti_{0.10}Zr_{0.90}O_3$ (PLZT1) and $Pb_{0.92}La_{0.08}Ti_{0.20}Zr_{0.80}O_3$ (PLZT2). The XRD study shows pure phase for both precursor powders. Dense ceramics with relative density of 95–98% and homogeneous microstructures have been obtained for all the compositions

The dielectric properties were investigated by Impedance Spectroscopy in the temperature range of (20, 270) °C at heating/cooling cycles. An increase of dielectric constant was observed at room temperature for PLZT_BT_SS and a reduction of permittivity was obtained in case of PLZT_BT_CS for both antiferroelectric phases.

The tunability properties determined at room temperature showed a strong nonlinear character and a hysteretic behavior for all the composite ceramics and reduced permittivity, to be compared with almost zero tunability found in the pure PLZT ceramics.

As a conclusion, the advantages of combining FE and AFE properties in composites towards a high tunability and lower permittivity properties of this kind of composite can be controlled by the preparation method.

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M2

MAGNETOELECTRIC COUPLING IN THE 2D ANTIFERROMAGNET: β-$NaMnO_2$

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Spin-driven ferroelectricity on the two-dimensional (2D) antiferromagnet β-$NaMnO_2$, is reported for the first time. Tuning the dielectric/ferroelectric properties of materials by applying external electric or magnetic fields is a major challenge in fundamental physics and a great necessity in the technology of multifunctional devices. Neutron powder diffraction shows that β-$NaMnO_2$ undergoes two magnetic phase transitions, a commensurate at 200 K and an incommensurate one at 90 K. Clear dielectric anomalies that occur at each magnetic transition indicate significant spin/lattice coupling. The complex non-collinear antiferromagnetic structure induced by the frustrated interactions of the corrugated triangular network of the Mn cations, breaks the inversion symmetry and induces magnetodielectric coupling, since sharp dielectric anomaly appears concurrently with the 90 K transition. The most striking feature of this dielectric anomaly is the unusually large dependence of the dielectric constant under different magnetic fields. HRTEM studies reveal structural heterogeneity due to coherent intergrowth of two near equivalent in energy polymorphs (distorted α-$NaMnO_2$ and β-$NaMnO_2$ phases). We argue that the various intergrown nanodomains, make the local and global symmetries different with important consequences in the manner with which magnetic interactions are established and magnetodielectric coupling appears in the bulk compound. The above findings provide new insight on the importance of nanodomains in bulk oxides associated with the appearance of the enchanced magnetodielectric effect that can be controlled by external fields.

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M3

FIRST-PRINCIPLES MODELLING OF $SrTiO_3$ BASED OXIDES FOR THERMOELECTRIC APPLICATIONS

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Oxide compounds are often considered as the most promising solution for hightemperature thermoelectric (TE) applications. Good candidates include doped-$SrTiO_3$, which shows a $ZT \sim 0.4$ in $SrTi_{0.8}Nb_{0.2}O_3$ films at 1000 K [1]. Different strategies have been proposed to further increase the TE efficiency. By performing first-principles electronic and transport calculations, we engineer the electronic band structure of $SrTiO_3$ alloys with Nb(V) and that of $LaVO_3$($KNbO_3$) nanostructures embedded in a $SrTiO_3$ matrix in order to design new oxide materials with high TE efficiency. These calculations have been performed within the recently proposed B1-WC hybrid functional [2]. This hybrid is able to describe both structural and electronic (band gaps) properties of prototypical ferroelectrics and multiferroics [3]. The TE properties of $SrTiO_3$ based oxides will be discussed.

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M4

USING 3D-IMAGING BY X-RAY MICROTOMOGRAPHY TO CHARACTERISE FUNCTIONAL CERAMICS INTERNAL STRUCTURE

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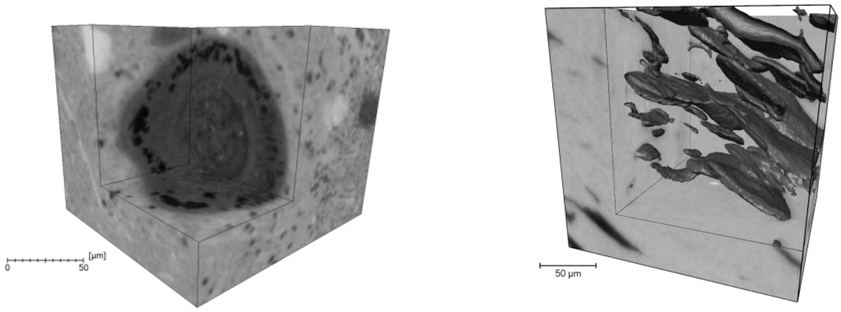
Functional ceramics such as ferroelectric composite materials feature more and more complex structures at various scales, and their performances are directly connected to the well-controlled architecture of their components. Classical 2D-imaging approaches (i.e. scanning electron microscopy, SEM) are commonly used to validate the final layout of these composites, but the real shape of the different phases is hardly known, especially in the case of anisotropic functional materials. X-ray computed microtomography

(XCMT) is a non destructive characterisation technique providing direct images of the 3D microstructure of multi-materials. The possibilities offered by XCMT to quantify the 3D architecture are exposed in this presentation. We have processed by Spark Plasma Sintering (SPS) composites made of MgO inclusions dispersed in a ferroelectric matrix ($Ba_{0,6}Sr_{0,4}TiO_3$) [1] and developed an innovative procedure [2] in order to obtain a complete quantitative description of the ferroelectric composites at their initial state (mixing powder) and final processed state (Fig. 1).



a) b)

Figure 1. a) 3D rendering with multiple 2D sections of MgO granule (corresponding to the dark spheroid) inside the ferroelectric matrix before sintering. MgO features porous structures at the perimeter. b) 3D rendering of the composite material after sintering by SPS (inclusions in dark grey).

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M5

INVESTIGATION OF THE ROLE OF POROSITY ON THE SWITCHING PROPERTIES OF Nb-PZT CERAMICS: EXPERIMENT AND MODELING

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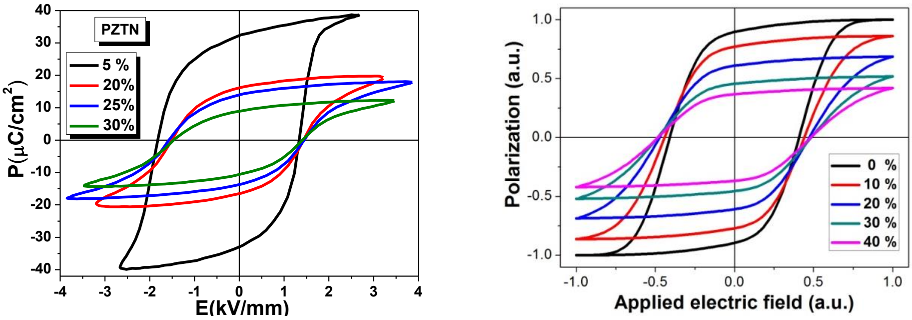
A combined Finite Element Method (FEM) - Preisach model is proposed to theoretically explain the dependences of the polarization on the applied electric field in porous ferroelectric systems. As a first step, various 2D porous systems were numerically generated. For these systems with different porosities the local electric fields were computed by FEM solving the Poisson's equation: $\nabla \cdot (\varepsilon \nabla V) = 0$, were ε is the local permittivity: 1000 for ferroelectric bulk and 1 for pores. By comparison with a dense system, a highly inhomegeneous local field distribution was obtained for a porous structure. Considering these local electric field distributions, $P(E)$ hysteresis loops and First Order Reversal Curves (FORC) were simulated by Preisach model applied locally per elements. A very good agreement between experimental and simulated hysteresis loops was observed: the decrease of the saturation/remanent polarization, decrease of the hysteresis area and the tendency towards a more tilted hysteresis with increasing porosity (Fig. 1).

