Electroceramics XIII

June, 24th-27th 2012

University of Twente, Enschede,
The Netherlands
Welcome

It’s our pleasure to welcome you to the Electroceramics XIII conference, held in Enschede, the Netherlands, from June 24 – 27, 2012. We wish you a pleasant stay during the conference, which is hosted by the University of Twente. This booklet provides information about your participation in the scientific and social activities of the conference.

The aim of this conference is to provide an interdisciplinary forum for researchers, theorists as well as experimentalist on the design, fabrication, theory, analysis and applications of functional materials and (epitaxial) thin films.

Electroceramics materials and applications thereof have become an important field of research within materials science. Major breakthroughs in the synthesis of electroceramic materials, in bulk and (epitaxial) thin films, as well as the understanding of the structure-property relation of these materials have been realized in the last decades. This has led to many exciting new concepts, which are nowadays used in many technological applications.

The series of Electroceramics conferences have become an important forum to discuss recent advances and emerging trends in this developing field. New research areas have been adopted, such as the epitaxial thin film research, and it is the aim to further develop the field by adopting other interesting research fields.

We hope that you will enjoy the presentations and will also take the opportunity to attend the conference reception and banquet. On behalf of the international advisory board, the national organizing committee, the local organizing committee, and the many volunteers —Welcome to the University of Twente, Enschede.

On behalf of the organizing committees,
Guus Rijnders

Chairman of the Electroceramics XIII conference.
Organization

National Organizing Committee
Chairman: Guus Rijnders (The Netherlands)

Dave Blank
Bernard Boukamp
Henny Bouwmeester
Bernard Dam
André ten Elshof
Pim Groen
Gertjan Koster
Beatriz Noheda
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L. Li (China) J. Wang (Singapore)
I-Nan Lin (Taiwan) H. Wang (China)
F. Marques (Portugal) W. Wolny (Denmark)
L. Mitoseriu (Romania) W.G. Zhu (Singapore)
M. Miyayama (Japan)
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Sponsors
MESA+ Institute for Nanotechnology

MESA+ is one of the largest nanotechnology research institutes in the world, delivering competitive and successful high quality research. It uses a unique structure, which unites scientific disciplines, and builds fruitful international cooperation to excel in science and education. MESA+ has created a perfect habitat for start-ups in the micro- and nano-industry to establish and to mature.

MESA+ Institute for Nanotechnology is part of the University of Twente, having intensive cooperation with various research groups within the University. The institute employs 525 people of which 300 are PhD’s or postdocs. With its NanoLab facilities the institute holds 1,250 m² of cleanroom space and state of the art research equipment. MESA+ has an integral turnover of 50 million euro per year of which 60% is acquired in competition from external sources.

For more information visit us at www.utwente.nl/mesaplus
The Applied-Piezo.com foundation is a group of cooperating industrial companies, research institutes and universities in The Netherlands and Belgium with expertise in the field of piezo technology.

Applied-Piezo.com will support companies from idea to production.

The aim of Applied-Piezo.com is to define and execute new projects together, to promote piezo technology, to stimulate knowledge development and innovation and to provide a network where knowledge, expertise and products can be exchanged.

Applied Piezo Foundation
PO Box 4176, 7320 AD
Apeldoorn, The Netherlands
www.applied-piezo.com
info@applied-piezo.com

Applied-Piezo.com is the coordinator of the SMARTPIE research program on piezo technology funded by the Dutch government.

SmartPie is an acronym for "SMART systems based on integrated PIEzo".

Within the program industrial companies, research institutes and universities work together to strengthen the innovative position and perception of the Dutch high tech industry by providing it with new piezo-based technology and applications.

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PI Ceramics

From the Piezoeffect to Operational Sensors and Actuators: Development, Manufacture and System Support all from the Specialist

Piezoelectric materials convert electrical energy directly into mechanical energy and vice versa. This effect can be used for both sensor and actuator applications. High-precision positioning tasks can be undertaken with piezo-based drives, for example. PI Ceramic from Lederhose in Thuringia is one of the global leaders for piezo actuators and sensors. Its extensive product portfolio includes a range of piezoceramic materials, piezoceramic components in the form of rings or discs, multilayer piezo actuators (translators or benders), stack actuators and shear modules. Special DuraAct transducers can be used as sensors, actuators and for energy harvesting. Ultrasonic generators round off this broad spectrum of products, which also includes the matching electronics - from OEM circuit boards and power drivers through to cased controllers. At the same time, high priority is given to realizing customer-specific solutions as fast as possible.

Customer-Specific Adaptations

PI Ceramic is the subsidiary of Physik Instrumente (PI) in Karlsruhe and currently employs around 200 staff, including 30 engineers in research, development and production alone. Customer focus is one of its top priorities. Early contact between users and application or development engineers is the key to producing solutions which are technically first class, matched to the application and which also make commercial sense. Advice on system integration is as matter of course as comprehensive after-sales service, which is seen not as a mere repair service, but as a user advice service. Many branches of industry benefit from this: The company supplies piezoceramic solutions for all important high-tech markets from industrial automation and the semiconductor industry, medical engineering, mechanical engineering, high-precision engineering and the automotive sector through to the aeronautics industry.

Production under Control

A broad range of expertise in the complex development and manufacturing process of functional ceramic components combined with state of the art equipment ensure high quality, flexibility and adherence to supply deadlines. The production is exclusively in-house, which results in an extremely low complaint rate of 0.11%. This also enables it to react quickly to customer requirements, when engineering samples are to be manufactured or preproduction series are to be produced. Process flexibility ensures fair prices, even for small production runs. The company philosophy of the piezo specialists is tried and tested and, the company has experienced constant growth despite the recent “years of crisis”, a development which manifests itself in growing staff numbers and extensions to its premises.

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E-mail info@piceramic.de, www.piceramic.com
Twente Solid State Technology

What is PLD?

Pulsed Laser Deposition (PLD) is a thin film technique using laser ablation from a target acting as the particle source. A pulsed highly energetic laser beam is focused on a target, resulting in ablation of material. At the early stage of the laser pulse, a dense layer of vapor is formed at the target surface. Energy absorption during the remainder of the laser pulse causes both the pressure and the temperature of the vapor to increase. This vapor expands from the target surface due to the high pressure and forms the so-called ‘plasma plume’.

The background pressure can be independently controlled with ranges from UHV up to several mbar. Stoichiometric deposition at these high pressures is easily obtained with PLD, which is essential during epitaxial growth of multi-component complex oxides.

The high deposition rates obtained during the deposition pulse and the variable range of the kinetic energy of the deposited particles are, in fact, more unique for PLD and can be exploited to improve thin film properties, like crystallinity and surface smoothness. Taking advantage of the growth kinetics at the high supersaturation reached during the deposition pulses, atomically flat film surfaces can be easily achieved.

Twente Solid State Technology B.V.
P.O. Box 256
7500 AG, Enschede
the Netherlands

Phone: +31 53 2030 244
Fax: +31 53 2030 248
E-mail: info@TSSST.nl
WWW: www.TSSST.nl

1) Usually an excimer laser or high-power Nd:YAG laser is used. Both produce high-intensity laser pulses in the UV range at repetition rates up to several hundred Hz.
How do you get to the University of Twente?

BY CAR
From the A1 motorway, take the A35 motorway in the direction of Enschede
Take the exit 'Enschede – West / Universiteit' (exit no 26)
Follow the signs for 'Universiteit'

BY TRAIN / BUS
The University of Twente can be reached by bus from the railway stations in Hengelo, Enschede and Enschede Drienerlo; the services usually run every half hour

From Enschede railway station: line number 1 in the direction of 'Universiteit Twente'
line number 9 in the direction of Hengelo
From Enschede Drienerlo railway station: line number 1 in the direction of 'Universiteit Twente'
line number 9 in the direction of Enschede
line number 15 in the direction of 'Universiteit Twente'
(Lines number 17, 18 and 19 also pass the University)

For more information, please call the information service number for Public Transport: 0900-9292
Map of building Waaier
Ground floor

WAAIER
Ground plan

Electroceramics XIII
University of Twente.
Map of building Waaier
First floor
Map of city centre Enschede
Tutorial lectures
Sunday, June 24, 2012

Session 1, location Waaier 3
09.00-10.30h Electrochemical impedance spectroscopy (Bernard Boukamp, University of Twente)
11.00-12.30h Defect chemistry (Henny Bouwmeester, University of Twente)
Lunch break
13.30-15.00h Quantitative high-resolution electron microscopy (Sara Bals, University of Antwerp)
15.30-17.00 Advanced x-ray diffraction (Arturas Vailionis, Stanford University)

Session 2, location Waaier 4
09.00-12.30h Piezoelectric (bulk ceramics and thin film) applications (organized by Applied Piezo Foundation)

Electrochemical Impedance Spectroscopy (EIS).
Tutor: Bernard A. Boukamp, University of Twente, the Netherlands

Impedance measurements have become an important tool in the study of mass and charge transport in many electrochemical systems, such as solid state ionics, fuel cells and batteries. Although EIS can be very effective in obtaining information on the various processes in a system, its use requires understanding of the underlying principles and often actual experience as well. In this tutorial the participant will be guided through the principles and methods of impedance spectroscopy. The following topics will be presented:
- Basic principles of frequency domain measurements
- Data validation with Kramers-Kronig
- Brief discussion of circuit elements
- Diffusion transfer functions
- Building a sensible equivalent circuit
- Brief description of CNLLS-analysis procedures
- Obtaining starting parameters from an impedance spectrum (pre-analysis)

There will be ample time for discussion and participants are encouraged to provide specific questions and problems beforehand by E-mail (b.a.boukamp@tnw.utwente.nl).

Defect chemistry
Tutor: Henny Bouwmeester, University of Twente, the Netherlands

This tutorial gives an introduction into the equilibrium defect chemistry of solid inorganic materials, with emphasis on metal oxides. Topics discussed include lattice and electronic defects, defect notations, defect structures, point defect concentrations in dependence of temperature, partial pressure and doping level, and the correlation between defect chemistry and transport properties of materials. Also covered are underlying concepts like structure elements versus building blocks, size exclusion effect, chemical potentials of ionic and electronic defects, virtual versus true chemical potentials, etc. Attendees are invited to present and discuss problem cases encountered in their own research practice.
Quantitative high-resolution electron microscopy
Tutor: Sara Bals, Physics, University of Antwerp, Belgium

Nanosystems that are being investigated within the field of physics, biology and chemistry are becoming smaller and more complex. As a consequence, higher demands are being put to microscopic and nanoscopic characterization techniques as well. New developments in the field of transmission electron microscopy (TEM) allow to investigate these systems at the atomic scale, not only structural, but also from chemical and electronic point of view. The new double aberration corrected Qu-Ant-EM microscope that was installed at the University of Antwerp even enables one to obtain 2D images with a spatial resolution of 50 pm. However, one should never forget that all these techniques only provide a 2D projection of a 3D object. To overcome this problem, electron tomography has been used in an increasing number of studies over the last decennium. Nevertheless, it is still not straightforward to push the resolution below the nanoscale in 3D. This relies on the combination of state-of-the-art electron microscopes and advanced computational procedures to transform the 2D images into a 3D reconstruction. In this tutorial, the evolution from qualitative TEM to quantitative TEM will be discussed. Also some recent case studies will be presented in which advanced 2D and 3D TEM techniques enable us to obtain more insight on the connection between properties and structure of a broad range of nanostructures, including oxide multilayers.

Advanced x-ray diffraction
Tutor: Arturas Vailionis, Stanford University, USA

The tutorial will focus on advanced x-ray diffraction techniques that are or can be used in thin film analysis. It will mainly cover topics that are not commonly addressed in regular text books or class lectures. We will start with the thin film sample and learn how strained, relaxed, epitaxial and polycrystalline films can be represented in reciprocal space. How reciprocal lattice points are affected by mismatch, strain, mosaicity, thickness, modulations, etc. Then we will introduce the diffractometer and will learn how scattering vector is used to probe the reciprocal space. Scan directions - reciprocal vs. real space scenarios. Choosing right scans for your measurements. What x-ray optic components are available in today’s commercial diffractometers for advanced thin film analysis. The importance of the instrumental resolution. What can we learn using different x-ray diffraction techniques such as reciprocal space maps, grazing incidence diffraction, in-plane diffraction, x-ray reflectivity. Making use of 1-dimensional detector for high-speed spatial mapping of epitaxial thin films.
Piezoelectric (bulk ceramics and thin film) applications
organized by Applied Piezo Foundation

09:00-10:30h Introduction to piezoelectric materials and applications
- piezoelectric effect
- history of piezoelectricity
- overview and characterisation of piezoelectric materials
- overview of applications

11:00-12:30h Example applications
- bulk ceramics: piezoelectric actuation and sensing for active vibration control
- thin film application
### Monday, June 25, 2012
Parallel session 1, location Waaier 1