The macroscopic FORC distributions were computed for different porosity levels, and only for the dense structure the macroscopic distribution is identical with the one used in the Preisach model. For porous structures, broader distributions were obtained macroscopically even if the local distributions are independent on the porosity. The results predicted by the FEM-Preisach model were experimentally confirmed by the case of the Nb-doped PZT with various levels of porosity.



a) b)

Figure 1 (a) Experiemental P(E) hysteresis loops for Nb-doped PZT with different porosity levels; (b) Simulated P(E) hysteresis loops by combine Preisach-FEM model

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M6

PREPARATION AND CHARACTERIZATION OF SPHERICAL TiO_2 MICRORESONATORS BY SPRAY DRYING FOR THz APPLICATION

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Over the last decade, metamaterials have attracted a great attention in many potential applications such as sub-diffraction-limited imaging, biosensing, medical imaging, and so on. The so-called all-dielectric metamaterials are very promising as novel three dimensional isotropic metamaterials exhibiting desired electromagnetic properties for terahertz applications [1]. In this study, we focus on the elaboration of TiO_2 micro-resonators using spray drying method. Starting with TiO_2 commercial nano-particles dispersed in water, spherical micro-sized particles with a size ranging from 10 up to 65 µm, are prepared by adjusting the synthesis parameters (solid concentration, gas flow, suspension composition). The influence of each parameter on the size, the shape and the microstructure of particles are discussed.

The crystallinity control of TiO_2 µ-spheres is achieved by multi step sintering under O_2 flow. SEM micrographs and 3D X-ray tomography analysis are used to study both the bulk and the surface of particles. THz characterizations conducted on metamaterials made of a layer of TiO_2 spherical particles will be presented.

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M7

PHASE TRANSITIONS IN Ba/Sr TITANATE AND $BaTiO_3/TiO_2$ NANOSTRUCTURES STUDIED BY RAMAN SPECTROSCOPY

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Barium titanate is widely used for electronic devices in technological ceramic industry because of its ferroelectric, thermoelectric and piezoeletric properties when it assumes the tetragonal structure [1]. As such it have application in production of capacitors, positive temperature coefficient resistors, dynamic random access memories, electromechanics and nonlinear optics [2,3]. On the other hand, Strontium titanate with perovskite structure is known for its dielectric, thermoelectricity, magnetoresistivity and optical non-linearity [4,5].

In this work Ba/Sr titanate nanostructures will be synthesized using hydrothermal treatment. The aim of the study is influence of the molar ratio of Ba^{2+}/Sr^{2+} in starting solution for hydrothermal synthesis on structural properties and ferroelectric phase transitions of synthesized materials.

For the synthesis of barium/strontium titanate, nanostructures aqueous solutions containing different molar ratio of barium and strontium salts were hydrothermally treated with titanium dioxide nanoparticles and NaOH. $BaTiO_3/TiO_2$ was synthesized by hydrothermally from 1 M aqueso solution of barium octahydrate and TiO_2 nanotubes on Ti foil. Obtained nanostructures were characterized by micro-Raman spectroscopy (RS), X-ray powder diffraction. Temperature dependent micro-RS measurements were done *in situ* at different temperature using Linkam heating stage.

In situ low and high temperature RS was used for study of ferroelectric phase transitions from tetragonal to cubic structure in Ba/Sr titanate nanostructures and $BaTiO_3/TiO_2$ having different phase purity and relation. The influence of the morphology, the formation of solid solutions, phase relation and purity to the temperature of phase transitions will be discussed.

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M8

Y-TYPE HEXAFERRITE $Ba_2Mg_2Fe_{12}O_{22}$ POWDERS – OBTAINING AND CHARACTERIZATION

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Multiferroic materials in which long-range magnetic and ferroelectric orders coexist have recently been of great interest in the fields of both basic and applied sciences. The Y-type hexagonal ferrites are an important type of high-frequency soft magnetic materials due to their strong planar magnetic anisotropy. The Y-type hexagonal ferrite $Ba_2Mg_2Fe_{12}O_{22}$ is a multiferroic material. It has a relatively high spiral-magnetic transition temperature (~200 K), shows multiferroic properties at a zero magnetic field, and the direction of the ferroelectric polarization can be controlled by a weak magnetic field (< 0.02 T). Due to the fact that the Y-type hexaferrites are an intermediate phase during the synthesis of Z-type ferrites, which is suitable for multy-layer chip inductors, not much attention has been paid to their synthesis and magnetic investigation especially what concerns powders. We present the structural and magnetic properties of multiferroic $Ba_2Mg_2Fe_{12}O_{22}$ hexaferrite powders containing a small amount of $MgFe_2O_4$. The samples were obtained by auto-combustion or by sonochemical co-precipitation. The XRD spectra of the powders showed the characteristic peaks corresponding to the Y-type hexaferrite structure ($Ba_2Mg_2Fe_{12}O_{22}$) as a main phase and some impurity of $MgFe_2O_4$ less than 2%. The Rietveld refinement of the crystal structure of the $Ba_2Mg_2Fe_{12}O_{22}$ revealed that the Mg^{2+} cations are distributed over all cation sites leading to mixed occupancies of sites in the cation sublattice. The particles obtained by sonochemical co-precipitation had an almost perfect hexagonal shape in contrast with those prepared by auto-combustion. Two magnetic phase transitions related to the composite's multiferroic properties were seen: at 183 K and 40 K for the auto-combustion sample, and at 196 K and 30 K for the sonochemical co-precipitation one. The change at higher temperature is brought about by a phase transition from ferromagnetic state to spiral spin order state. This transition determines the multiferroic properties of $Ba_2Mg_2Fe_{12}O_{22}$. We believe that the transition at lower temperature is related to spin reorientation along the *c* axis into a longitudinal conical state. No magnetic phase transitions in these temperature ranges appeared for $MgFe_2O_4$ sample, i.e., magnesium ferrite does not affect this material's multiferroic properties.

M9

AUTOCOMBUSTION SYNTHESIS AND CHARACTERIZATION OF MULTIFERROIC BISMUTH FERRITE CERAMICS

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Bismuth ferrite is one of the most promising single multiferroic materials. It exhibits ferroelectric and antiferromagnetic behavior in wide range of temperatures. Many new applications arise due to possibility of magnetization reorientation by electric field and polarization reorientation by magnetic field [1]. Main problem in usage of $BiFeO_3$ is difficulty of obtaining pure phase ceramic and high conductivity as a result of Fe non-stoichiometry.

$BiFeO_3$ (BFO) powders were prepared by auto-combustion and soft chemical methods starting from iron and bismuth nitrates. After the synthesis, fine precursor powders were thermally treated for various periods at different temperatures and heating rates. In case of auto-combustion synthesis, several fuels (citric acid, sucrose and urea) and fuel to oxidizer ratios (F/O) were examined, while for soft chemical synthesis two complexing agents were tested: citric and tartaric acids. Low temperature synthesis was also tested without any complexing agent. XRD measurements showed presence of

Bi_2O_3, $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$ secondary phases in all powders, and pure perovskite BFO phase for several sintered samples. Powders and ceramics were characterized by SEM/EDS, TG/DTA, particle size distribution and BET surface area measurements. Impedance and magnetic measurements were performed in order to define electrical and magnetic properties of BFO ceramics.