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<td>Chair: Gertjan Koster</td>
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<tr>
<td>Pl.1</td>
<td>09.00-09.45</td>
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<td></td>
<td>Changing Dielectrics into Ferroelectrics—Alchemy Enabled By Strain</td>
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<td>Chair: Gertjan Koster</td>
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<tr>
<td>Applications I</td>
<td>Chair: Bernard Boukamp</td>
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<td>O.1</td>
<td>10.00-10.20</td>
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<td></td>
<td>Electrode kinetics of mixed conducting oxides in H₂/H₂O and O₂ atmosphere</td>
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<td>O.2</td>
<td>10.20-10.40</td>
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<td></td>
<td>Conductivity relaxation experiments in pure and Sr/Bi-doped Ca₃Co₂O₉ electrode materials</td>
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<td>O.3</td>
<td>10.40-11.00</td>
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<td>Cathode performance of spray pyrolysis-deposited La₀.₅₈Sr₀.₄Fe₀.₈Co₀.₂O₃₋δ and La₀.₅₈Sr₀.₄Fe₀.₈Ni₀.₂O₃₋δ thin films for intermediate temperature solid oxide fuel cells</td>
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<td>11.00-11.30</td>
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<td>Applications II</td>
<td>Chair: André ten Elshof</td>
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<tr>
<td>I.1</td>
<td>11.30-12.00</td>
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<td></td>
<td>Piezoelectric nano-wires: formation, properties, and possibilities</td>
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<td>O.4</td>
<td>12.00-12.20</td>
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<td></td>
<td>Composition control of piezoelectric PZT thin films deposited onto Cu-coated polymer substrates</td>
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<td>O.5</td>
<td>12.20-12.40</td>
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<td>Ferroelectrics for energy storage: the role of dielectric nonlinearities</td>
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<td>O.6</td>
<td>12.40-13.00</td>
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<td>BaMg₁/₃Ta₂/₃O₃ Thin Films Obtained by PLD or Sol-Gel</td>
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<td>13.00-14.00</td>
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<td>Applications III</td>
<td>Chair: Nava Setter</td>
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<td>I.2</td>
<td>14.00-14.30</td>
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<td></td>
<td>Effects of sintering temperature on specific grain boundary properties of CGO</td>
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<td>O.7</td>
<td>14.30-14.50</td>
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<td></td>
<td>Nano-structuring of SOFC anodes by reverse current treatment</td>
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<td>O.8</td>
<td>14.50-15.10</td>
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<td></td>
<td>Increased ionic conductivity in microwave hydrothermally synthesized rare–earth (RE) doped ceria Ce₁ₓREₓO₂₋ₓ/₂</td>
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<td>O.9</td>
<td>15.10-15.30</td>
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<td>Critical issues for the development of 3rd generation fuel cells with proton conducting electrolyte</td>
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<td>15.30-16.00</td>
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<td>16.00-18.00</td>
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<td>08.45</td>
<td>Opening</td>
<td>Dr. Anne Flierman</td>
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<tr>
<td>09.00-09.45</td>
<td>Plenary</td>
<td>Darrell Schlom</td>
<td>Changing Dielectrics into Ferroelectrics—Alchemy Enabled By Strain</td>
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<td>Chair: Pim Groen</td>
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<tr>
<td>09.00-09.20</td>
<td>Synthesis I</td>
<td>Yanling Gao</td>
<td>Low-temperature synthesis and characterization of ceramics driven from amorphous and nanocrystalline barium titanate powders</td>
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<td>10.00-10.20</td>
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<td>Jurij Koruza</td>
<td>Microstructure Design of Sodium Niobate Ceramics</td>
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<td>10.40-11.00</td>
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<td>Horng-Yi Chang</td>
<td>Blue light excited nanophosphors synthesized by soft wet methods</td>
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<td>10.40-11.00</td>
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<td>Chair: Arturas Vaillionis</td>
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<td>11.30-12.00</td>
<td>Characterization I</td>
<td>Sara Bals</td>
<td>Aberration corrected transmission electron microscopy for ceramic (multi)layers: advances and challenges</td>
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<td>12.00-12.20</td>
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<td>Armin Feldhoff</td>
<td>Phase stability of oxygen-transporting ceramic membranes in the intermediate temperature range</td>
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<td>12.20-12.40</td>
<td></td>
<td>Andris Sutka</td>
<td>A route towards more sensitive ZnFe₂O₄ gas sensors</td>
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<td>12.40-13.00</td>
<td></td>
<td>Mara Bernardo</td>
<td>Microstructure control in bulk Ti-doped BiFeO₃ ceramics</td>
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<td>13.00-14.00</td>
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<td>Lunch break</td>
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<tr>
<td>14.00-14.30</td>
<td>Characterization II</td>
<td>Dietrich Hesse</td>
<td>Nanodomain vertex arrays in BiFeO₃ single crystals</td>
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<tr>
<td>14.30-14.50</td>
<td></td>
<td>Tobias Klande</td>
<td>Investigation of doped Ruddlesden-Popper La₃NiO₄ and La₉Ni₉O₄₁₀ phases as oxygen-transporting materials</td>
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<td>14.50-15.10</td>
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<td>Simon Kraschewski</td>
<td>Characterization of grain boundaries in iron-doped SrTiO₃ by analytical transmission electron microscopy</td>
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<td>15.10-15.30</td>
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<td>Andreas Pavitschitz</td>
<td>Microstructural characterisation of ZnO varistor ceramics</td>
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<td>15.30-16.00</td>
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<td>Chair: Roger De Souza</td>
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<td>16.00-18.00</td>
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<td>Poster sessions</td>
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<td>19.00</td>
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### Monday, June 25, 2012
Parallel session 3, location Waaier 3. Opening and plenary in Waaier 1.

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<td>09.00-09.45</td>
<td><strong>Darrell Schlom</strong> (plenary) Changing Dielectrics into Ferroelectrics—Alchemy Enabled By Strain</td>
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<td>Chair: Henny Bouwmeester</td>
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<td>O.19</td>
<td>10.00-10.20 <strong>Anatolii Belous</strong> Nature of Ionic Conduction in Li_{0.5-y}Na_{y}La_{0.5}V(Nb,Ta)<em>{2}O</em>{8} System</td>
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<tr>
<td>O.20</td>
<td>10.20-10.40 <strong>Andrei Kovalevsky</strong> High-temperature conductivity, stability and redox properties of (Fe,Mg,Al)<em>{2}O</em>{3} spinel-type materials</td>
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<td>O.21</td>
<td>10.40-11.00 <strong>Melanie Kuhn</strong> Defect chemistry and transport properties of Ba_{x}Sr_{1-x}Ti_{1-y}Fe_{y}O_{3-d} solid solutions</td>
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<td>11.00-11.30 Coffee break</td>
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<tr>
<td>I.5</td>
<td>11.30-12.00 <strong>Jürgen Fleig</strong> Interfacial ion transport in oxides: principles, methods and examples</td>
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<td>O.22</td>
<td>12.00-12.20 <strong>Stefan Wagner</strong> Equilibration Kinetics of Mixed Ionic-Electronic Conducting Materials at Different Oxygen Partial Pressures</td>
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<td>O.23</td>
<td>12.20-12.40 <strong>Henny Bouwmeester</strong> Oxygen surface exchange kinetics of mixed oxide ionic-electronic conductors</td>
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<td>O.24</td>
<td>12.40-13.00 <strong>Rose-Noëlle Vannier</strong> Oxygen Transport in Ba_{2}CoO_{9}O_{14} cobaltite</td>
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<td></td>
<td>13.00-14.00 Lunch break</td>
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<tr>
<td>I.6</td>
<td>14.00-14.30 <strong>Sean Bishop</strong> Probing Pr_{x}Ce_{1-x}O_{2-d} thin film defect concentrations using in-situ optical absorption and impedance spectroscopy techniques</td>
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<td>O.25</td>
<td>14.30-14.50 <strong>Stefanie Huber</strong> Investigation of charge transport in Fe-doped SrTiO_{3} thin films by means of impedance spectroscopy and ^{18}O tracer diffusion</td>
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<td>O.26</td>
<td>14.50-15.10 <strong>DI Chen</strong> The chemical capacitance of praseodymium-cerium oxide thin films and relationship to nonstoichiometry</td>
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<td>O.27</td>
<td>15.10-15.30 <strong>Veronika Metlenko</strong> Oxygen Transport In Model Thin Film SrTi_{1-x}Fe_{x}O_{2-d} Mixed Conducting Cathodes For Solid Oxide Fuel Cells</td>
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<tr>
<td>08.45</td>
<td>Opening by Dr. Anne Flierman, president University of Twente</td>
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<td>Chair: Gertjan Koster</td>
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<tr>
<td>Pl.1</td>
<td>09.00-09.45 Darrell Schlom (plenary) Changing Dielectrics into Ferroelectrics—Alchemy Enabled By Strain</td>
</tr>
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</table>
| Fundamentals I | Chair: Gustau Catalan |}
| O.28  | 10.00-10.20 Zarel Valdez Nava Bulk and local electrical properties of the colossal dielectric constant materials: the case of the CaCu$_3$Ti$_4$O$_{12}$ |
| O.29  | 10.20-10.40 Hitoshi Ohsato Fabrication of Indialite Glass Ceramics with Low dielectric Constant for Millimeterwave dielectrics |
| O.30  | 10.40-11.00 Jan Petzelt Giant dielectric constant and effective dielectric spectra of dielectric-conductor composites |
|       | 11.00-11.30 Coffee break                                                              |
| Fundamentals II | Chair: Darrell Schlom |}
| I.7   | 11.30-12.00 Andrew Bell Nanopolar behaviour in bismuth-based ferroelectrics           |
| O.31  | 12.00-12.20 Jyrki Lappalainen Phase-coexistance phenomenon in Metal-Insulator-Transition of VO$_2$ Thin Films |
| O.32  | 12.20-12.40 Pin Yang Elastic properties of a tin-modified lead zirconate titanate ceramic |
| O.33  | 12.40-13.00 Elena Buixaderas Low-frequency phonons and phase transition dynamics in Pb(Zr$_{1-x}$Ti$_x$)$_3$O$_7$ |
|       | 13.00-14.00 Lunch break                                                               |
| Fundamentals III | Chair: Andrew Bell |}
| I.8   | 14.00-14.30 Gustau Catalan Flexoelectricity: Controlling Polarity at the Nanoscale    |
| O.34  | 14.30-14.50 Lavinia Curecheriu A new approach for tayloring tunability and permittivity values by using grain size reduction at nanoscale |
| O.35  | 14.50-15.10 Héctor Beltrán Mir Structural and Electrical Properties of a New Ba$_2$NdTi$_{2+x}$Nb$_3$O$_{15+x/2}$ Solid Solution with Tetragonal Tungsten Bronze Phase |
| O.36  | 15.10-15.30 Juan Nino Lessons from Bi$_2$Ti$_2$O$_7$: one step closer to finally understanding dielectric relaxation in pyrochlores |
|       | 15.30-16.00 Coffee break                                                              |
|       | 16.00-18.00 Poster sessions                                                           |
|       | 19.00 BBQ                                                                           |
## Parallel session 1, location Waaier 1

**Chair:** Mark Huijben

**08.30-09.15**

**Plenary Session**

**Jean-Marie Tarascon**

*Materials and synthesis approaches for developing sustainable batteries*

**Chair:** Jan Peters

**09.30-11.30**

**Industrial presentations**

*TBA*

**10.30-11.00**

**Coffee break**

## Heteroepitaxial structures: Interfaces and properties I

**Chair:** Jorge Frade

**I.9**

**11.00-11.30**

**Susanne Stemmer**

*Two-dimensional Electron Gases at Mott/Band Insulator Interfaces*

**O.37**

**11.30-11.50**

**Yunzhong Chen**

*Atomically designed oxide interfaces for nanoionics and nanoelectronics: extraordinary conductivity at complex oxide interfaces*

**O.38**

**11.50-12.10**

**Pep Fontcuberta**

*Multiferroic epitaxial thin film and heterostructures*

**O.39**

**12.10-12.30**

**Raoul Scherwitzl**

*Metal-insulator transition and interface phenomena in nickelate heterostructures*

**12.30-14.00**

**Lunch break**

## Heteroepitaxial structures: Interfaces and properties II

**Chair:** Susanne Stemmer

**I.10**

**14.00-14.30**

**Rossitza Pentcheva**

*Tuning the two-dimensional electron gas at the LaAlO$_3$/SrTiO$_3$(001) interface by metallic contacts*

**O.40**

**14.30-14.50**

**Umberto Scotti**

*Two dimensional electron gas at the SrTiO$_3$ surface and interfaces*

**O.41**

**14.50-15.10**

**Alexey Kalabukhov**

*A comparative study of polar oxide interfaces: correlation between electrical and microstructural properties*

**O.42**

**15.10-15.30**

**Josée Kleibeuker**

*Electron transfer from LaTiO$_3$ to LaFeO$_3*

**15.30-16.00**

**Coffee break**

**16.00-18.00**

**Poster sessions (P.71 - P**

**19.00**

**Conference Banquet**
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<td>Jean-Marie Tarascon (plenary)</td>
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<td>09.30-09.50</td>
<td>O.43 Multiferroics I</td>
<td>Doped Ga$_{2-x}$Fe$_x$O$_3$ ceramics towards magnetoelectric applications</td>
<td>François Roulland</td>
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<td>09.50-10.10</td>
<td>O.44 Multiferroics I</td>
<td>New aspects concerning the tunability and dielectric anomalies of BiFeO$_3$ ceramics</td>
<td>Felicia Gheorghiu</td>
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<td>10.10-10.30</td>
<td>O.45 Multiferroics I</td>
<td>Effect of particles size on the cosintering of multiferroic composites</td>
<td>Petra Jenuš</td>
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<td>Fundamentals IV</td>
<td>Effect of octahedral distortions on magnetic and transport properties in epitaxial oxide thin films</td>
<td>Arturas Vailionis</td>
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<td>11.30-11.50</td>
<td>O.46 Fundamentals IV</td>
<td>Electron Microscopy investigations of zirconium-, yttrium- and scandium-doped (Ba$<em>{0.5}$Sr$</em>{0.5}$)(Co$<em>{0.8}$Fe$</em>{0.2}$)$<em>{0.97}$Y$</em>{0.03}$O$_{3-d}$ (BSCFX5582)</td>
<td>Philipp Müller</td>
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<td>O.47 Fundamentals IV</td>
<td>Characterization of the Alignment of Acceptor-Oxygen Vacancy Defect Complexes Under dc Bias in Fe Doped SrTiO$_3$ Using TSDC and EPR Techniques</td>
<td>Russell Maier</td>
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<td>Electronic and ionic transport properties IV</td>
<td>Grain boundaries in proton-conducting BaZrO$_3$ proton conductors: evidence for space charge effects</td>
<td>Rotraut Merkle</td>
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<td>Electronic and ionic transport properties IV</td>
<td>Oxide ion transport in Ca$_5$Co$<em>4$O$</em>{2+δ}$, a promising SOC electrode</td>
<td>Caroline Pirovano</td>
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<td>Electronic and ionic transport properties IV</td>
<td>Electrical conductivity, thermal expansion and stability of Y- and Al-doped SrVO$_3$ as prospective SOFC anode material</td>
<td>Aleksey Yaremchenco</td>
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<td>15.10-15.30</td>
<td>Electronic and ionic transport properties IV</td>
<td>Impact of sulfur contamination on oxygen transport through BSCF: relevant issues in the development of capillary and hollow-fiber membranes</td>
<td>Aleksey Yaremchenco</td>
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<td>Jean-Marie Tarascon (plenary)</td>
<td>Materials and synthesis approaches for developing sustainable batteries</td>
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<tr>
<td>09.30</td>
<td>Synthesis II</td>
<td>Sjoerd Veldhuis</td>
<td>One-step Low-temperature Synthesis of Nano-crystalline BaTiO3: Structural Features and Reaction Mechanism</td>
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<td>María Verde Lozano</td>
<td>Controlled growth of ZnO nanoarrays by a combination of EPD and hydrothermal processing</td>
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<td>David Calatayud</td>
<td>Synthesis and characterization of nanostructured anatase TiO₂ with high-energy facets obtained by a mild method</td>
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<td>11.00</td>
<td>Synthesis IV</td>
<td>Marlies Van Bael</td>
<td>Solution based deposition of nanostructured oxides: strategies to address current challenges</td>
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<td>11.00</td>
<td>Synthesis IV</td>
<td>Chae Il Cheon</td>
<td>Effect of sintering conditions on ferroelectric properties of BiFeO₃ ceramics</td>
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<td>11.00</td>
<td>Synthesis IV</td>
<td>Kazuo Yuki</td>
<td>Fabrication and Evaluation of Anatase Titanium Dioxide Films using Aerosol Deposition Method</td>
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<td>Synthesis IV</td>
<td>Karsten Rachut</td>
<td>The B/A ratio in tunable BST thin films: evidence for two phase mixture and impact on dielectric properties</td>
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<td>14.00</td>
<td>Fundamentals V</td>
<td>Matthijn Dekkers</td>
<td>Misfit strain dependence of ferroelectric and piezoelectric properties of clamped (001) epitaxial Pb(Zr₀.₅₂,Ti₀.₄₈)O₃ thin films</td>
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<td>14.00</td>
<td>Fundamentals V</td>
<td>Tor Grande</td>
<td>Anisotropic chemical and thermal expansion of nano-crystalline rhombohedral perovskites</td>
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<td>Fundamentals V</td>
<td>Roman Korobko</td>
<td>The Mechanism of Electrostriction in Gd-doped Ceria</td>
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<td>Matjaz Spreitzer</td>
<td>Influence of synthesis conditions on the electrical properties of the Na₀.₅Bi₀.₅TiO₃-KTaO₃ ceramics</td>
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<td>Synthesis III</td>
<td>Jae-Ho Jeon</td>
<td>The Growth Mechanism of (K,Na)NbO₃-based Lead-Free Piezoceramic</td>
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<td>Andreja Bencan</td>
<td>Lead zirconate titanate-zirconia composites prepared by hetero-agglomeration of constituent particles</td>
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<td>Oleg Ovchar</td>
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<td>Ian Reaney</td>
<td>Structural and magnetic phase transitions in Bi₁₋ₓNdₓFeO₃ ceramics</td>
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<td>Christopher Kavanagh</td>
<td>Rare earth doped bismuth ferrite: A neutron diffraction study</td>
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<td>Annette Bussmann-Holder</td>
<td>From Quantum Paralectric To Antiferromagnetic: The Phase Diagram Of Almost Multiferroic Sr₁₋ₓEuₓTiO₃</td>
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<td>11.50-12.10</td>
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<td>Tomasz Stawski</td>
<td>Evolution of inhomogeneities in alkoxide-carboxylate precursor sols and amorphous xero-gel films of barium titanate and lead zirconate titanate</td>
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<td>11.30-12.00</td>
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<td>Andrei Kholkin</td>
<td>Nanoscale phenomena in relaxor ferroelectrics via Scanning Probe Microscopy</td>
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<td>14.00-14.30</td>
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<td>Liliana Mitoseriu</td>
<td>New insights on grain size and interface effects in nanostructured ferroelectric ceramics</td>
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<td>14.30-14.50</td>
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<td>Nadejda Horchidan</td>
<td>High-field dielectric properties and Raman spectroscopic investigation of the ferroelectric-to-relaxor crossover in BaSnₓTi₁₋ₓO₃ ceramics</td>
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<td>Mark Stewart</td>
<td>The effect of tensile strain on the piezoelectric output of soft PZT actuator materials</td>
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**Wednesday, June 27, 2012**
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<td><strong>Paul Muralt</strong> (plenary) <strong>Paul Muralt</strong>&lt;br&gt;Recent progress in materials issues for piezoelectric MEMS</td>
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<td><strong>O.70</strong></td>
<td><strong>Dieter Stender</strong>&lt;br&gt;Zigzag-structured yttria stabilized zirconia thin films grown by pulsed laser deposition</td>
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<td><strong>O.71</strong></td>
<td><strong>Pier Paolo Aurino</strong>&lt;br&gt;Patterning of LAO/STO interfaces using dry ion beam etching</td>
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<td><strong>O.72</strong></td>
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<td>11.00-11.30</td>
<td><strong>Fundamentals VII</strong></td>
<td><strong>I.17</strong></td>
<td><strong>Clive Randall</strong>&lt;br&gt;Point defects and their impact in dielectric and piezoelectric ceramics</td>
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<td><strong>O.73</strong></td>
<td><strong>Dario Marrocchelli</strong>&lt;br&gt;The origins of chemical expansion in non-stoichiometric oxides</td>
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<td><strong>Fundamentals VII</strong></td>
<td><strong>O.74</strong></td>
<td><strong>Saeedeh Farokhipoor</strong>&lt;br&gt;Selective conduction through ferroelastic domain walls in epitaxial BiFeO₃ thin films</td>
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<td>12.10-12.30</td>
<td><strong>Fundamentals VII</strong></td>
<td><strong>O.75</strong></td>
<td><strong>Pascal Marchet</strong>&lt;br&gt;Electrical Properties in BiFeO₃ Based Solid Solutions</td>
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<td><strong>Fundamentals VIII</strong>&lt;br&gt;<strong>Fundamentals VIII</strong></td>
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<td>14.00-14.30</td>
<td><strong>Fundamentals VIII</strong></td>
<td><strong>I.18</strong></td>
<td><strong>Roger De Souza</strong>&lt;br&gt;The behaviour of oxygen vacancies in the perovskite oxide SrTiO₃ and at its extended defects</td>
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<td><strong>Fundamentals VIII</strong></td>
<td><strong>O.76</strong></td>
<td><strong>Peter Supancic</strong>&lt;br&gt;Fully ferroelectric/ferroelastic coupled FE model for piezoceramic including the effect of a weak electrical conductivity</td>
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<td><strong>O.77</strong></td>
<td><strong>Anna-Karin Axelsson</strong>&lt;br&gt;Structural and functional analysis of newly discovered pyrochlores from Bi₂O₃-Fe₂O₃-TeO₃ system</td>
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<td><strong>Laurent Baudry</strong>&lt;br&gt;Nucleation and growth of an exotic ferroelectric domain structure in PZT close the morphotropic phase boundary</td>
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**Chair: Guus Rijnders**

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#### Lead free materials I

**Chair: Tor Grande**

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<td>Lead-free piezoceramic materials for industrial applications</td>
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<td>09.50-10.10</td>
<td>Ekaterina Politova</td>
<td>Bismuth-based perovskite-related piezoelectric ceramics</td>
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<td>Klaus Reichmann</td>
<td>The electro-mechanical properties of BNT based multilayer actuators</td>
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10.30-11.00 Coffee break

#### Lead free materials II

**Chair: Paul Muralt**

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<td>Brady Gibbons</td>
<td>Bi-based Piezoelectric Thin Films via Chemical Solution Deposition</td>
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<tr>
<td>11.30-11.50</td>
<td>José Fernández</td>
<td>In situ ferroelectric domain structure by Confocal Raman Microscopy accompanied by Atomic Force Microscopy</td>
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<td>11.50-12.10</td>
<td>Marco Deluca</td>
<td>Temperature-dependent Raman spectroscopy of unmodified, Fe- and Ba-modified sodium bismuth titanate lead-free ferroelectric ceramics</td>
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<td>12.10-12.30</td>
<td>Denis Schütz</td>
<td>Lone-pair induced covalency as the cause for the extended strain in BNT based solid solutions</td>
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12.30-14.00 Lunch break

#### Lead Free materials III

**Chair: Brady Gibbons**

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<td>Barbara Malic</td>
<td>Vapour pressure over alkali niobate ceramics followed by Knudsen effusion mass spectrometry as a tool for optimisation of processing and properties</td>
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<td>14.30-14.50</td>
<td>Toshio Ogawa</td>
<td>Poling Field Dependence of Young’s Modulus and Poisson’s Ratio in Lead-Free Piezoelectric Ceramics</td>
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<tr>
<td>14.50-15.10</td>
<td>Florian Jean</td>
<td>Epitaxial growth and properties of lead-free ferroelectric (\text{Na}_0.5\text{Bi}_0.5\text{Ti}_3\text{O}_9) thin films on various single crystal substrates</td>
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<td>Dulce Perez-Mezcua</td>
<td>Solution derived lead-free (\text{Bi}<em>{0.5}\text{Na}</em>{0.5}\text{Ba}_{1-x}\text{Ti}_3\text{O}_9) thin films in the proximity of the Morphotropic Phase Boundary (MPB)</td>
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### Wednesday, June 27, 2012
Parallel session 3, location Waaier 3. Plenary in Waaier 1

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#### Functional materials I

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#### Applications IV

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<td>Madhu Jambunathan</td>
<td>Energy Harvesters for Intelligent Tires using AlN and PZT Thin Films</td>
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Changing Dielectrics into Ferroelectrics—Alchemy Enabled By Strain

Darrell Schlom
Cornell University, Department of Materials Science and Engineering, Ithaca, USA

Using epitaxy and the misfit strain imposed by an underlying substrate, it is possible to strain dielectric thin films to percent levels—far beyond where they would crack or plastically deform in bulk. Under such strains, the properties of dielectrics can be dramatically altered. For example, materials that are not ferroelectric in their unstrained state can be transmuted into ferroelectrics. We have applied such strain engineering to the challenge of making a low-loss tunable microwave dielectric. The miniaturization and integration of frequency-agile microwave circuits—tunable filters, resonators, phase shifters and more—with microelectronics offers tantalizing device possibilities, yet requires thin films whose dielectric constant at GHz frequencies can be tuned by applying a quasi-static electric field. Appropriate systems, e.g., Ba$_x$Sr$_{1-x}$TiO$_3$, have a paraelectric-to-ferroelectric transition just below ambient temperature, providing high tunability. Unfortunately such films suffer significant losses arising from defects. Recognizing that progress is stymied by dielectric loss, we start with a system with exceptionally low loss—Sr$_{n+1}$Ti$_n$O$_{3n+1}$ phases—where in-plane crystallographic shear (SrO)$_2$ faults provide an alternative to point defects for accommodating non-stoichiometry. Although low $n$ is advantageous for minimizing defects, it also quenches (incipient) ferroelectricity and thus tunability even in strained Sr$_{n+1}$Ti$_n$O$_{3n+1}$ films. Suppression of spontaneous polarization perpendicular to the (SrO)$_2$ faults is expected from depolarization fields; size effects suppressing an in-plane polarization are, however, unprecedented. Here we show both experimentally and theoretically the emergence of a ferroelectric and highly tunable ground state in biaxially strained Sr$_{n+1}$Ti$_n$O$_{3n+1}$ phases with $n \geq 3$ at frequencies up to 40 GHz. With increasing $n$ the (SrO)$_2$ faults are separated further than the ferroelectric coherence length perpendicular to the in-plane polarization, enabling tunability with a figure of merit at room temperature that rivals all known tunable microwave dielectrics.
Abstracts Keynote speakers

Pl.2  Materials and synthesis approaches for developing sustainable batteries

Jean-Marie Tarascon
Laboratoire de Réactivité et Chimie des Solides, Université de Picardie Jules Verne, CNRS (UMR-7314), 33 rue Saint-Leu, 80039, Amiens, France

Although today’s Li-ion technology has conquered the portable electronic markets, and is still improving, it falls short of meeting the demands dictated by both electric transportation and grid applications. There is room for optimism as long as we pursue paradigm shifts while keeping in mind the concept of materials sustainability. Some of these concepts relying i) on new ways to prepare known or new inorganic phosphates, fluorophosphates or fluorosulfate electrode materials via eco-efficient processes enlisting dry solid state reactions and ionothermal, or bio-inspired approaches, will be discussed. Similarly, our strategy towards the search for new Na-insertion compounds in order to enable, as an alternative to Li-ion, the development of the Na-ion technology will be presented with a few recent results.
Piezoelectric materials play a crucial role in a large number of applications modern society would not like to miss. Mobile communication and ultrasonic imaging are just the most prominent ones. Since two decades, miniaturization of mechanical devices in silicon technology is a major research direction in engineering known under name of MEMS, which stands for micro-electro-mechanical systems. Piezoelectricity fits very well into this concept and was expected right from the beginning to play its role in MEMS. However, there was a long way to go, specifically with the strongest piezoelectric materials, the ferroelectric ones. The first breakthrough was hence made with the non-ferroelectric AlN thin films in RF duplex filters for mobile phones. What counts here is acoustic quality and stability for achieving high quality factors of thickness mode resonances. The force champion among piezoelectric thin film materials, Pb(Zr,Ti)O$_3$ gave more problems in processing, and requires more patience to meet requirements and needs for mass applications. It seems, however, that the breakthrough is imminent. PZT thin films are now rapidly making the step from research laboratories to industry. The struggling for optimal films, and the best integration schemes is still going on, involving new companies and established ones. Sputtering, pulsed laser deposition and sol-gel techniques are delivering a neck and neck race. This talk attempts to give an overview of the field, give a snapshot of the present status, highlighting recent achievements, introduce operation principles, and describe some applications.
The cubic (or pseudo-cubic) crystalline structure of perovskite ferroelectrics does not lend itself easily to one-dimensional growth. For this reason only rare reports exist on growth and properties of these materials in the form of nano-wires. On the other hand, those rare reports intrigue us to pursue growth in order to study the properties of these nanowires with particular attention to size dependent properties and their potential implications.

The hydrothermal synthesis and processing of PZT and KNbO₃ nanowires are summarized based on own work and work reported in the literature. The origins of the nano-fibrous morphologies are discussed. The structure of the wires is discussed next, including the orientation of the spontaneous polarisation relative to the crystallographic orientation of the geometrical axes of the wires. The piezoelectric properties are reported for both PZT and KNbO₃. The situation in which the polarization axis is inclined to the axis of the wire in a mono-domain nanowire is analysed theoretically. Such a situation corresponds, for example, to a practical case where the nanowire axis of a tetragonal PZT is not [001]. In this configuration, the depolarisation field, opposing the spontaneous polarization leads to a polarization rotation. In particular diameters and orientations, the appearance of new phases is predicted. Size effect on properties is discussed with both positive an negative effect possible. Comments are made in regards to potential applications.

Effects of sintering conditions often exceed the expected dependence of grain boundary resistance on reciprocal grain size of CGO ceramics. Although the scatter in literature data might be also related to the grade of precursors and/or differences in powder preparation, these arguments are inconclusive, when grain boundaries are very clean. The purpose of this contribution is, thus, to re-examine effects of sintering temperature on specific grain boundary properties.