M10

VISCOELASTIC BEHAVIOR OF NEW ANIONIC CLAY – POLYMER HYBRID MATERIALS

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Nanocomposites (PVA/LDHs) based on matrices of hydrotalcite-like clays type MgAlLDH and FeAlLDH and poly(vinyl alcohol) (PVA) were prepared by using the structural reconstruction of the calcined clays. The physical-chemical characteristics of the LDHs-polymer hybrids were studied by using rheological measurements and SEM analysis. The PVA/LDHs nanocomposites were submitted to freezing/thawing cycles and the rheological behavior of the samples was investigated for different freezing periods (0, 7, 14 days).

The viscoelastic parameters (such as: the storage and loss moduli, the loss tangent as well as the complex viscosity) were determined in frequency or temperature sweep tests, in the linear viscoelastic regime, giving information about the evolution of the polymer/clay network as a function of the material composition or experimental conditions. The experimental data show that for a freezing time of 7 days there is a noticeable increase in viscosity; furthermore, after 14 days of freezing the viscosity increases up to 10^4 times. Also, the dependences of the viscoelastic moduli as a function of the oscillation frequency are considerably changed with increasing the freezing time, indicating a transition from a liquid-like behaviour to a solid-like one for the studied hybrids. The yield stress and the tixotropy are sensibly dependent on the freezing time and the aging temperature.

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M11

CHARACTERIZATION OF $BiFeO_3$ NANOPOWDER OBTAINED BY HYDROTHERMAL SYNTHESIS

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The influence of processing parameters on phase formation and particle size of hydrothermally synthesized $BiFeO_3$ powders was investigated. $BiFeO_3$ powder was synthesized by dissolving bismuth nitrate and iron nitrate in KOH solution. Single-phase perovskite $BiFeO_3$ has been formed at a temperature of 200 °C in a 6 h reaction period. The phase composition of the samples was studied by micro-Raman spectroscopy (RS) and was compared with X-ray powder diffraction (XRD) results. It revealed that synthesized material crystallize in space group $R3c$ with cell parameters $a = b =$ 5.5780(10) Å and c = 13,863(3) Å. The particle size and distribution was determined by small-angle X-ray scattering (SAXS). The powders behavior was characterized by TG/DTA. The magnetic behavior of synthesized material is done by means of SQUID device and using a vibrating sample magnetometer (VSM).

M12

MULTIFERROIC PFN MATERIALS ENERGY CONVERSION CHARACTERIZATION

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Multiferroic materials energy conversion characterization is concerned with multifunctional properties of materials, a topic that is fascinating from the scientific point of view and important for the modern technology. We are present a detailed report of the relationships between magnetic field intensity and output characteristics of fabricated one phase $PbFe_{1/2}Nb_{1/2}O_3$, for magnetic field driven energy transducers. $PbFe_{1/2}Nb_{1/2}O_3$ (PFN) pervskite multiferroic materials exhibit magnetic and ferroelectric ordering and coupling between them in a single phase at room temperature. In the PFN ceramics, ions of iron (Fe), niobium (Nb) are substituted randomly at the octahedral B positions in pervskite ABO_3 structure, whereas lead (Pb) goes into the A position. Iron has a naturally magnetic moment, consequently, the angles between the connecting lines between B cation and oxygen are equal to 180 degree, providing optimum conditions for magnetic ordering due to the indirect exchange interaction. So that, the coupling between magnetization and polarization is achieved due to ferrum ions addition, that rise sufficiently sensitivity to magnetic field not decreasing the dielectric losses.

M13

MULTIFERROIC Ba(Sr)TiO$_3$-NiFe$_2$O$_4$ COMPOSITE CERAMICS FROM CORE/SHELL NANOPARTICLES

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Even though single-phase multiferroics have been profoundly investigated in recent years, none of the known materials exhibit satisfactory Magneto Electric (ME) effect at room temperature. On the other hand, composite multiferroic materials (consisting of ferroelectric and ferromagnetic separate phases) offer a wide variety of design and tuning possibilities and accordingly, have drawn rising attention in recent years. Recently, with the aim to achieve a more intimate contact between the phases in bulk solid composites, novel synthesis methods to obtain multiferroic core-shell nanostructures have been reported. This work presents a possible approach for preparation of dense ceramic with specific electrical and magnetic properties, from nanoparticles with core-shell structure. Barium or strontium titanate (BaTiO$_3$, SrTiO$_3$) was used as a core material, while shell was created of nickel ferrite (NiFe$_2$O$_4$) nanoparticles, i.e. spinnel ferrite, showing ferrimagnetic behaviour. (Sr,Ba)titanate nanoparticles were synthesized by sol-gel method in two-step process, while shell of nickel ferrite nanoparticles were synthesized by co-precipitation route using stable ferric and nickel salts with sodium hydroxide as precipitating agent. Synthesis procedure and process parameters (pH, temperature, core/shell mass ratio) were varied with the aim of preparation nanoparticles of good morphology and shell coverage. Core-shell nanoparticles were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). Core-shell nanoparticles were further isostatically pressed and sintered at different temperatures in order to obtain dense ceramic with desired electrical and magnetic properties. Microstructure of prepared ceramics was various titanate:ferrite ratio was characterized by SEM, and functional (dielectric and ferroelectric) properties were investigated. Ferroelectric behavior was measured at room temperature and dielectric properties at elevated temperature (room temperature – 450 °C) and in the frequency range of 100 Hz–1 MHz.

M14

THERMAL TREATMENT EFFECTS IN PbTiO$_3$ STUDIED BY XPS AND ELECTRIC CONDUCTIVITY

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The PbTiO$_3$ is a material needed for industry from point of view of their stability, since it shows high value of the spontaneous polarisation P_S [1] and the ferroelectric phase stable up to T_C = 746 K. The as-grown aged and thermally treated PbTiO$_3$ crystal samples were prepared [2]. The samples were heated, for several hours in ambient air, at 723 K and 873 K, i.e. below and above T_C. Migration of defects was presumed, caused by such processing. The thermal treatment induced changes in shape of the Pb 4f, Ti 2p, O 1s, and also valence band lines. The main effect of the thermal treatment was seen in narrowing of these lines (FWHM). The narrowing of the core lines indicated the decreasing disorder of the crystal lattice. Moreover we deduced that higher temperature of thermal treatment, the lower contribution of the surface states occurred [3]. This effect was ascribed to a migration of ions, that occurred at high temperature. Dielectric permittivity $\varepsilon'(T,f)$, *measured at radio frequencies,* of the aged samples of the PbTiO$_3$ crystals shown marked dispersion. A frequency dependent broad peak in plot of dielectric loss coefficient $tan\delta(T,f)$ occurred in 300–500 K range. Both real and imaginary parts of electric permittivity reached high values ~10^5 in high temperature range. The expected Curie-Weiss type anomaly at FE-PE phase transition was masked by steep increase in $\varepsilon'(T)$, in case of as-grown and aged PbTiO$_3$ crystals. The thermal procedure influenced electric properties and two effects occurred. The samples heated at 723 K shown still marked dispersion in electric permittivity. However, the resistive switching to non-semiconductor type temperature dependence in electric conductivity $\sigma(T,f)$ was obtained and confirmed by DC conductivity $\sigma_{DC}(T)$ measurements [4]. The samples heated at 823 K exhibited well resolved Curie-Weiss dependence above T_C = 750 K. The electric conductivity $\sigma(T,f)$ shown semiconductor dependence on temperature with activation energy values E_a = 0.15, 0.35, and 0.84 eV. Such values of E_a, lower than optical energy gap, indicated that defects determined electrical properties. Thermal treatment induced change in the activation energy values. A correspondence of the electrical features, induced by high temperature effects, to electronic structure changes, determined with XPS test, was discussed. We discuss the obtained results in framework of charged defect migration toward and from FE domain walls [5], space charge effects, and chemical capacitance of solids which contain traps distributed in energy gap [6,7].