Different CGO10 precursor powders were used, including commercial powders, and powders prepared by freeze drying and sol-gel. Ceramic samples were processed by conventional sintering at 1400-1600°C, hot pressing at 1150-1200°C, at temperatures down to 1000°C by the use of sintering aids. Microstructure-property relations were analysed on combining microstructural characterisation with impedance spectroscopy, to de-convolute the electrical response of grain boundaries from bulk and electrode contributions.

One found consistent correlations between the temperature dependence of specific grain boundary conductivity or space charge potential and oxygen nonstoichiometry changes, estimated by extrapolating the temperature dependence of oxygen nonstoichiometry to sintering temperatures. This suggests that increase in space charge potential is promoted.
by the onset of significant reducibility at the highest sintering temperatures, or corresponding changes in point defect chemistry, possibly determining frozen-in conditions upon cooling. Coulometric titration of samples quenched from different sintering temperatures confirms differences in oxygen nonstoichiometry.

### 1.3 Aberration corrected transmission electron microscopy for ceramic (multi)layers: advances and challenges

**Sara Bals**  
Physics, University of Antwerp, Belgium

Recent developments in the field of transmission electron microscopy (TEM) have transformed this technique into a versatile tool for nanocharacterization. Aberration correctors nowadays enable us to obtain a spatial resolution below 1 Å. In addition to structural data, one is able to acquire chemical and valence information, all at the atomic scale. Clearly, this opens up a new level of experiments when investigating ceramic multilayer systems. Using a combination of advanced TEM techniques, the structure and chemical composition at interfaces and grain boundaries can be precisely determined. In this presentation we will show recent results obtained for LaAlO$_3$-SrTiO$_3$ systems grown using different experimental parameters as well as interface engineered (La,Sr)MnO$_3$-SrTiO$_3$ layers. Also the investigation of PbTiO$_3$-SrRuO$_2$-DyScO$_3$ multilayer systems, including strain mapping, will be presented. Finally, early results on band gap mapping in these systems will be discussed.

### 1.4 Nanodomain vertex arrays in BiFeO$_3$ single crystals

**Dietrich Hesse, Andreas Berger, Angelika Hähnel, Miryam Arredondo, Marin Alexe**  
Exp. Dept. II, Max Planck Institute of Microstructure Physics, Halle (Saale), Germany, D-06120

**Background:**  
BiFeO$_3$ (BFO) is a unique example of an intrinsic multiferroic, simultaneously showing antiferromagnetic, ferroelastic, and ferroelectric properties at room temperature. Polarization values of about 100 μC/cm$^2$ along the diagonals of the perovskite unit cell were reported for thin films and bulk single crystals. The domain structure is known to include three main domain types, viz. two ferroelastic domains, 71° and 109° domains, and one 180° pure ferroelectric domain.

**Methods and Results:**  
We report on a new type of regular domain patterns in BFO single crystals. They consist of triangular nanodomains of <50 nm size, arranged into long regular vertex arrays separated by stripe domains. They were observed by (scanning and high-resolution) transmission electron (STEM; HRTEM) and piezoresponse force (PFM) micro-copies in single crystals grown from solution flux. PFM together with crystallographic analysis by selected area and nano-beam electron diffraction indicate that these patterns consist of ferroelectric 109° domains. Geometry and orientation of the domain walls are analyzed, and a reasonable domain model is derived.

**Conclusions:**  
The observations clearly point to the presence of arrays of 109° nanodomain vertexes of new type in BFO single crystals that have hitherto not been described. A possibility for conserving Kittel’s law of domain size is discussed in terms of the patterns being confined to the skin layer observed recently on BiFeO$_3$ single crystals.
Ion transport in oxides is essential in many electrochemical devices such as fuel cells or batteries but may also play an important role in dielectric and piezoelectric applications where defect motion is often related to degradation phenomena. Moreover, resistive memory devices are partly based on ion transport processes. In all cases, interfacial ion transport may be of crucial importance: Owing to structural differences and violation of charge neutrality, interfaces such as grain boundaries, surfaces and hetero-phase interfaces exhibit ion transport properties which differ from those of the bulk.

In this contribution, basic principles of interfacial ion transport will be discussed including methodological aspects dealing with impedance spectroscopy and tracer diffusion studies. Numerous experimental results will then exemplify relevance (and partly also irrelevance) of interfaces for ion transport in lead zirconate (PZT), BaTiO₃, SrTiO₃ and yttria stabilized zirconia (YSZ). Among others, vacancy accumulation space charge layers in perovskite-type oxides probed by tracer diffusion and SIMS (secondary ion mass spectrometry) as well as ion transport phenomena along and across interfaces of YSZ thin films will be presented.

Thin film electroceramics are of great interest in gas sensors and solid oxide fuel cells (SOFCs), where, the small dimensions lead to more rapid response times in gas detection and low ionic resistance in SOFC electrodes and membranes. The nature and concentrations of point defects play a key role in determining device electrical properties, and hence, performance. As a consequence of the larger surface and interface to volume ratios and the potential for stress/strain from film/substrate lattice mismatch, thin films often exhibit electrical behavior largely different from their bulk counterparts, frequently attributed to differences in defect structure of the films. To test this hypothesis, two complementary methods, optical absorption and chemical capacitance, are used to examine defect concentrations in PrₓCe₁₋ₓO₂₋₄ (PCO) thin films. At relatively high oxygen partial pressures (∼ air, > 500 °C), Pr is multivalent (4+/3+), resulting in mixed ionic electronic conductivity. Optical absorption in the visible (measured in-situ), proportional to the concentration of Pr⁴⁺ is observed, and is used to extract the relevant defect concentrations in these thin films. Additionally, the Pr redox couple results in a significant chemical capacitance, reflecting potential storage/release of oxygen, which is probed by impedance spectroscopy and used to extract the oxygen nonstoichiometry in the PCO films. The optical and chemical capacitance measurements show good mutual agreement and are found to differ little from the corresponding defect properties of bulk specimens.
The search for lead-free piezoelectrics is uncovering a number of systems with unusual dielectric and electromechanical behaviour of which the origin is currently uncertain. This behaviour includes: (i) relaxation peaks in the temperature dependence of permittivity that do not coincide with the Curie temperature, (ii) large electric field induced strain that is not reflected in the piezoelectric coefficients of poled samples, and (iii) unusual frequency or time dependence of polarization hysteresis loops and field-induced phase transitions.

It has been postulated that many of these characteristics are due to a combination of polar nano-regions (PNRs) and ferroelectric macro-domains. To explore this hypothesis, a model has been developed of the low field complex permittivity of ensembles of PNRs through a statistical mechanics determination of the influence of thermal fluctuations on both the size and direction of the polarization vector in PNRs. The model has been tested using data from the \((Na_{1/2}Bi_{1/2})TiO_3-(K_{1/2}Bi_{1/2})TiO_3\) system (NBT-KBT). It is shown that the size distribution of PNRs is critical to developing the properties observed. Employing the same assumptions the high field properties, in terms of the frequency dependence of coercive field and remanent polarization, are also modelled. Whilst demonstrating that frequency dependence of polarization-field behaviour may not always be attributed to conduction currents, the results of the model are inconclusive when applied to the example of NBT-KBT.

In recent years, strain engineering has proved to be a very effective tool to tune the functional properties of ferroelectrics. But while strain can be used to modify the magnitude or the symmetry of the ferroelectric polarization, it cannot be used to change its sign. On the contrary, strain gradients couple linearly to polarization and are therefore capable to orient it, thanks to the so-called flexoelectric effect. In this talk, besides providing some basic outline of the key aspects of flexoelectricity, I will discuss two recent results concerning the use of flexoelectricity in ferroelectric thin films. In the first of them, we show how strain gradients inherent in the domain structures that arise when epitaxially growing ferroelectric thin films can be used to point the polarization away from the normal direction; thus, strain gradient engineering provides a physical route for achieving ferro/piezoelectrics with tilted polarization, long thought to be a requirement for enhanced piezoelectricity. The second recent result concerns the use of pure mechanical pressure in order to achieve inversion of polarization. By pushing the sharp tip of an AFM onto the surface of a ferroelectric film, the stress concentration leads to strong enough deformation gradients that their associated flexoelectricity is able to switch the sign of the polarization. This provides an alternative way to operate a ferroelectric memory, which can be written mechanically and read electrically. The results illustrate how flexoelectricity can be used to actively control not just polarization but polarity in ferroelectrics.
Two-dimensional electron gases at interfaces between Mott insulators and band insulators have attracted significant attention because they can exhibit unique properties, such as strong electron correlations, superconductivity and magnetism. Interfaces between the band insulator SrTiO$_3$ and the rare earth titanates (RTiO$_3$, where R is a trivalent rare earth ion), which are Mott insulators, are particularly interesting, because both the oxygen and Ti sublattices are continuous across the interface. An interfacial fixed polar charge arises because of a polar discontinuity at the interface. This interfacial charge can be compensated by a two-dimensional electron gas, residing in the bands of the Mott and/or band insulator and bound to the interface by the fixed interface charge. In this presentation, we report on intrinsic electronic reconstructions, of approximately 1/2 electron per surface unit cell at a prototype Mott/band insulator interface between GdTiO$_3$ and SrTiO$_3$ grown by molecular beam epitaxy. The sheet carrier densities of all GdTiO$_3$/SrTiO$_3$ heterostructures containing more than one unit cell of SrTiO$_3$ are approximately 1/2 electron per surface unit cell (or 3×10$^{14}$ cm$^{-2}$), independent of layer thicknesses and growth sequences. These carrier densities closely meet the electrostatic requirements for compensating the fixed charge at these polar interfaces. We will report on correlation effects in extremely high carrier density SrTiO$_3$ quantum wells that can be obtained using these interfaces, such as magnetism. Models of the charge distribution and measurements of transport coefficients, such as the Seebeck effect, provide insights into the nature of the two-dimensional electron gas, the importance of band alignments, background doping and different electrostatic boundary conditions. We will also discuss new experimental approaches to probe the Mott insulating state, using modulation doping with heterointerfaces for electrostatic control of large carrier densities in Mott materials.

The interface between the two band insulators LaAlO$_3$ and SrTiO$_3$ shows a range of fascinating properties such as conductivity, magnetism, superconductivity and even their coexistence. Using density functional theory calculations we explore the impact of a metallic overlayer on LaAlO$_3$/SrTiO$_3$(001) and reveal that it alters significantly the electric field within the polar LaAlO$_3$ film. For Al or Ti metal contacts the electric field is eliminated, leading to a suppression of the thickness-dependent insulator-to-metal transition observed in uncovered films. Independent of the LaAlO$_3$ thickness, both the surface and the interface are metallic, with an enhanced interface carrier density relative to LaAlO$_3$/SrTiO$_3$(001) after the metallization transition. Monolayer thick contacts of Ti, nonmagnetic in bulk, develop a finite magnetic moment and induce a spin-polarized 2D electron gas at the n-type interface, due to confinement effects in the SrTiO$_3$ slab. In contrast to the simple metals, noble metal contacts (Cu, Ag, Au) exhibit a finite and even enhanced internal electric field. Results for a series of metallic overlayers on LaAlO$_3$/SrTiO$_3$(001) show broad variation of band alignment, size of Schottky barrier and
carrier concentration and provide guidelines how to control the properties of the quasi-two dimensional electron gas at the LaAlO3/SrTiO3(001) interface.

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<th>I.11</th>
<th>Effect of octahedral distortions on physical properties of La_{0.67}Sr_{0.33}MnO_3 films</th>
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<td></td>
<td>Arturas Vailionis</td>
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<td>GLAM, McC 227, 476 Lomita Mall, Stanford University, Stanford, CA 94305</td>
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Strained La_{1-x}Sr_xMnO_3 (LSMO) films exhibit rich variety of electronic and magnetic phenomena that are closely coupled to lattice distortions. Among many structural degrees of freedom MnO_6 octahedra distortions represent an important tuning mechanism of the physical properties in LSMO thin films [1]. Here we demonstrate that magnetic and electric properties of LSMO (x = 0.33) thin films are strongly coupled to the sign and degree of MnO_6 octahedra rotations. We observe 90 degree switching of the in-plane magnetic easy axis in LSMO thin films grown on (La,Sr)(Al,Ta)O_3 substrates as compared to those grown on NdGaO_3 [2]. The change in magnetic easy axis direction can be explained by distinct MnO_6 octahedral rotations that are induced in epitaxial LSMO thin films by compressive biaxial strain. The result shows that the magnetic anisotropy can be effectively controlled by a fine-tuning of the octahedral rotations.

The octahedral distortions also have an effect on conductivity of LSMO films. We demonstrate that the conducting LSMO films grown on STO(110) become insulating as film thickness is reduced below 10 unit cells [3]. X-ray diffraction data show that, as films get thinner and reach 10 uc, the unit cell symmetry increases from monoclinic to orthorhombic. The symmetry change alters octahedral distortions at the interface which originate from dissimilar BO_6 rotational patterns between the substrate and the coherently grown layer. We believe that insulating phase of LSMO films is related to the stabilization of static Jahn-Teller distortions due to the symmetry mismatch between substrate and the layer.


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<th>I.12</th>
<th>Grain boundaries in proton-conducting BaZrO_3 proton conductors: Evidence for space charge effects</th>
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<td>Mona Shirpour¹, Rotraut Merkle¹, Behnaz Rahmati¹, Wilfried Sigle², Peter A. van Aken², Joachim Maier²</td>
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<tr>
<td></td>
<td>¹Max Planck Institute for Solid State Research, Stuttgart, Germany; ²Stuttgart Center for Electron Microscopy, Max Planck Institute for Intelligent Systems, Stuttgart, Germany</td>
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Proton-conducting Y-doped BaZrO_3 combines high chemical stability with good bulk conductivity. Nevertheless, the small grain size (approx.1 micrometer) and blocking character of the grain boundaries still impede a broader application, e.g. in intermediate temperature fuel cells.

Dense Y- and Sc-doped BaZrO_3 ceramics were obtained by “Spark-Plasma-Sintering” at 1600°C. While grain size and bulk conductivity remain constant, additional annealing (20h at 1700°C) decreases the grain boundary resistance by 1-3 orders of magnitude. TEM-EDXS indicates a pronounced dopant accumulation in the grain boundary region for the annealed samples [1]. The comparable degree of segregation for Sc³⁺ (negligible size mismatch) and Y³⁺ (large mismatch) suggests a positive excess charge in the grain boundary core as main driving force for segregation. Within the space charge model, this
dopant accumulation to grain boundary core and/or space charge zone will decrease proton depletion and thus increase total conductivity. Further evidence for the validity of the space charge model is obtained from impedance measurements under large DC bias [2]. An extremely large-grained sample with >100 micrometer grain size and Pt microcontacts allows to measure impedance spectra across individual grain boundaries. DC bias values of up to 1 V per boundary strongly decrease grain boundary resistance as well as capacitance. Both findings support the model that a space charge depletion zone for protons (and oxygen vacancies) is the origin of the blocking grain boundaries.