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M15

SELF-ASSEMBLIES OF NANOPARTICLES OF Cr_2O_3-ZnTi LDHs AND THE DERIVED MIXED OXIDES AS NOVEL PHOTOCATALYSTS FOR PHENOL REMOVAL

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Phenol is a major pollutants of aquatic environment. Phenol may occur in aquatic environment due to its widespread use in agricultural, petrochemical, textile, paint, plastic and pesticide chemical industries. Defined by a high carcinogenic and mutagenic potential, phenol poses a high risk to mammalian and aquatic life. Owing to its stability and solubility in water, its removal to a safety level (0.1–1.0 mg/L) is a difficult process. A growing interest exists nowadays to develop new photocatalysts able to use the light energy for generating strongly oxidizing hydroxyl radicals (•OH), which oxidize not only phenol but also a broad range of organic pollutants from wastewaters.

This work reports the synthesis and characterization of the nanostructured assemblies of Cr_2O_3-ZnTi-layered double hydroxides (LDHs) and the derived mixed oxides as novel nano-photocatalysts for phenol photodegradation under UV light.

Cr_2O_3 exhibits a strong absorption in the UV and Vis range and shows photocatalytic response mainly based on two features. Layered double hydroxides have a number of advantages over other materials for environmental applications, as they are nontoxic, cheap and easy to prepare. These materials are currently employed on a wide scale as catalysts and catalyst precursors in fine organic syntheses as well as for the oxidation of organic compounds in wastewaters.

The self-assembly of Cr_2O_3 nanoparticles and ZnTi-LDH was obtained by taking advantage of the remarkable *memory effect* property of this type of material. It was demonstrated that the layered structure could be regenerated and the obtained nanosized Cr_2O_3-ZnTi-LDH self-assembly can form under mild temperature conditions a combined nanosized Cr_2O_3-Zn_2TiO_4 photocatalytic system with specific properties. The photocatalytic efficiency of the obtained products was evaluated for the degradation of phenol under UV irradiation. The phenol degradation pathway was rationalized using UV-vis spectroscopy. The advantage of using a LDH type matrix assembled to metal oxide nanoparticles stands in the versatility of the brucite-like sheets composition which may allow the insertion of key cations, like Zn^{2+} and Ti^{4+}, within the LDH network. The LDHs materials can supply a good dispersion of the metal cations within the layers which may act as charge separation centers enhancing the efficiency in photocatalytic applications.

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M16

SYNTHESIS AND CHARACTERIZATION OF NICKEL ZINC FERRITES

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In this study we have prepared nickel ferrite (NF) and nickel zinc ferrite (NZF) nanoparticles by auto-combustion method starting from nickel, zinc and iron nitrates. After the process of self-ignition, fine precursor powder was thermally treated at 1000 °C for 1 h, forming nickel zinc ferrite powders, with molar ratio of Zn 0, 0.3, 0.5, 0.7. XRD characterization showed the formation of well crystallized nickel ferrite and nickel zinc ferrite inverse spinel structure without presence of secondary phases. Ceramic materials were obtained by uniaxial pressing at 196 MPa and sintering at 1250 °C for 4 h in the tube furnace. SEM images at the free surface showed that substitution of Ni^{2+} ions with

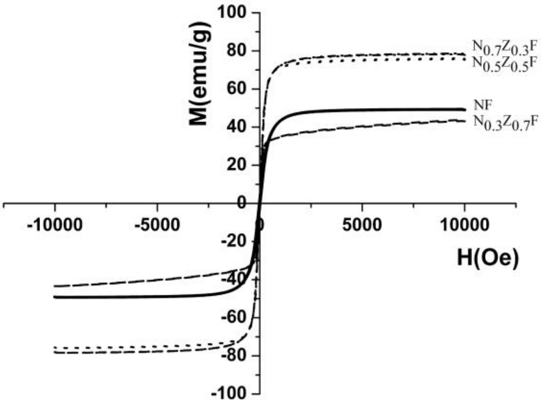

Figure 1. Magnetic measurements of $Ni_{1-x}Zn_xFe_2O_4$ ceramics

Zn^{2+} ions results in larger grains and lower porosity, confirmed by density measurements.

Magnetization results showed ferromagnetic behavior of the NF and NZF materials. Magnetic measurements of ferrites were carried out and presented in Fig. 1. Saturation magnetization moment of NF was lower than for $N_{0.7}Z_{0.3}F$ and $N_{0.5}Z_{0.5}F$, but slightly higher than for $N_{0.3}Z_{0.7}F$. With increasing the ratio of Zn to 0.3, magnetization increases, because the Fe^{3+} ions in the octahedral site interact with other Fe^{3+} ions. The fields at which saturation occur was almost the same for all materials.

M17

DIELECTRIC PROPERTIES OF NANOGRAIN BSPT CERAMICS

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Ferroelectric materials are of high interest for both researchers and engineers due to their remarkable properties. Their switchable electric polarization [1] is ideal for use in devices for memory storage and integrated microelectronics. Advanced devices tend to nanoscale, that raises necessity to research new cheaper and more durable materials.

BSPT (xBiScO$_3$–(1-x)PbTiO$_3$, $x = 0.36$ and 0.375) ceramics with micron, submicron and nanoscale grains were produced from nanocrystalline powders obtained by mechanosynthesis [2] in different milling media (WC and stainless steel). From Fig. 1

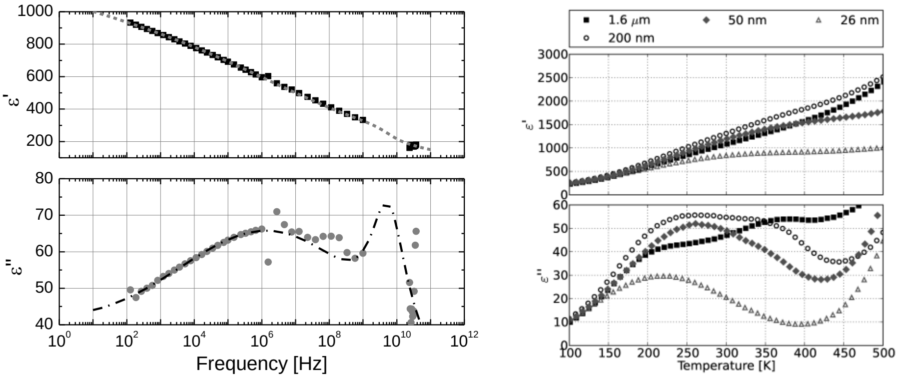

Figure 1. Frequency dependence and fit curves of real (top left) and imaginary (bottom left) part of dielectric permittivity at 225 K temperature for BSPT 200 nm grain size and temperature dependence at 1 kHz frequency of real (top right) and imaginary (bottom right) of different grain size BSPT ceramics produced in WC milling media

we can see that several processes are observed. Furthermore, their strength depends on grain size. A more detailed discussion of dielectric properties of ceramics and grain size effects will be presented.

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M18

DIELECTRIC RESPONSE OF $(Bi_{1-x}La_xFeO_3)_{0.5}(PbTiO_3)_{0.5}$ CERAMICS PREPARED FROM MECHANICALLY SYNTHESIZED POWDERS

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$(Bi_{1-x}La_xFeO_3)_{0.5}(PbTiO_3)_{0.5}$ nanoceramics with high La content was reported to exhibit improved ferroelectric and ferromagnetic properties and relatively great magnetoelectric coupling [1,2]. We studied dielectric response of $(Bi_{1-x}La_xFeO_3)_{0.5}$ $(PbTiO_3)_{0.5}$ (x = 0, 0.1, 0.2, 0.3 and 0.5) prepared from powders obtained by mechanical activation of Bi_2O_3, La_2O_3, Fe_2O_3, PbO and TiO_2 in stoichiometric ratios. The synthesis was carried out in SPEX 8000 Mixer Mill (weight ratio of stainless steel balls/to oxides = 2:1) for 48 h at room temperature. The synthesis was controlled by XRD studies and the obtained compounds can be considered as single-phase materials with tetragonality decreasing with increasing x. Dielectric response of the ceramic samples (with gold electrodes) was studied using an Alpha-A High Performance Frequency Analyzer (Novocontrol) combined with Quatro Cryosystem from 125 K to 575 K on heating at a rate of 1 K/min and the oscillating voltage of 1 V.

At low frequencies one can dielectric anomalies at 430 K related by us to oxygen vacancies. The Curie point anomaly appears at ~500 K for the ceramics with x = 0.5. Relaxor-like behavior with ε''_{max} increasing with increasing frequency was found below 250 K. The effect that random lattice disorder produced by chemical admixtures in highly polarizable host lattice can lead to formation of polar nanoregions has been predicted earlier by Samara [3].

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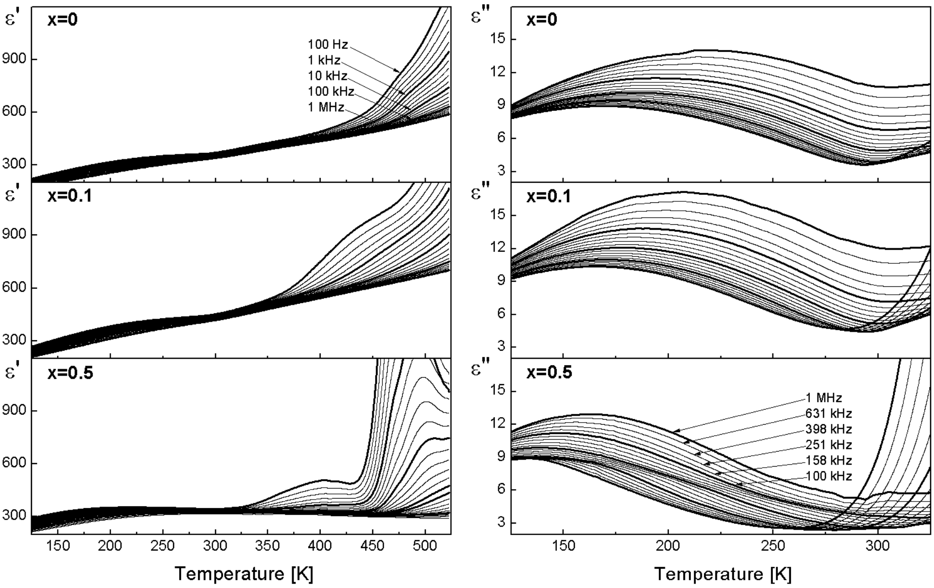

Figure 1. Dielectric response of $(Bi_{1-x}La_xFeO_3)_{0.5}(PbTiO_3)_{0.5}$ ceramics

M19

TEMPERATURE DEPENDENCE OF THE MAIN PIEZOELECTRIC PARAMETERS IN VERY SOFT, SOFT AND HARD PIEZOELECTRIC CERAMIC DISCS

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A systematic study of the temperature dependence of the main piezoelectric parameters in very soft PZTN (conventional Nb doped PZT), soft PLZTN (La and Nb doped PZT) and hard PZTNMML (Nb, Mg, Mn, and La doped PZT) piezoelectric ceramics was done between -30 °C and 150 °C. Using the Impedance Resonance Technique electromechanically coupling factors k_{31}, k_p, k_t, quality factor Q_m, dielectric permittivity coefficients ε_{33}^T and ε_{33}^S, the piezoelectric coefficient, d_{31}, elastic compliance coefficients s_{11}^E, s_{12}^E, as well as the elastic constants c_{33}^E and c_{33}^D were determinates both on cooling and subsequent heating in investigated temperature range for all three ceramics disks. The comparative study reveals that increasing temperature appear significant differences in dielectric behavior and piezoelectric constants between very soft and hard piezoelectric ceramics. Thermal hysteresis was observed for all parameters temperature dependences over the temperature range. Experimental results were discussed in terms of extrinsic, intrinsic and domain wall motion contribution to the dielectric and piezoelectric response of materials [1,2].

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M20

BROADBAND DIELECTRIC SPECTROSCOPY OF A-SITE SUBSTITUTED PEROVSKITE CERAMICS

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Relaxors are disordered materials which exhibit fascinating properties and have been a subject of researches for already more than 60 years. Many models and concepts starting from superparaelectric model [1] were developed to explain the unique features of relaxor ferroelectrics. As a canonical relaxor material B-site substituted system $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) is usually studied. It is known that disorder in the B-site sub-lattice is responsible for the behavior of PMN [2]. The relaxor behaviour is not unique to B-site substituted perovskites but is in general a consequence of charge and ion disorder and random fields occuring in the material [3]. That is why the relaxor behaviour is also observed in A-site substituted materials like $x$$Na_{0.5}Bi_{0.5}TiO_3$– (1-$x$)$SrTiO_3$ [4], xNBT–(1-x)KBT [5] etc.

Relaxors also exhibit similar features to glassy materials and it is well established in the community that the glassy component in relaxors exists [6]. Despite of similarities theese two types of materials have many different properties as well. One of the main differences is observed in dielectric properties and distribution of relaxation times [7]. Relaxors usually have two peaks in the distribution of relaxation: one very broad lying in the long relaxation time part and one sharp peak in the short relaxation times [8,9]. Dipolar glasses, on the other hand, have only one peak [7].

In this contribution we present dielectric measurements of several systems based on sodium bismuth titanate (NBT): ternary solid solutions $Na_{0.5}Bi_{0.5}TiO_3$–(0.6-x)$SrTiO_3$–

$x\mathrm{PbTiO_3}$, $(1\text{-}x)\mathrm{Na_{0.5}Bi_{0.5}TiO_3}$–$0.6\mathrm{SrTiO_3}$–$x\mathrm{PbTiO_3}$, $x\mathrm{Na_{0.5}Bi_{0.5}TiO_3}$–$(1\text{-}x)\mathrm{Sr_{0.7}Bi_{0.2}TiO_3}$, which exhibit very wide range of properties: from dipolar glass-like behaviour to relaxor-like to ferroelectric behaviour. Also, the comparison with canonical relaxors will be made. It will be shown that lead ions in A-site plays an important role for relaxor behaviour to occur.