In order to meet with the demand of increasing speed and improving performance, but also in view of 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. New fundamental questions related to composition-morphology-property relations at the nanoscale need to be addressed as well. For this, it is required that interesting nanostructured oxides are synthesized with the desired purity and in the specific appearance in which their functional properties need to be established. This tendency towards nanostructured materials, together with the increasing economical and environmental awareness on production processes, imposes important opportunities for solution based synthesis methods. They are put forward as an economically efficient alternative for high temperature solid state synthesis or vacuum based methods.

In this presentation, we will address current challenges in the solution based synthesis of complex oxide nanostructures based on our recent work. We discuss our experimental strategies towards using non-toxic solvents, lowering thermal budgets, and using vacuum-free deposition and nanostructuring by self assembly or soft lithography.

A. Hardy is a postdoctoral research fellow of the Research Foundation-Flanders (FWO Vlaanderen).

Ferroelectric oxides, such as Pb(Zr,Ti)O3 (PZT), are very useful for electronic and photonic devices, as well as piezomechanical actuators and sensors. The ferro- and piezoelectric properties are strongly related to the crystal orientation as well as the strain state of the PZT layer. Successful integration of these devices into silicon technology is therefore not
only dependent on the ability of epitaxial growth on silicon substrates, but also the control of the crystallographic orientation and the residual strain state of the deposited PZT thin film.

A study on the effects of the residual strain in Pb(Zr_{0.52}Ti_{0.48})O_3 (PZT) thin films on the ferroelectric and piezoelectric properties is presented. Pulsed laser deposited epitaxial (001)-oriented PZT thin film capacitors are sandwiched between SrRuO_3 electrodes. The thin film stacks are grown on different substrate-buffer-layer combinations. Compressive or tensile strain caused by the difference in thermal expansion of the PZT film and substrate influences the ferroelectric and piezoelectric properties. These properties are consistent with the theoretical model for strained thin films in the ferroelectric r-phase. In this contribution, the control of the crystalline orientation and misfit strain state of epitaxial PZT, as well as the resulting ferroelectric and piezoelectric properties will be discussed. From theoretical models it will be explained that these PZT films must be in the monoclinic phase.

I.15 Structural and magnetic phase transitions in Bi_{1-x}Nd_xFeO_3 ceramics
Jan M. Reaney
Materials Science and Engineering, University of Sheffield, United Kingdom, S13JD

The magnetic and structural phase transitions as a function of Nd concentration are investigated in Bi_{1-x}Nd_xFeO_3 based ceramics. Paraelectric (PE) to ferroelectric (FE) transitions were observed for compositions with x <=0.125 which manifested themselves as sharp peaks in permittivity. In contrast, PE to antiferroelectric (AFE) transitions for 0.15 <=x <=0.20 gave rise to a step-like change in the permittivity with x = 0.25 exhibiting no sharp anomalies and remaining PE until room temperature. The large volume change at the PE to FE/AFE transitions, reported by Levin and co-workers [Phys. Rev. B 81, 020103, 2010] and observed by dilatometry, coupled with their 1st order character, constrain the structural transitions to occur uniformly throughout the material in an avalanche-like manner. However, despite the large volume change and eye-catching anomalies in DSC, the latent heats for the transitions in Bi_{1-x}Nd_xFeO_3 are similar to Pb(Zr,Ti)O_3 (1-3 KJ/mol) with each an order of magnitude greater than BaTiO_3 (<0.2 KJ/mol).

The Neel temperature (T_N) and magnetic order remained broadly unaffected by the substitution of Bi by Nd. However, the onset of a structural phase transition below T_N resulted in rotation of the magnetic dipoles through 90 degrees with a commensurate anomaly in magnetisation [Levin et al. Phys. Rev. B 81, 020103 2010]. Compositions with x = 0.15 gave a comparatively robust ferromagnetic response suggesting that magnetic dipoles are not completely antiparrallel and are either canted or exhibit helical ordering.

I.16 Nanoscale phenomena in relaxor ferroelectrics via scanning probe microscopy
Andrei Kholkin
DECV & CICECO, University of Aveiro, Portugal

Ferroelectric relaxors have been a puzzling problem since the discovery of their unusual dielectric and electromechanical properties. Recent years witnessed a tremendous interest in relaxor materials due to the unique combination of useful functional properties offered by miniaturization and modern deposition techniques. However, the central problem of relaxors –the origin and properties of polar nanoscale regions (PNRs) that are responsible for their dielectric and piezoelectric phenomena remain elusive. Until now the properties of PNRs have been only assessed via indirect scattering techniques.
New possibilities are offered by the advancements in Scanning Probe Microscopy where the PNRs can be probed via their local piezoelectric response. In this presentation, recent SPM results on Pb-based perovskite relaxors will be presented and analyzed. Clear correlation between the grain size and SPM response was observed in PLZT ceramics thus allowing to link macroscopic properties and local piezoelectricity. Depth-resolved measurements show that the surface properties of relaxors are different from the bulk. Using extensive imaging and spectroscopic studies by variable-temperature and time resolved SPM, we found that the observed mesoscopic behavior is consistent with the presence of two order parameters describing dynamic and static parts of polarization. The static component gives rise to rich spatially ordered systems on the 100 nm scale, and are only weakly responsive to electric field. The surface of relaxors undergoes a mesoscopic symmetry breaking leading to the freezing of polarization fluctuations and shift of corresponding transition temperature.

In this presentation, we consider the impact of point defects on electrical properties in a variety of different dielectric and ferroelectric materials. We will consider the impact of equilibrium defect concentrations in the BaTiO$_3$ material with respect to partial Schottky and reduction reactions on the paraelectric-ferroelectric phase transition temperature, the heat of transformation, and the Curie Constant. We will also consider the impact of defect formation enthalpy in solid solution within the BaTiO$_3$-BaZrO$_3$ system, noting a non-Vegardian trend in the defect formation energetics with composition. Defect association and dissociation behaviour will also be considered with thermally stimulated depolarization current (TSDC) characterization approaches with a number of ionically compensated acceptor dopants in paraelectric SrTiO$_3$ and ferroelectrics, such as BaTiO$_3$ and Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$. Doping and defect interactions on non-linear domain wall motion will also be discussed in important non-lead systems, such as (Na,K)NbO$_3$.

There is renewed interest in the behaviour of point defects in bulk SrTiO$_3$ and at its interfaces due to the material’s possible application in all-oxide electronics and as a memristive device. The combination of $^{18}$O/$^{16}$O exchange and Secondary Ion Mass Spectrometry (SIMS) analysis constitutes a powerful tool for probing the behaviour of oxygen vacancies in oxides. In this contribution, after a brief introduction to the technique and its capabilities and limitations, I demonstrate the application of this method to investigating the behaviour of oxygen vacancies in SrTiO$_3$ and at its extended defects (dislocations, surfaces, hetero-interfaces). Three systems will be examined: (1) single crystal SrTiO$_3$ substrates; (2) low-angle grain boundaries in SrTiO$_3$ comprising periodic arrays of edge dislocations; and (3) heterostructures based on SrTiO$_3$ (e.g. LaAlO$_3$|SrTiO$_3$, SrRuO$_3$|SrTiO$_3$). Two aspects regarding the behaviour of oxygen vacancies
Bi-based perovskites have been investigated as promising candidates to replace lead-based piezoelectrics. Notably, compositions near the morphotropic phase boundary in \((\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3 \sim (\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\) (BKT-BNT) display promising behavior such as high \(P_{\text{max}}\) and \(P_r\). Recently, \(\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3 \sim (\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3\) (BZnT-BKT) ceramics have also been explored for their piezoelectric response and showed a high dielectric constant \((K \approx 4000\text{ at } T_c)\) and \(P_{\text{max}}\) above 25 \(\mu \text{C/cm}^2\). Although bulk material research is useful, many applications require thin film embodiments. To date most thin film studies indicate these materials are generally very leaky dielectrics, with hysteresis measured (if at all) at frequencies greater than 1 kHz.

Here, BKT-BNT near MPB composition and BZnT-BKT thin films are deposited on Pt-Si substrates via chemical solution deposition. Strict attention was paid to precursor solutions and process conditions to understand and control the multiple volatile cations present. “Layer-by-Layer crystallization” resulted in single phase perovskite development and depending on cation overdoping, changes in grain size were observed. Dense columnar morphologies were found, with microcracking present when using non-ideal solution stoichiometry. For BKT-BNT, optimal conditions resulted in maximum polarization of 45 \(\mu \text{C/cm}^2\), remanent polarization of 16.3 \(\mu \text{C/cm}^2\), coercive field of \(\sim 90\) kV/cm, and dielectric constant and loss of 600-750 and 3-5%.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Much of the current research has been oriented towards lead-free materials due to environmental concerns. Sodium potassium niobates represent a group of lead-free piezoelectrics. The problems related to synthesis and sintering of alkali-niobate based ceramics persist and they are connected to assumed deficiency of alkalines stemming either from hygroscopicity of the alkali reagents, and/or from the sintering where the alkali losses could be evidenced by the appearance of secondary niobium-rich phases which are in some cases humidity sensitive.

Knudsen effusion mass spectrometry (KEMS) was used to determine the equilibrium vapour pressures of sodium over selected compositions in the \(\text{Na}_2\text{O–Nb}_2\text{O}_5\) system at 1100–1470 K. Different two-phase regions were investigated and the vapor pressures of sodium above selected compositions were calculated. For \(\text{NaNbO}_3\), the sodium vapor pressure at typical sintering conditions was found to be substantial \((p_{\text{Na}} \sim 2.14\) Pa at 1350 K).
The estimated alkali loss at 1350 °C could explain the observed alkali deficiency in the ceramics. The approach was extended to the pseudo-binary KNbO₃–NaNbO₃ system. Results are discussed from the viewpoint of their applicability to processing and properties of this family of lead-free piezoelectric ceramics.

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<th>I.21</th>
<th>Ageing phenomena in negative temperature coefficient thermistors: A review for different oxide ceramics</th>
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<tr>
<td></td>
<td>Sophie Guillemet-Fritsch, Christophe Tenailleau, Abel Rousset</td>
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<td>Material Science, CIRIMAT/CNRS, Toulouse, France, 31062</td>
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Transition metal manganites are interesting semiconductor ceramics used as negative temperature coefficient (NTC) thermistors. These materials crystallize in the spinel structure, a cubic close packing of oxygen anions in which the cations are located on the tetrahedral (A) sites and the octahedral (B) sites. The electrical transport phenomena in these materials are interpreted in terms of a phonon-assisted jump of carriers among localized states, the so-called hopping conductivity. Much work has been done in order to develop high performance thermistors. However, under thermal constraint, most of the thermistor resistivity increases with time. This phenomenon, called “ageing,” is still the subject of controversy explanations. The drift of resistivity depends on the chemical composition, the crystal structure, and the thermal history of the ceramics. The ageing phenomenon has been explained by cationic migration and/or electronic changes between the sublattices of the spinel structure and by formation of Mn³⁺ clusters on the octahedral sites. The aim of the work is to give an overview of the mechanisms that have been given to explain the ageing phenomenon in different systems (nickel manganites, iron manganites, zinc nickel manganites..) and to discuss them.

<table>
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<tr>
<th>I.22</th>
<th>Piezoelectric PZT-polymer composites processed using an electric field: Materials and applications</th>
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<td>Daan A. van den Ende¹,², Wilhelm (Pim) A. Groen¹,², Sybrand van der Zwaag²</td>
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<td>¹Holst Centre, TNO, Eindhoven, Netherlands; ²Novel Aerospace Materials, Delft University of</td>
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Piezoelectric ceramics have excellent electromechanical coupling, making them very suitable as sensors and actuators. However, their practical applications are limited, especially where robustness is important. Piezoelectric polymer–PZT composites containing dispersed particulates are intrinsically tougher and easy to process into complex shapes. However, their electromechanical coupling is severely compromised due to limited connectivity of the PZT particles.

To overcome this problem, composites with microstructures of highly aligned, well connected particulates were manufactured by electric field assisted processing. The dielectrophoretic effect (DEP) causes particles to align during curing of the matrix. Piezoelectric properties of the composite resemble 1-3 composite properties, with much better coupling than dispersed 0-3 particulate composites.

Using this technique, sensitive composites were manufactured for cost-effective, robust pressure sensors and switches. The composites also show potential for energy harvesting, especially in high strain applications, such as direct strain energy harvesting inside automobile tires. The composites are robust enough to survive the strains in the tire during operation. The charge output of the energy harvesters is coupled to the power output. At relatively modest driving speeds these energy harvesters provide an output high enough for in-tire sensing and wireless signal transmission.
Structured composites of classic 1-3 configuration were obtained using aligned PZT fibers. An all solid-state device with controllable surface roughness was manufactured. In-situ switching of the friction coefficient, is demonstrated by sliding against a Si wafer counter surface. Some potential applications for the electronics industry are demonstrated.
Abstracts oral contributions

O.1 Electrode kinetics of mixed conducting oxides in H₂/H₂O and O₂ atmospheres

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Compared to common Ni|yttria stabilized zirconia (YSZ) cermet anodes, oxide anodes are expected to exhibit improved properties in solid oxide fuel cells (SOFC) in terms of redox cycling and coking stability. Owing to their mixed ionic and electronic conductivity, acceptor doped oxides are particularly attractive. However, mechanistic studies on the polarization behavior of such electrodes are still rare.

Methods
Anode kinetics of La₀.₆Sr₀.₄FeO₃₋ₓ and SrTi₀.₇Fe₀.₃O₃₋ₓ in humid hydrogen atmosphere was investigated by means of impedance and dc studies on geometrically well-defined thin film electrodes, which were deposited on YSZ single crystal substrates by pulsed laser deposition. An additional platinum thin film grid was used to support the rather weak electronic conductivity of both materials under reducing conditions.

Results and Conclusions
These model electrodes showed rather low polarization resistances for H₂ oxidation/H₂O splitting. The electrocatalytic performances of both materials under reducing conditions are compared to that in oxygen atmosphere. Considering two different reactions on the same electrode allows an in depth analysis of the relation between defect chemistry and electrode kinetics of thin film electrodes. The resistive and capacitive features of the electrode impedance are discussed in terms of equivalent circuits and attributed to different transport, reaction and storage processes.