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M21

CHARACTERIZATION OF THE DIELECTRIC PROPERTIES OF BARIUM TITANATE AND NICKEL-ZINC FERRITE COMPOSITE CERAMICS

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In recent years, there is a tendency to search for novel multifunctional materials. Various technologies that could be used in designing and constructing new devices for electric as well as magnetic field applications simultaneously are very promising and quickly growing fields of interest. It is not surprising that multifunctional multiferroic materials, in which at least two of the main ferroic properties coexist in the same range of temperatures, have gained a lot of attention and are being intensively studied globally. In reality, d-orbital occupancy creates restrictions for the synthesis of new single-phase multiferroic materials, therefore the latter are not very common. Solution to overcome this problem is the synthesis of two-phase multiferroic composites, being nowadays the most extensively studied multifunctional materials.

The present work is dedicated to the comparison of broadband dielectric spectroscopy results of the multiferroic barium titanate and nickel-zinc ferrite (BT-NZF) composite ceramics. The magnetic properties of these materials can be found elsewhere [1]. xBaTiO$_3$–(1-x)Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ceramics were synthesized from powders prepared by using two different methods – co-precipitation and core-shell. Particle morphology and composite microstructure was confirmed in each case by XRD, SEM and other devices [2,3]. Co-precipitation samples were prepared in compositions of $x = 0.5$, 0.6 and 0.7, and core-shell – with $x = 0.7$, but by using two different sintering temperatures – 1050 and 1150 °C. In such case, it is possible to compare properties of the materials in 3 different directions: co-precipitation and core-shell materials, different compositions and different sintering temperatures. Various devices and broadband dielectric spectroscopy methods were used in experiments to cover the wide range of temperatures and frequencies, spanning from 100 K to 500 K and from 20 Hz up to 50 GHz.

The samples prepared by co-precipitation method display significantly higher values of dielectric permittivity than those having core-shell structure. Moreover, three peeks in the temperature dependencies of co-precipitation samples are observed and can be associated with phase transitions occurring in pure barium titanate, while in core-shell samples such behavior is not present anymore. It is noticeable that conductivity is also higher in composites prepared by co-precipitation method. The behavior at low frequencies is primarily determined by more conductive low-permittivity material (nickel-zinc ferrite). In the non-dispersive region, the dielectric permittivity regularly increases with increasing level of high-permittivity material (barium titanate) as a result of "sum property". At higher frequencies, a nearly Debye-type relaxation process can be observed. This shows that the preparation methodology is able to modify dielectric properties significantly in a very broad frequency range.

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M22

IR AND RAMAN STUDIES OF STRUCTURAL, MAGNETIC AND FERROELECTRIC PHASE TRANSITIONS IN MULTIFERROIC CaMn$_7$O$_{12}$

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CaMn$_7$O$_{12}$ is an unusual material which exhibits a rich sequence of structural, ferroelectric and magnetic phase transitions. At high temperatures, (CaMn$_3$)Mn$_4$O$_{12}$ crystallizes in the cubic perovskite structure (space group $Im\bar{3}$) and upon cooling below T_{C1} ~ 450 K charge and orbital ordering occurs which induce a structural phase transition to a trigonal phase with the space group $R\bar{3}$ (Z=3). Below $T_{C2} = 250$ K, the trigonal structure becomes incommensurately modulated with a propagation wavevector $q_c = (0,0,2.077)$ [1]. Upon further cooling below $T_{N1} = 90$ K, an incommensurately modulated magnetic structure emerges with a magnetic modulation vector $q_m = ½q_c$ [1] Very recently, it was reported [2] that the magnetic structure is also ferroelectric with a spontaneous polarization attaining up to $P_s = 2870$ μCm^{-2} oriented parallel to the *c* axis. This is the highest spin-induced polarization among all multiferroics. At $T_{N2} = 50$ K, another magnetic transition occurs, giving rise to a second propagation vector along the *c* axis. Both propagation vectors q_{m1} and q_{m2} change with temperature, but their average value corresponds exactly to $½q_c$.

We have investigated far-IR reflectivity and Raman scattering spectra of $CaMn_7O_{12}$ and found significant changes in the spectra at structural and ferroelectric phase transitions. The IR reflectivity and a Raman scattering spectra changes abruptly at $T_{C1} = 450$ K, giving evidence of the first-order character of the phase transition. Moreover, the conductivity seen in the high-temperature IR spectra disappears below T_{C1}, proving the metal-insulator character of this phase transition due to charge ordering. New polar phonons appear in the IR spectra in the incommensurate phase below 250 K due to a change of selection rules. Raman spectra seem to be less sensitive on the incommensurate and magnetic phase transitions probably due to high absorption and luminescence of the material.

Close to T_{N1}, a new mode develops in IR spectra near 50 cm^{-1}; another one near 30 cm^{-1} appears below T_{N2}. Since the modes appear near the magnetic phase transitions, they can be spin waves (magnons). Nevertheless, IR reflectivity spectra reveal a transfer of the oscillator strengths from the phonons to the excitations seen below 50 cm^{-1}. Thus, the modes at 30 and 50 cm^{-1} contribute to the dielectric permittivity and not to the magnetic susceptibility. This is a typical signature of electromagnons, i.e. electric active magnons, which are activated in THz dielectric spectra due to dynamical magnetoelectric coupling. It is interesting, that the electromagnons are not Raman active, even if the selection rules for phonons are the same for Raman and IR spectra in the ferroelectric phase.

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M23

DIELECTRIC PROPERTIES OF A NEW $Ba_{6-2x}Nd_{2x}Fe_{1+x}Nb_{9-x}O_{30}$ TTB SYSTEM

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Ferroelectric relaxor systems with tetragonal tungsten bronze (TTB) structure is one of the largest oxygen octahedral ferroelectric families next to the ferroelectric perovskites [1]. Three types of open channels that develop within its octahedral framework give raise to its unique properties. More open crystalline network compared to perovskites makes TTB a more flexible material. A wide range of substitutions available in TTB framework enables scientists to synthesize many different compounds. including relaxors, ferroelectrics and even multiferroics.

In this work we present broadband dielectric spectroscopy results of a new $Ba_{6-2x}Nd_{2x}Fe_{1+x}Nb_{9-x}O_{30}$ (TTB) relaxor system. Dielectric measurements were performed in 30–425 K temperature region and 20 Hz–46 GHz frequency range. The investigations were carried out for samples $x = 0.95$, 0.8 and 0.6. A LCR-meter HP4284 was used to measure capacitance and loss tangent of samples in 20 Hz–1 MHz frequency range and model of flat dielectric capacitor was used to obtain a complex dielectric permittivity. Measurements of complex transmission and reflection coefficients were performed using Agilent 8714ET network analyzer in 1 MHz–3 GHz frequency range. In this case a multimode capacitor model was used to obtain complex dielectric permittivity. Measurements in 10–46 GHz frequency range and were performed using scalar network analyser R2400 produced by "Elmika" company by placing the thin dielectric rod in the centre of a waveguide and monitoring the reflection and transmission coefficients from it. All measurements were performed in cooling cycle with temperature change rate of about 1 K/min.

Broad relaxation is observed in all concentrations ($x = 0.95$, 0.8 and 0.6). The values of dielectric permittivity are influenced by conductivity at low frequencies below 100 kHz.

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M24

SELF-ASSEMBLED $BaTiO_3$-$CoFe_2O_4$ AND $BiFeO_3$-$CoFe_2O_4$ FILM COMPOSITES: STRUCTURE AND MAGNETIC STUDIES

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The coexistence of ferroelectric and ferromagnetic properties, as well as the coupling between the ferroic orders makes multiferroic composites very attractive for possible applications in multifunctional devices. Two extreme forms of the composites in a film-on-substrate geometry are multilayer and self-assembled nanostructures. Self-assembled composites on single crystalline substrates show stronger magnetoelectric coupling in comparison with multilayer composites. The large areal distribution of three dimensional heteroepitaxy in two-phase heterostructures causes strong elastic interactions between the constituent phases. These interactions control the magnetic and electric responses of self-assembled multiferroic composites and are probably responsible for an enhanced magnetoelectric effect [1–4].

We prepared composite thin films using an aqueous chemical solution deposition method. Multimetal ion solutions with different molar ratios of ferroelectric/ ferrimagnetic phases: xBaTiO$_3$–(1-x)CoFe$_2$O$_4$ and xBiFeO$_3$–(1-x)CoFe$_2$O$_4$ with $x = 0.5$, 0.6 or 0.7 were spin coated on different types of substrates ($LaAlO_3$ (100), $SrTiO_3$ (100) and $SrTiO_3$ (111)). The films were subjected to a thermal treatment in order to remove the organic residues and to obtain the desired crystalline phases.

This study focuses on the structural and functional characterization of composite films from aqueous solutions. During the film crystallization, spontaneous phase separation occurs resulting in two-phase composites where both phases show a high degree of crystallographic orientation in respect of the substrate. Hysteresis loops obtained by to SQUID measurements, demonstrate mostly isotropic magnetic properties in the $BaTiO_3$–$CoFe_2O_4$ composite films with a magnetization saturation around 270 emu/cm^3. On the other hand, the enhanced ferromagnetic response of $BiFeO_3$–$CoFe_2O_4$ samples points out the presence of ferromagnetic parasitic phases, probably due to the decomposition of $BiFeO_3$.

In conclusion, we have shown that aqueous solution based processing is an easily accessible way to grow self-assembled, thin film composites.

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M25

CRYSTALLINE STRUCTURE AND COMPOSITIONAL DEPTH PROFILE OF SOLUTION DERIVED LEAD-FREE $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ (BNBT) THIN FILMS AROUND THE MORPHOTROPIC PHASE BOUNDARY

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$(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ (BNBT) is considered a promising lead-free alternative to MPB - $Pb(Zr_x,Ti_{1-x})O_3$(PZT). It shows the coexistence of rhombohedral (*R3c*) and tetragonal (P4mm) crystalline structures in the proximity to the MPB ($x \sim 0.06$). In this work, BNBT thin films were fabricated by chemical solution deposition (CSD) with a wide range of compositions ($x = 0.050–0.150$) onto $Pt/TiO_2/SiO_2/(100)Si$ substrates, from hybrid precursor solutions. Stoichiometric thin films (hereinafter BNBT) and others containing Na^++Bi^{3+} excesses (BNBTxs) were prepared. Na^+ and Bi^{3+} are highly volatile at the crystallization temperatures, and traditionally small excesses of these elements are added to the precursor solution to compensate any possible loss. Structural studies by X-ray diffraction using the $\lambda_{Cu} = 1.54$ Å and synchrotron radiation with $\lambda = 0.97354$ Å were performed to determine the crystalline structure of the films and of the powders derived from the corresponding solutions. Rietveld analysis of the experimental X-ray patterns showed different phase volume fractions of the rhombohedral-tetragonal phases as a function of the Ba^{2+} content and an apparent shift of the position of the MPB with the introduction of Na^++Bi^{3+} excesses. MPB was around nominal values of $x \sim 0.055$ and

x~0.10 for the BNBT and BNBTxs, respectively. Rutherford backscattering experiments (RBS) were performed to study the compositional profile of the films. This study revealed bismuth excess is not volatilized during crystallization of the BNBTxs films, but forming instead thick Bi_xPt bottom interfaces. However, the BNBT films with x~0.055 have a homogeneous compositional profile. This joined to the coexistence of rhombohedral and tetragonal phases result in films with well-defined ferroelectric hysteresis loops and comparatively high values of remnant polarizations.

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M26

PLD DEPOSITION AND CHARACTERIZATION OF COMPRESSIVELY-STRAINED HETEROEPITAXIAL $SrTiO_3$ THIN FILMS

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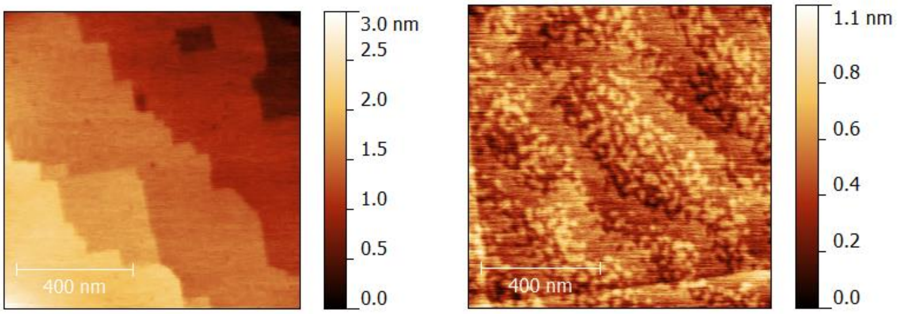
The aim of this work was to investigate processing conditions and deposit heteroepitaxial STO ($SrTiO_3$) thin films with smooth and well defined interfaces for further research. Influence of deposition temperature, laser fluence and repetition rate, ambient pressure on growth mode and film quality was studied.

Heteroepitaxial STO thin films were deposited on LSAT ($(LaAlO_3)_{0.3}$-$(Sr_2AlTaO_6)_{0.7}$) single crystal substrates with LSMO ($La_{0.8}Sr_{0.2}MnO_3$) electrode and STO buffer layer (Fig. 1a) by pulsed laser deposition with KrF excimer laser ($\lambda = 248$ nm). STO and LSMO ceramics were used as the targets. Substrates were cleaned with acetone and isopropanol and annealed in oxygen flow at 1250 °C at the same time controlling La vapour pressure at LSAT substrate surface [1] to get atomically flat surface. Best quality STO films were obtained at 780 °C deposition temperature, with 2 Hz laser repetition rate and 39 mJ energy. The oxygen pressure was 0.1 mBar during deposition and was raised to 1 mBar during cool down. Both LSMO electrode and STO thin films showed good epitaxy (Fig. 1b) and crystallinity, XRD STO 002 reflex rocking curve FWHM was 0.039° (STO film thickness 100 nm, LSMO electrode thickness 17 nm, STO buffer layer thickness 10 nm).

Obtained thin films were analysed by structural characterization techniques – XRD, AFM (Fig. 1 a,b) and RHEED.



a) b)

Figure 1. AFM images of a) STO buffer layer after annealing, b) $SrTiO_3$ heteroepitaxial thin film STO/LSMO/STO//LSAT (STO thickness - 100 nm, LSMO - 17 nm, STO buffer - 10 nm)

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M27

TEMPERATURE DEPENDENT LOCAL ELECTROMECHANICAL INVESTIGATIONS OF ATOMIC VAPOUR DEPOSITION (AVD) GROWN AURVILLIUS PHASE $Bi_6Ti_3Fe_2O_{18}$ THIN FILMS

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Lead-based piezoelectric materials are extensively used in piezoelectric and ferroelectric industries due to their strong piezoelectric properties[1]. However, due to toxicological and environmental concerns, there is a strong impetus to replace Pb-based materials with new materials having comparable piezoelectric properties, especially for use at elevated temperatures[2]. Bismuth layer-structured ferroelectric materials in the Aurvillius phase are considered as potential candidates to replace Pb-based materials with high Curie temperatures (T_c generally over 500 °C) and fatigue-free switching for memories. These materials are naturally 2-*D* nanostructured, consisting of $(Bi_2O_2)^{2+}$ layers alternating with $nABO_3$ perovskite units, described by the general formula $Bi_2O_2(A_{n-1}B_nO_{3n+1})$. On increasing the number of perovskite layers (n), the microstructural, ferroelectric, magnetic and other physical properties can be altered significantly.