O.2 Conductivity relaxation experiments in pure and Sr/Bi-doped Ca₃Co₄O₉ electrode materials

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Ca₃Co₄O₉ layered cobaltites have been presented recently as promising electrode materials in Solid Oxide Fuel Cells. Nevertheless, their mixed ion-electron conduction character has not been explored yet. Here, we performed conductivity relaxation measurements in order to determine Dchem and Kchem diffusion and exchange coefficients. These experiments are performed on fully dense sample prepared by spark plasma sintering. We studied here the influence of Sr and Bi dopants on diffusion and exchange properties and compare them to what has been found by tracer diffusion after determining the thermodynamic coefficient.

We found that Diffusion and exchange coefficients are much lower than those found in state-of-the-art materials for fuel cells. This study underlines then the importance for controlling oxygen content in these materials to improve these properties and make these materials competitive compared to more classical LSF or BSCF electrode compounds.

Cathode performance of spray pyrolysis-deposited La$_{0.58}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-\delta}$ and La$_{0.58}$Sr$_{0.4}$Fe$_{0.8}$Ni$_{0.2}$O$_{3-\delta}$ thin films for intermediate temperature solid oxide fuel cells

Per Martin Rørvik$^1$, Filip Lenrick$^2$, Yngve Larring$^1$, L. Reine Wallenberg$^2$, Camilla Haavik$^1$

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Conventional solid oxide fuel cells (SOFCs) typically operate at 800-1000 °C. If the operating temperature can be reduced to 600 °C or below SOFCs become relevant for new markets such as portable devices, but under such condition cathode performance is crucial. This challenge opens up possibilities of nanoscale structuring of the cathode by using lower processing temperatures than in traditional powder-based fabrication methods.

Methods

Thin amorphous films of La$_{0.58}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-\delta}$ (LSFC) and La$_{0.58}$Sr$_{0.4}$Fe$_{0.8}$Ni$_{0.2}$O$_{3-\delta}$ (LSFN) were deposited onto heated substrates by air blast spray pyrolysis using a homogenous solution. The films were subsequently crystallized by annealing at 650 °C. The cathode performance was studied by impedance spectroscopy using symmetrical cells with YSZ as electrolyte. Microstructure and phase composition were studied by SEM, TEM, XRD and EDXS.

Results

The thin films were porous with particle size ~20 nm. The electrochemical properties of the cathodes were studied and compared to the microstructure and the material composition in order to optimize the cathode performance. The area specific resistance (ASR) of 2-5 μm thick LSFC cathodes made with carbon black as pore former was 0.59 Ω cm$^2$ at 600 °C. Detailed TEM/EDXS studies revealed Co- or Ni-rich regions and regions with connected crystallographic orientation.

Conclusions

Spray pyrolysis is a useful technique for deposition of thin porous LSFC and LSFN cathodes. The low processing temperature results in nanoscale particle size and low ASR.

Composition control of piezoelectric PZT thin films deposited onto Cu-coated polymer substrates

Anja Kleiner, Gunnar Suchaneck, Barbara Adolphi, Gerald Gerlach

Solid State Electronics Lab, TU Dresden, Germany

Recently, we demonstrated reactive sputter-deposition of Pb(Zr, Ti)O$_3$ (PZT) thin films directly on copper-coated polymer films without intentionally substrate heating. Here, the low pressure plasma carries energy to the deposition substrate, which leads to an increase of the substrate surface temperature without sufficiently heating the substrate itself.

In this work, we investigate film composition of such nanocrystalline Pb(Zr, Ti)O$_3$ (PZT) thin films in dependence on deposition parameters. Large area film deposition was performed by means of reactive magnetron sputtering from 200 mm diameter metallic targets. Pulsed DC sputtering has been employed for the Ti-target (or alternatively for the Zr-target), RF-sputtering for the Pb-target and high-power pulse sputtering for the Zr-target (or alternatively the Ti-target). The pulsed-DC mode was optimized to avoid arc events. RF-sputtering provided the best result in terms of preventing droplet formation at the Pb-
target. Repetition frequency and duty cycle of the high-power pulse were selected to provide a high current discharge with ions impinging on the substrate at energies of a few 10 eV. Composition profiling was carried out by XPS and RBS. Film composition was analysed in a ternary TiO$_2$-ZrO$_2$-PbO diagram. The as-deposited films had a lead-enriched layer at the surface. Lead enrichment was obtained also at the PZT/Cu interface, but not at a PZT/Pt one. The bulk film composition was in rhombohedral range near the morphotropic phase boundary of the PZT phase diagram. The impact of deposition parameters on bulk film composition is discussed.

Ferroelectrics for energy storage: The role of dielectric nonlinearities

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Functional Materials Group, National Physical Laboratory (NPL), London, United Kingdom

Ferroelectrics are promising materials for energy storage due to their high energy and power density. Yet, overestimated values of recoverable energy have been reported in ferroelectrics, as dielectric nonlinearities have not been considered when calculating energy density. This talk first puts forward a model linking energy density in ferroelectrics with linear and nonlinear Landau coefficients. This model is extended to provide a complete picture of energy density in ferroelectrics, whereby extrinsic polar mechanisms, like domain walls, polar nanoregions and interfaces, can also strongly affect the material’s nonlinear dielectric properties. This multipolarization mechanism model, is used to evaluate the interplay of intrinsic and extrinsic polarization in energy density in composites, multi-phased ceramics and homogeneous and multilayer thin films. The model proposed in this work for energy density will support the development of new high energy density systems and heterostructures for energy storage applications.

BaMg$_{1/3}$Ta$_{2/3}$O$_3$ thin films obtained by PLD or sol-gel

Cristina Busuioc$^{1,2}$, Liviu Nedelcu$^2$, Marian Gabriel Banciu$^2$, Cristina Dragoi$^2$

Nicu Doinel Scarisoreanu$^3$, Sorin-Ion Jinga$^1$, Ecaterina Andronescu$^1$

$^1$Faculty of Applied Chemistry and Materials Science, University "Politehnica" of Bucharest, Romania; $^2$Multifunctional Materials and Structures, National Institute of Materials Physics, Bucharest-Magurele, Romania; $^3$Photonic Processing of Advanced Materials, National Institute for Laser, Plasma and Radiation Physics, Bucharest, Romania

BaMg$_{1/3}$Ta$_{2/3}$O$_3$ (BMT) complex perovskite has stimulated a large interest due to its excellent dielectric properties in microwave communications systems. Thin films of dielectric materials offer the advantages of much lower crystallization temperature and larger capacitance than bulk samples, being easily integrated in microelectronic devices. In this work, we have fabricated BMT thin films by two different methods: pulsed laser deposition (PLD) and sol-gel (SG). PLD technique started from a bulk ceramic target synthesized by the solid state reaction method, with 1:2 ordered hexagonal structure, while SG method involved barium carbonate, magnesium acetate and tantalum butoxide as chemical precursors, followed by spin-coating and heat treatment. Platinum-coated silicon wafers were used as substrates.

XRD, AFM, SEM, TEM, EDS and electrical investigations were employed for structural, morphological, compositional and dielectric characterization of BMT samples. All BMT thin films exhibit polycrystalline single-phase structure, with cubic symmetry. SEM investigation revealed a columnar microstructure in the case of PLD and a granular one in the case of SG. BMT films tend to crystallize with small grains, sized below 50 nm. The dielectric permittivity ($\varepsilon_r$) of BMT thin films presents values around 18, smaller than those of BMT target ($\varepsilon_r \sim 24$). The temperature dependence of the dielectric permittivity ($\varepsilon_r$) of
BMT samples was recorded at 100 kHz, in the (−100 °C +100 °C) temperature range, resulting in a moderate thermal stability of BMT thin films. Opposite to BMT target, all BMT films show relatively high, positive values.

Solid Oxide Fuel Cells (SOFC) convert the chemical energy of various fuels directly into electrical energy. However, a performance limiting factor are the polarisation losses occurring at the cathode (air electrode) and the anode (fuel electrode). In this contribution we present an effective method for increasing the anode performance of anode supported cells (ASC). It is based on a short-time application of a high current density in reverse direction (reverse current treatment, RCT) intermittent to normal cell operation mode.

The performance change of ASCs is evaluated with a parameter variation for the RCT (current density, humidity, duration, number of treatments). The performance indicator area specific resistance (ASR) is measured by electrochemical impedance spectroscopy and assigned to the different polarisation processes. The contribution attributed to the anode electrochemistry is reduced by up to 40 % after the RCT.

Post-test analysis with FIB/SEM revealed the formation of a nano-structured interlayer (thickness ~200nm) at the interface electrolyte/anode functional layer. The reverse current treatment during operation is seen as valuable method to further increase performance of anode supported SOFCs.

\[ \text{Ce}_{0.85}\text{RE}_{0.15}\text{O}_{1.925} \ (\text{RE} = \text{Gd}, \text{Sm}) , \text{Ce}_{0.8}\{\text{Gd}_{0.1}\text{Sm}_{0.1}\}\text{O}_{1.9} \] and CeO\textsubscript{2-\delta} nano-powders were synthesized by microwave-assisted hydrothermal synthesis in a time and energy efficient way. The fluorite-type crystal structure was confirmed by powder X-ray diffraction and Rietveld refinement. The Brunauer-Emmett-Teller (BET) method was used to confirm high powder surface area. The morphology of the nano-powders was investigated by Transmission Electron Microscopy (TEM) and the observed nano-metric particle size was consistent with calculations of the line width broadening in the XRD pattern. Sintered ceramics were confirmed to show high density and low surface porosity using Scanning Electron Microscopy (SEM), as a result of the high sintering activity of the microwave-assisted hydrothermally synthesized nano-powders. In the sintered ceria ceramics the grain boundary (GB) areas were found to constitute ionic charge transport barriers, because the resistance of GBs was found to be larger than the bulk areas by separately analyzing GB and bulk dielectric relaxations using impedance spectroscopy. The high sintering activity of the nano-powders lead to optimal and highly increased GB ionic conductivity in the doped ceria sintered ceramics, with the highest values encountered in the Sm doped composition. The undoped CeO\textsubscript{2-\delta} sample showed clear signs of a dominating electronic charge transport mechanism, possibly due to incomplete
oxygenation and mixed valent Ce⁴⁺/Ce³⁺ electron hopping. The strongly increased and pure ionic conductivity detected in rare-earth doped ceria may facilitate application of these materials in intermediate-temperature solid oxide fuel cells (IT-SOFC).

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<th>O.9</th>
<th>Critical issues for the development of 3rd generation fuel cells with proton conducting electrolyte</th>
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<td>Christelle Denonville¹, Agnieszka Gorzkowska-Sobas², Marit Stange¹, Yngve Larring², Marie-Laure Fontaine¹, Truls Norby²</td>
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<td>¹SINTEF Materials and Chemistry, Oslo, Norway; ²University of Oslo, Norway</td>
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Metal-Supported Solid Oxide Fuel Cells (MS-SOFC), wherein the supporting component of the cell is made of a porous alloy, are referred to as 3rd gen SOFC operating at temperature down to 500-650°C. This technology is expected to decrease significantly capital and operational costs, while increasing lifetime due to lower operating temperature and higher redox stability. Furthermore use of proton conducting electrolyte is expected to provide additional advantages. This presentation reviews briefly metal supported cell development with focus on main issues affecting production, performance and longevity of single cells. It addresses critical issues for selection of alloys based on cost, thermal expansion, corrosion rate, particle size and Cr evaporation issues. From these considerations, cell architectures and fabrication processes investigated in the EU project EFFIPRO are presented to illustrate the level of technical refinement required to produce MS-PCFC. Porous stainless steel substrates are produced by water based tape casting and scaled up to 5*5 cm². Various anodic architectures are investigated in order to optimize electrochemical performance and ensure good thermo-chemical compatibility with the alloy and La₆₋ₓWO₁₂ electrolyte material. These include NiO-LSC electrodes and other ceramic oxides. The anodes are deposited by various techniques, including spray-coating and screen-printing. The thin electrolyte is deposited by EPD or PLD. The various architectures for MS-PCFC are characterized and main issues for their production are discussed. This work is partially funded by the EU FP7 EFFIPRO project.

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<th>O.10</th>
<th>Low-temperature synthesis and characterization of ceramics driven from amorphous and nanocrystalline barium titanate powders</th>
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<tr>
<td></td>
<td>Yanling Gao, Viadimir Shvartsman, Doru C. Lupascu, Institute for Materials Science, University of Duisburg-Essen, Essen, Germany, 45141</td>
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In this report, we describe a low temperature synthesis procedure for the synthesis of barium titanate (BaTiO₃) nanoparticles in organic media. The difference in size and shape of BaTiO₃ particles is attributed to the combined effects of surfactant oleic acid (OA) and precipitant tetramethylammonium hydroxide (TMAH) or sodium hydroxide (NaOH). The method allows tailor-made preparation of powder particles with different stoichiometries and grain sizes. The mechanism of the formation of the pure perovskite BaTiO₃ nanoparticles is discussed in detail. Characterization with respect to morphology or grain size, and behavior on sintering was performed in order to determine appropriate process conditions for the preparation of pure, dense nanocrystalline ceramics. The BaTiO₃ particles are characterized by powder X-ray diffraction (XRD), Raman scattering, scanning electron microscopy (SEM) and high-resolution TEM (HRTEM). As for BaTiO₃ ceramics, the effect of sintering temperature on relative density and the temperature dependence of dielectric properties are further investigated.
Antiferroelectrics have recently gained increased attention due to their large energy storage capacity, required for high-performance capacitors, and a large volume change accompanying the field-induced phase transition, which may be used in high-strain actuator and transducer applications. Sodium niobate (NaNbO₃) belongs to the group of prototype antiferroelectrics, showing the largest amount of temperature induced phase transitions among all oxygen perovskites. In addition NaNbO₃ can be transformed to a ferroelectric phase upon application of an external electric field or by changing the grain size. Understanding the polymorphism of NaNbO₃ is fundamental for estimating its suitability for the above mentioned applications.

In order to study the size-induced phase transition behaviour and properties it is necessary to prepare dense NaNbO₃ ceramics with a wide grain size range. This requires a careful control of densification and grain growth processes. In order to design NaNbO₃ ceramics with different grain sizes we have first prepared solid-state synthesized NaNbO₃ powders ranging from 80 nm up to 400 nm. These powders were subsequently sintered using various sintering techniques, such as conventional sintering, two-stage sintering and hot-forging. The different techniques were systematically investigated and the process was optimized, resulting in a successful preparation of dense NaNbO₃ ceramics with grain sizes ranging from submicron sizes up to 50 μm. The effect of the grain size on the dielectric permittivity of NaNbO₃ ceramics will also be reported.

Solvothermal is a feasible method to synthesize nanophosphors with various morphologies and well crystallization. The blue light excited yttrium oxides nanophosphors were prepared by microemulsion combined isopropanol-solvothermal (MIS) process. The morphologies were determined by the added surfactant, pH value and centrifugation runs. The well-crystallized Y₂O₃: 9 mol% Eu nanophosphors were obtained from 180°C/24 h along with 500°C/2 h heat treatment. The 611 nm red emission was excited by 466 nm blue light to show high photoluminescence (PL). Furthermore, the more iso-morphological yttrium oxides were obtained by the urea-hydro-deposition (UHD) method. Those hydrolyzed nanophosphors possessed nearly isotropic particles after 80°C water bath heating for 2 h. Such nanophosphors prepared processing might keep the small phosphor particles about 80 nm without much growth even post-heat treatment up to temperature of 1000°C. Combine the MIS and UHS processes, the well crystallized and isolated red and green yttrium oxides nanophosphors could be achieved with high photoluminescence excited by blue light for applications in LED and LCD industries.
The mixed conducting cubic perovskite \((\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_3-\delta\) (denoted BSCF) is the state-of-the-art ceramic membrane material for oxygen separation technologies above 1150 K. In the intermediate temperature range (750 - 1100 K), however, BSCF suffers from a slow decomposition of the cubic perovskite into hexagonal perovskite and a modified 15R structure, which is accompanied by a degradation of oxygen transport. Temperature-dependent electron energy-loss spectroscopy (EELS) showed that, in the BSCF compound, redox stability of cobalt is remarkably lower than that of iron. At intermediate temperature, low-spin 3+ cobalt results, which has small ionic radius (54.5 pm) and is not tolerated by the cubic perovskite structure. After long-term oxygen permeation at intermediate temperature, BSCF membrane shows different occurrence of the aforementioned secondary phases at the oxygen feed side and the oxygen release side with respect to grain boundaries and grain volumes. Recently developed ferrites show improved phase stability at intermediate temperature as compared to BSCF, which can be understood by differences in redox stability (valence and spin-state) of cobalt and iron.

For enhancement of the sensitivity electron concentration in the n-type gas sensor material needs to be regulated in order to achieve equilibrium between optimal concentration of surface oxygen species and width of the depletion layer. The aim of the present work is to demonstrate that the sensing characteristics of a metal oxide semiconductor gas sensor using n-type zinc ferrite can be improved by controlling iron stoichiometry in composition.

The sol-gel auto-combustion has been used to produce nano-sized \(\text{ZnFe}_{2+z}\text{O}_4\) materials. The sensors were characterized by using XRD, SEM and DC gas sensing measurements. To identify contribution of the depletion layer and grain interior, ac impedance spectroscopy (IS) measurements were performed.

XRD analysis reveals a pure cubic spinel type structure for zinc ferrite samples tested as gas sensors. SEM micrographs of the samples reveal microstructures with nanosized grains and open pores. No morphological differences were apparent between samples with various iron content. The complex impedance spectra shows a presence of two gas sensitive phases with different electric properties attributed to grain interior and depletion layer. Depletion layer of the grain gives higher signal due to higher influence of test gas to the electron concentration at the boundary layer. Overall, sensitivity by going from iron deficient to excess can be improved for the four times due to increase adsorbed oxygen states on grain surface. By reaching \(z > 0.1\) sensitivity again drops due to remarkable decrease of depletion layer width, as concluded from IS analysis.
BiFeO$_3$ is one of the most promising multiferroic materials since it could exhibit both ferroelectric and ferromagnetic order at room temperature. However, BiFeO$_3$ materials usually present high electrical conductivity hampering its practical applications. Among the different possible strategies to avoid these problems, doping with Ti$^{4+}$ at Fe positions is related as a propitious method to enhance the properties of the BiFeO$_3$. Although a decrease in the electrical loss through Ti-doping is generally accepted, in literature usually appears controversy regarding the properties of the Ti-doped BiFeO$_3$ materials which, besides, are very sensitive to the process conditions.

In this work, undoped and Ti-doped BiFeO$_3$ bulk ceramics have been prepared by a conventional mixed-oxide method with the aim of carry out a detailed study which provides a well understanding about the Titanium effect in the BiFeO$_3$ properties. Microstructural analysis shows a nanostructure in the Bi(Fe,Ti)O$_3$ ceramics related with the dopant segregation at grain boundaries. Moreover, electrical characterization shows that Ti-segregation decreases the grain-boundary conductivity playing a key role in the properties of the Bi(Fe,Ti)O$_3$ materials.

The Ruddlesden-Popper series is formed by a variation of LaNiO$_3$ perovskite and LaO rock-salt layers depending on the La/Ni ratio. The lanthanum nickel oxides offer long-term stability even under harsh conditions such as CO$_2$ containing atmospheres, which is demonstrated by thermodynamical calculations via an Ellingham diagram. This favors their possible application to produce high-purity oxygen or in oxyfuel combustion power plants. The Ruddlesden-Popper type materials were synthesized by a sol-gel route using stoichiometric amounts of metal oxides, ethylenediaminetetraacetic acid and citric acid. The samples were investigated using in-situ $^{57}$Fe-Mossbauer spectroscopy at elevated temperatures and varying oxygen partial pressures, X-ray diffraction, oxygen permeation tests, scanning electron microscopy, transmission electron microscopy, and electronic conductivity measurements. The Ni-site of La$_2$NiO$_4$ can be doped with a variety of cations, which however result in a slight decrease of ionic transport properties. The La$_2$Ni$_0.9$Fe$_{0.1}$O$_4$ sample shows phase decomposition into higher order Ruddlesden-Popper phase La$_4$Ni$_2$Fe$_{0.9}$O$_{10}$ and La$_2$O$_3$, which was detected by transmission electron microscopy. However, the iron nucleus allows to investigate the iron valence and environment with Mossbauer spectroscopy at elevated temperatures for the iron-doped phase La$_3$Ni$_{0.9}$Fe$_{0.1}$O$_4$, which show stable iron valence of 3$^+$ up to 1023 K. The loss of interstitial oxygen at elevated temperatures results in a change of the quadrupolar interaction at the iron nucleus. Similar results were obtained for La$_3$Ni$_{0.98}$Fe$_{0.02}$O$_4$ and La$_4$Ni$_2$Fe$_{0.9}$O$_{10}$.
Characterization of grain boundaries in iron-doped SrTiO$_3$ by analytical transmission electron microscopy

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Microstructure and especially interfaces like, e.g., grain boundaries (GBs) have strong impact on materials properties. This is especially true for the vast variety of ceramics with perovskite structure. Therefore, understanding the basic mechanisms of densification and grain growth during sintering of the materials is essential for tailoring microstructure and, hence, properties.

GBs in perovskites are characterized by the presence of charged defects, resulting in the formation of a space charge region where aliovalent dopants are either accumulated or depleted. There is still a lack of understanding concerning the impact of those space charge regions on grain growth. In the present study iron-doped SrTiO$_3$ was used as model material because defect chemistry and diffusion is well known. The goal of this study was to measure the distribution of elements at different GBs with respect to grain size (grains of same size, grains of different size).

A set of samples varying in iron-dopant content and dwell time upon sintering was fabricated. Microstructure and GBs were investigated by conventional and analytical trans-mission electron microscopy employing quantitative energy-dispersive X-ray spectroscopy (EDXS). Some samples show strong bimodal grain growth. Common to all samples is strong iron segregation in the GB region with the iron atoms expected to occupy the B-site of the perovskite lattice. Comparing different GBs with known growth history, different element distribution profiles were measured. GBs adjacent to larger grains show higher iron content compared to GBs between small grains.

Microstructural characterisation of ZnO varistor ceramics

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Background

Varistors are electroceramic components used as over voltage protection in electronic devices. The standard varistor material is polycrystalline ZnO which shows highly non-linear current-voltage characteristics with rapidly decreasing resistance above a specific voltage. This effect is caused by so called Schottky barriers at grain boundaries. Therefore, electrical and structural characterization of the microstructure is essential for the understanding of the varistor effect and the improvement of varistor materials.

Methods

In this study, the electrical properties of ZnO multilayer varistors (MLV) were investigated on the microscopic scale employing conductive atomic-force microscopy (C-AFM), Kelvin probe force microscopy (KPFM), and KPFM with biased MLV electrodes (biased KPFM) as well as four-point probe measurements. Additionally, the
crystallographic orientation of the single grains was determined with electron backscatter diffraction (EBSD).

**Experimental**

Individual grain boundaries as well as ZnO metal-electrode contacts were investigated using C-AFM, KPFM, and biased KPFM. This data was compared with I-V characteristics obtained from four-point-probe measurements. The electronic properties were associated with the crystallographic orientation data from EBSD. Employing KPFM on an MLV with an applied bias between the electrodes reveals a step-like voltage drop with steps at the grain boundaries. The relative height of these steps is not uniform. Also a dependence of the relative step-height on the direction of the applied bias was observed.

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### Nature of ionic conduction in Li\(_{0.5-y}\)Na\(_y\)La\(_{0.5}\)V\(_x\)(Nb,Ta)\(_2\)O\(_6\) system

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Lanthanum-lithium titanates, niobates and tantalates with defect perovskite structure are fast Li\(^+\) conductors (\(\varepsilon = 10^{-3}-10^{-5}\) S cm\(^{-1}\)). In lanthanum-lithium titanate (Li\(_{0.5-y}\)Na\(_y\)La\(_{0.5}\)TiO\(_3\)), a percolation transition in the conductivity is observed. The percolation threshold depends on the content of conducting ions (Li), blocking ions (Na) and vacancies (V). Niobates and tantalates have a higher concentration of vacancies than titanates; however, the nature of ionic conduction in such materials is unknown. The aim of this work was to elucidate the nature of ionic conduction in Li\(_{0.5-y}\)Na\(_y\)La\(_{0.5}\)V(Nb,Ta)\(_2\)O\(_6\) system in which lithium ions are partially substituted by sodium ions.

The samples were prepared by solid-state reaction technique. To characterize the samples, X-ray diffraction, nuclear magnetic resonance, chemical analysis and impedance spectroscopy were used.

Sintered materials were single-phase ones and had an orthorhombic defect perovskite structure (sp. gr. \(Pmmm\)). Niobates have an ordered structure within the entire concentration range, whereas in tantalates increasing the Na content leads to partial disordering. The conductivity of Li\(_{0.5-y}\)Na\(_y\)La\(_{0.5}\)VNb\(_2\)O\(_6\) samples on Na content pass through a maximum due to two competing factors: the increase in unit cell volume and the decrease in Li concentration. The ionic conductivity of Li\(_{0.5-y}\)Na\(_y\)La\(_{0.5}\)VTa\(_2\)O\(_6\) samples decreases with sodium content. This difference occurs because in tantalates, Na ions occupy both La plane and vacant plane, whereas in niobates they occupy only La plane. In addition, the higher synthesis temperature of tantalates leads to higher lithium losses. In lanthanum-lithium niobates and tantalates, no percolation transition is observed due to considerable vacancy content.

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### High-temperature conductivity, stability and redox properties of (Fe,Mg,Al)\(_3\)O\(_4\) spinel-type materials

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Molten oxide electrolysis was recently proposed as a breakthrough low-CO\(_2\) steel technology to overcome the environmental impact of classical extractive metallurgy. Spinel-type iron-based oxides, possessing relatively high electronic conductivity, are considered as promising consumable anode materials for high temperature pyroelectrolysis. However, their phase stability domains, refractoriness and thermo
stability are limited due to the redox changes. The present work was focused on the analysis of phase relationships, thermal expansion and high-temperature electrical conductivity in the (Fe,Mg,Al)$_3$O$_4$ in oxidizing and inert atmospheres, in order to determine the most promising material composition, with emphasis on electrical conductivity and appropriate stability at elevated temperatures in mildly oxidizing atmospheres.

Spinel-type (Fe,Mg,Al)$_3$O$_4$ oxides were prepared via solid state route followed by sintering of corresponding ceramics at 1753-1773 K in argon and air. Introducing both aluminium and magnesium suppresses the thermal expansion of Fe$_3$O$_4$ spinel ceramics. Increasing aluminium content in Fe$_3$O$_4$ spinel lattice was found to decrease the tolerance against oxidative decomposition, confirmed by XRD, SEM/EDS and electrical conductivity vs p(O$_2$) measurements, whilst doping with Mg increases the stability of Al-containing Fe$_3$O$_4$-based spinels in oxidizing conditions. Atomistic simulation was performed to predict cation distribution between octahedral and tetrahedral sublattices, in order to explain the conductivity dependence on Al and Mg concentration in (Fe,Mg,Al)$_3$O$_4$. Simultaneous doping with aluminium and magnesium was found to be a promising strategy for improvement of refractoriness and phase stability of Fe$_3$O$_4$-based spinels at elevated temperatures without significant reduction in the electrical performance.

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<th>Defect chemistry and transport properties of Ba$<em>x$Sr$</em>{1-x}$Ti$_{1-y}$Fe$<em>y$O$</em>{3-\delta}$ solid solutions</th>
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<td>Melanie Kuhn$^1$, Jae Jin Kim$^1$, Sean R. Bishop$^{1,2}$, Harry L. Tuller$^2$</td>
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<td>$^1$Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA, 02139; $^2$International Institute for Carbon Neutral Energy Research (I2CNER), Kyushu University, Nishi-ku Fukuoka, Japan, 819-0395</td>
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Mixed ionic electronic conducting (MIEC) oxides are being investigated for solid-state electrochemical applications such as solid oxide fuel cells (SOFCs) and gas permeation membranes. SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ (STF), a potential SOFC cathode material, has been studied as a model MIEC by our group. A detailed defect chemical model was established representing the effects of the mixed-valence states of the B-site cations, resulting in MIEC behavior in high oxygen partial pressure and predominant ionic conductivity in intermediate oxygen partial pressure. Increasing iron content further enhanced the ionic conductivity and caused a decrease in band gap energy and reduction enthalpy. The aim of this study is to investigate the effect of isovalent substitution of the A-site cations by larger cations, such as Ba, on the kinetic and thermodynamic properties of the material. The variation in lattice parameter is expected to impact both defect formation and transport. Ba$_x$Sr$_{1-x}$Ti$_{1-y}$Fe$_y$O$_{3-\delta}$ (BSTF) powders with different Ba and Fe doping concentration were fabricated by the Pechini method. Thermogravimetry is performed to measure the oxygen content as a function of oxygen partial pressure and temperature. The defect model established for STF is extended to BSTF to enable extraction of key defect thermodynamic parameters and a direct comparison with already published values for STF.
For an application of mixed ionic-electronic conducting (MIEC) oxides, e.g., as solid oxide fuel cell (SOFC) cathodes, as high-temperature gas sensors or as oxygen-transport membrane (OTM) material, the kinetics of oxygen transport — namely the chemical diffusion coefficient $D^\delta$ and the surface exchange coefficient $k^\delta$ are of fundamental importance as they determine the performance of the materials. A common setup for the determination of $D^\delta$ and $k^\delta$ values is the conductivity relaxation method where the conductivity response of a bulk MIEC sample is monitored (and evaluated according to Crank’s theory) after the ambient oxygen partial pressure $p_{O2}$ is abruptly changed using different gas mixtures. In the present study an alternative setup — a closed tubular zirconia “oxygen pump” with Pt electrodes — was employed to precisely control the $p_{O2}$ continuously within the entire range between $10^{-20}$ ... 1 bar at temperatures above 700 °C.