In this work, we will present the synthesis and electromechanical investigations of novel *n* = 5 layered $Bi_4Ti_3O_{12}$-$(BiFeO_3)_2$ thin films (B6FTO) on c-plane oriented sapphire substrates. B6TFO films were fabricated by an atomic vapour deposition (AVD) process which was further optimised in order to avoid and suppress the formation of the pyrochlore secondary phase ($Bi_2Ti_2O_7$) using excess bismuth. The local electromechanical properties were investigated with respect to temperature in order to assess the potential of B6TFO as a piezoelectric, ferroelectric and multiferroic material. Vertical PFM (piezoresponse force microscopy) confirms the out-of-plane piezoelectric and ferroelectric behaviour of the deposited film, however lateral PFM indicates that the major polarization vector in B6TFO lies along the plane of the film. Information on the local electromechanical domain switching behaviour (180 °) and hysteresis loops of B6TFO were collected as a function of temperature via switching-spectroscopy PFM and ferroelectric lithography. Piezoresponse increases slightly with increase in temperature (200 °C) confirming the suitability of B6TFO for application at elevated temperatures. The capability of the B6TFO films to be written and retain polarization will be presented via PFM lithography, demonstrating the material's suitability for potential memory storage applications.

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M28

IMPROVED PROPERTIES OF THE LEAD FREE SOLID SOLUTION $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ PREPARED AS MULTILAYER COMPOSITE THIN FILMS WITH $BiFeO_3$

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Due to the environmental regulations applied worldwide, lead free materials are banned in electronic devices. In the search for alternative lead free materials, the solid solution $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ (BNBT) with compositions close to the morphotropic phase boundary (MPB $x \approx 5.5\%$) stands out because of its large piezoelectric coefficients d_{33}: ~450 pC/N for single crystals, ~200–125 pC/N for ceramics[1]. The preparation of these materials in thin film form is indispensable for their integration into microelectronic devices. However a drastic decrease in the remnant polarization of BNBT thin films, respect to their bulk counterparts is reported [2], which is attributed to the stabilization of relaxor characteristics of the $(Bi_{0.5}Na_{0.5})TiO_3$ rich phase [3] in the films. As a possible solution to this strong reduction in the functional properties, multilayer composites in which the low remnant film is combined with hard ferroelectric layers have been proposed [4]. They induce an internal electric bias in the film, which increases the remnant polarization values. The combination of layers of different phases can also be used to solve one of the main problems of some multiferroic layers, like $BiFeO_3$, to take full advantage of their polarization: the appearance of large leakage currents. In this work a study of the improvement of the properties ferroelectric of BNBT and $BiFeO_3$ (BF) films when combined in a multilayer composite is performed. A considerable improvement in the ferroelectric properties has been observed in the composites multilayer of BF / BNBT, the remnant polarization in the single phase in thin films of BNBT is about $P_r = 12$ µC/cm^2 while in the composites multilayer with BF $P_r = 32$ µC/cm^2. The retention of the polarization ("remnant hysteresis") also shows significant improvement in the composite multilayers with respect to the single phase films of BNBT, and it is observed a decrease in the leakage currents associated with the BF films.

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M29

INVESTIGATION OF OPTIMAL PROCESSING PARAMETERS FOR MULTILAYER $BaTiO_3/NiFe_2O_4$ THIN FILMS FABRICATION

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Lately, multiferroic materials have attracted a lot of interest in microelectronic industry around the world. Because of their unique ability to exhibit more than one ferroic property, they have found various applications in fabrication of microchip components such as sensors, filters, oscillators, magnetoelectric devices, etc. In this paper, multilayer thin film system composed of $BaTiO_3$ and $FeNi_2O_4$ layers, in alternating order, was investigated. Films were obtained by wet chemical solution deposition on silicon and alumina substrates, than thermally treated at various temperatures to acquire detailed informations about process of crystallization and phase composition. Obtained films were about 600 nm thick, crack free, with dense structure. Reaction between different layers is indicated, thus secondary phases are present above 700 °C. Regarding phase composition, it is concluded that optimal sintering temperature is around 750 °C, and on higher temperatures presence of $BaFe_2O_4$, $BaFe_{12}O_{19}$ and two crystal forms of TiO_2 is confirmed. Layer structure is maintained up to 1000 °C, while sintering on higher temperatures bulk composite structure was obtained.

M30

DIELECTRIC PROPERTIES OF POLYMER MATRIX NANOCOMPOSITES

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Nowadays, there is a growing tendency in miniaturization and multi-functionality of electronic devices. Composite materials represent a viable alternative and especially polymer matrix composites. For this kind of materials there are two main possibilities: conductive fillers–polymer matrix composites or ferroelectric fillers-polymer matrix composites. The idea is to combine the better properties of the composite constituents. The combination of nanoparticles (ferroelectric, magnetic or metallic) in a polymer matrix with good dielectric performances is an approach expected to result in new electrical properties with potential use in supercapacitor structures, sensing applications, flexible non-volatile memory applications and optoelectronics.

In the present paper, the dielectric properties (frequency, temperature and high electric field dependences) in case of composite materials formed by nanoparticles (metallic and ferroelectric) embedded in a flexible nonlinear dielectric matrix (chitosan) were investigated.

The chitosan membranes with different filler materials (gold and barium titanate) and concentrations were prepared by dry phase inversion method from an aqueous solution of chitosan. The dielectric properties were investigated by impedance spectroscopy in the frequency range 20 Hz–2 MHz and temperature range of 25–150 °C. With addition of ferroelectric or metallic nanoparticles an increase of permittivity and tunability was obtained while maintaining relatively low dielectric losses. In the case of gold-chitosan composites the increase of permittivity can be explained with the percolation theory, while for barium titanate-chitosan composites the increase of permittivity can be a result of the sum property of the composite.

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PREPARATION AND FUNCTIONAL PROPERTIES OF PZT WITH FERRITE MAGNETOELECTRIC CERAMIC COMPOSITES

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The magnetoelectric composites with different composition of ferrite and Pb(Zr,Ti)O_3 (PZT) ferroelectric phases were prepared by citrate-nitrate combustion using PZT-based template powders. In order to ensure a better connectivity of dissimilar phases, we have used chemical methods for preparation in-situ composites, followed by adequate sintering procedure. The structural, microstructural and functional properties of di-phase magnetoelectric composites of ferrite-PZT are reported. The XRD analysis is demonstrating the synthesis of pure ferrite phase directly on the ferroelectric templates. An excellent mixing was obtained in the composite powders, as proved by a detailed SEM analysis.

The magnetic and dielectric behaviors of the ceramic composites vary with the ratio of the two phases. The magnetic properties measured at room temperature showed that the saturation magnetization and the remnant magnetization of the composites increase with increasing the amount of ferrite. The dielectric behavior is greatly influenced by the magnetic phase. Dielectric measurements with frequency showed a decrease of the dielectric constant at increasing ferrite addition as a consequence of the *sum* property. The dielectric constant *vs.* frequency at room temperature and at a few temperatures in the range (25–250) °C indicate the dielectric relaxation causing by space charge effects and Maxwell-Wagner phenomena, particularly at low frequency and high temperature, and Debye relaxation in the range of frequency (10^3–2×10^6) Hz. The magnetoelectric (ME) coefficient was measured as a function of applied *DC* magnetic field.

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