Conductivity relaxation measurements were performed on dense MIEC bulk samples of $\text{Ba}_0.5\text{Sr}_0.5\text{Co}_0.8\text{Fe}_0.2\text{O}_3-\delta$ (BSCF), $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3-\delta$ (LSCF), and $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3-\delta$ (LSC) at $p_{O2}$ values between $10^{-6}$ and 1 bar in small $p_{O2}$ steps (thus remaining close to chemical equilibrium) at temperatures between 700 and 900 °C in order to determine $D^\delta$ and $k^\delta$ values as a function of temperature and $p_{O2}$.

Mixed oxide ionic-electronic conductors find potential applications in ceramic devices including oxygen separation membranes and solid oxide fuel cells (SOFC). Besides fast ionic transport, the challenge to researchers is to design oxide materials showing fast surface oxygen exchange kinetics between the gaseous phase and the oxide, allowing operation at intermediate temperatures (500-700°C). However, present understanding of the exchange kinetics on the surface of fast oxide ion conductors is still rudimentary. Recently, we developed a novel method, referred to as pulse-response isotopic exchange technique (PIE), for rapid measurement of the surface exchange kinetics. The method is based upon isotope analysis of an $^{18}$O-enriched gas phase effluent pulse after passage of a continuous-flow packed-bed microreactor loaded with the oxide powder. The measurements are carried out under isothermal and iso-$p_{O2}$ conditions. Since the method relies on gas phase analysis of the fractions of oxygen isotopomers with masses 36, 34 and 32 ($^{18}$O$_2$, $^{16}$O$^{18}$O, and $^{16}$O$_2$, respectively) by mass spectrometry also mechanistic information on the exchange reaction can be extracted from experiment. Results of
recent studies on selected perovskite- and fluorite structured oxides are presented, showing the usefulness of the PIE method.

Promising performances as cathode for SOFC were recently evidenced for \( \text{Ba}_2\text{Co}_{2+\delta}\text{Co}_{3-\delta}\text{O}_{14} \) cobaltite[1]. This compound exhibits a 3D structure corresponding to the intergrowth of [\( \text{Ba}_{3n+1}\text{Co}_n\text{O}_{3n+3} \)] perovskite blocks and [\( \text{CoO}_8 \)] blocks also containing layers of CdI\(_2\) type. Ionic conduction was expected in the first blocks (oxygen vacancies) while the latter should display electronic conductivity (mixed valence). In this work, the \( \text{Ba}_2\text{Co}_{2+\delta}\text{Co}_{3-\delta}\text{O}_{14} \) cobaltite has been proved to be a Mixed Ionic Electronic Conductor. Dense ceramics were obtained thanks to Spark Plasma Sintering of \( \text{Ba}_2\text{Co}_{2+\delta}\text{Co}_{3-\delta}\text{O}_{14} \) powder prepared by conventional solid-state reaction between \( \text{BaCO}_3 \) and \( \text{Co}_3\text{O}_4 \). Here oxygen diffusion in these materials was confirmed by \(^{18}\text{O}/^{16}\text{O}\) Isotope Exchange and Depth Profiling using Secondary Ion Mass Spectrometry imaging [2]. The oxygen diffusion coefficient \( (D^*, \text{cm}^2\cdot\text{s}^{-1}) \) and the oxygen exchange coefficient \( (k^*, \text{cm}\cdot\text{s}^{-1}) \) were derived. The oxygen diffusion was confirmed by Electrical Conductivity Relaxation. Since the oxygen molecule dissociation at the surface may be strongly affected by the composition of the outermost atomic layer of the material, Low Energy Ion Scattering Spectroscopy was also carried out.


SrTiO\(_3\) is an excellent example for mixed conducting electroceramic materials. Single crystalline as well as polycrystalline bulk material was often investigated in the past. However as a result of the high technological relevance of thin films in new applications such as ferroelectric memories or resistive memories the investigation of thin layers in the range of a few 100nm becomes increasingly important.

In this contribution Fe-doped SrTiO\(_3\) thin films were prepared by pulsed laser deposition. Structural characterization was carried out by XRD, AFM and REM. The ionic conductivity in the thin SrTiO\(_3\) layers was investigated by means of \(^{18}\text{O} \) tracer experiments and subsequent SIMS. Diffusion profiles perpendicular to the surface were analyzed to gain access to the two parameters of interest, \( k \) and \( D \). The fitting procedure also gives information on interfacial space charge layers, which are characterized by decreased vacancy concentrations and thus spatially varying tracer diffusion coefficients.

In addition to the \(^{18}\text{O} \) tracer experiments, the SrTiO\(_3\) thin films were investigated by means of impedance spectroscopy. Special electrode geometries and the usage of
insulating substrates allowed partial pressure dependent conductivity measurements in lateral direction. The effect of the grain boundaries on the entire lateral conductivity was analyzed and compared with the results obtained from the perpendicular diffusion experiments. Accordingly not only space charge layers at the surface but also at the grain boundaries affect the diffusion and the associated conductivity of the thin films.

### The chemical capacitance of praseodymium-cerium oxide thin films and relationship to nonstoichiometry

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The chemical capacitance of dense Pr₀.₁Ce₀.₉O₂₋δ thin films is derived from impedance spectroscopic measurements, on electrochemical cells of the form Pr₀.₁Ce₀.₉O₂₋δ/YSZ/Pr₀.₁Ce₀.₉O₂₋δ over the temperature range of 450 to 800 °C, and the oxygen partial pressure range of 10⁻⁶ to 1 atm O₂. The capacitance was confirmed as being the chemical capacitance based on its linear dependence on both electrode thickness and area, and its very large magnitude (10⁻² F). The non-stoichiometry of PCO film, derived from the chemical capacitance was found to be comparable to values derived for bulk Pr₀.₁Ce₀.₉O₂₋δ as determined by thermogravimetric analysis (TGA). The study confirms the suitability of the chemical capacitance as a means for measuring the non-stoichiometry of thin oxide films.

### Oxygen transport in model thin film SrTi₁₋ₓFeₓO₃₋d mixed conducting cathodes for solid oxide fuel cells

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Progress in achieving improved solid oxide fuel cell (SOFC) performance, particularly at reduced temperatures (<600°C), is constrained by imperfect understanding of the cathode kinetics and by the resultant inability to further reduce cathode polarization loss. In this work, we studied oxygen transport in a model mixed ionic and electronic conductor, SrTi₁₋ₓFeₓO₃₋d. This perovskite-type oxide system offers the possibility to systematically control both the levels of ionic and electronic conductivity as well as the band structure.

Oxygen transport in two STF compositions (x = 0.5, SrTi₀.₅Fe₀.₅O₃₋d and x = 1.0, SrFeO₃₋d) was investigated by oxygen isotope exchange experiments with subsequent Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analysis and by Impedance Spectroscopy (IS) as a function of temperature T and oxygen partial pressure pO₂. The observed trends are discussed in relation to the defect and transport of the STF thin film electrodes.
During the last ten years, a lot of interest has been devoted to the so-called colossal dielectric constant (CDC) material. The first materials exhibiting this behavior were the perovskite–based ceramics based on the CaCu$_3$Ti$_4$O$_{12}$ composition (CCTO). Relative dielectric permittivity can attain values up to (or even larger than) $10^5$. Nevertheless, their losses are still high, the lower values ranging 10%, in a narrow frequency range, thus limiting their applications. Most work on this type of materials aims to reduce these losses and widen their useful frequency range. On the other hand, the underlying physical mechanisms responsible of the CDC are still under study. While the analysis of broadband impedance spectroscopy measurements leads most of the authors to propose an interfacial polarization mechanisms (at the electrodes or at internal barriers), there is a limited number of complementary electrical characterization techniques, for the moment, they comfort the proposed interfacial polarization mechanisms. In the present work, I-V and time-domain polarization are used to characterize these materials. One of our main results is the observation of a non-symmetrical response of these materials related to the direction of the polarization. These results are observed for both macroscopic level on bulk polycrystalline material and within individual grains of the same samples. These results do not fit current accepted models for CDC materials. Part of the electrical characteristics can be related to the electrode contacts.

Millimeterwave dielectrics for wireless communications with high data transfer and radar system for Pre-Crash Safety System are expected to be developed on the low dielectric constant and the high microwave $Q$. Cordierite (Mg$_2$Al$_4$Si$_5$O$_{18}$) is a candidate for millimeterwave dielectrics as it has high $Q_f$ of 40,000 GHz, and low dielectric constant of 6.2. Cordierite has two polymorphs cordierite and indialite. Cordierite with low symmetry is ordering, and indialite with high symmetry is disordering of Si and Al on (Si$_4$Al$_2$)O$_{18}$ ring. It is well known that indialite could not be synthesized by solid state reactions but crystallized from glass as intermediate phase. In this paper, indialite glass ceramics are fabricated by crystallization of glass, analyzed the crystal structure by Rietveld method and the millimeterwave dielectric properties are presented, comparing the properties depending on the ordering ratio.
Giant dielectric constant and effective dielectric spectra of dielectric-conductor composites

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The giant permittivity phenomena and the effective dielectric and ac conductivity spectra will be discussed for the example of composite composed of a simple conductor with frequency independent conductivity and a lossless dielectric with frequency independent permittivity, particularly near the conduction percolation threshold, in the quasistatic effective medium approximation. Divergence of the static permittivity as the percolation threshold is approached will be analysed in terms of dynamic slowing down of a dielectric relaxation. Particular attention will be paid to the core-shell composites modelled by a coated-spheres (Hashin-Shtrikman) model and to a symmetrical Bruggeman model. Some related experiments showing up the increasing permittivity on approaching the percolation threshold from below will be mentioned. The full paper is published in [1].


Phase-coexistence phenomenon in metal-insulator-transition of VO$_2$ thin films

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Metal-insulator-transition (MIT) of VO$_2$ vanadium oxide has attracted strong attention as one candidate of new materials for nanostructured devices required for integration beyond present CMOS technology, such as memory cells, logic ports and sensors. In order to utilize VO$_2$ thin films in integrated components, the effects of parameters, for example, microstructure, temperature and mechanical properties, such as three-dimensional strain state on transition have to be understood to optimize component characteristics. Pulsed-laser-deposited highly oriented VO$_2$ thin films were grown using in situ conditions at 400°C in various oxygen partial pressures on a/r/c-Al$_2$O$_3$ and MgO(100) single crystal substrates. Microstructure of films was characterized using X-ray diffraction (XRD), Raman spectroscopy and Scanning Electron Microscopy (SEM). Resistivity of films was measured as a function of temperature to determine MIT temperature $T_{MIT}$. It was observed that $T_{MIT}$ of films increased and decreased from bulk $T_{MIT} = 68 \, ^\circ\text{C}$ under tensile or compressive strain, respectively. Shift of $T_{MIT}$ was dominated by the misfit strain state. Numerical modeling showed that films cannot be epitaxial due to huge misfit strains leading to unrealistic values of $T_{MIT}$ according to Clausius-Clapeyron law. However, Raman spectroscopy results indicated phase-coexistence of monoclinic P2$_1$/c (M1) and C2/m (M2) insulating phases in films reducing misfit strains and leading to relaxed structure which strain state correlated with $T_{MIT}$ predicted by Clausius-Clapeyron law. Phenomenon is analogous to adaptation of VO$_2$ nanofibres to applied strain by generating metal phase P4$_2$/mm regions to relax strain state of insulating phase.
Elastic properties of a tin-modified lead zirconate titanate ceramic

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The elastic properties of an unpoled and poled tin-modified lead zirconate titanate (PSZT) ceramic were measured from subambient to above its Curie temperature by an ultrasonic technique. Results indicate that the elastic behavior of the ferroelectric ceramic changes significantly near its phase transformations. Particularly, the Young's modulus, shear modulus and bulk modulus all reach a local minimum at the phase transformation temperature. These observations are consistent with a soft phonon behavior and give insights to an abnormal field-enhanced deformation and a field-induced paraelectric-to-ferroelectric behavior near its structural instability. Results will be compared to the dielectric resonant measurements to shed light on key issues governing the piezoelectric performance in ferroelectric ceramics.

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Low-frequency phonons and phase transition dynamics in Pb(Zr1-xTix)O3

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Raman spectra of nominally pure Pb(Zr1-xTix)O3 (PZT) ceramics with different Ti concentration (x=0.36–0.75) were measured and evaluated, in the temperature range 20 K–900 K, together with infrared reflectivity data, time-domain terahertz transmittance spectra, and dielectric measurements in selected compositions.

The analysis of the spectra show that, in the cubic and high-temperature ferroelectric phase, two overdamped modes are present: a soft mode and an anharmonic hopping central mode, both related to Pb vibrations. In the low-temperature ferroelectric phase, with doubled unit cell, three main Pb vibrations are present: the soft mode, a mode corresponding to antiphase vibrations of neighbouring Pb atoms in the terahertz range, and an antiferrodistortive mode which produces antiphase tilts of the oxygen octahedra. This last mode, located near 70 cm\(^{-1}\) appears in all the samples near and below room temperature, even in the tetragonal side.

Our measurements also confirm that the intrinsic permittivity (from phonons) of PZT has a maximum at the morphotropic phase boundary (MPB), as predicted by theory; although this represents just a small percent of the total permittivity at lower frequencies due to extrinsic contributions. The permittivity maximum is assigned to the THz softening of the anharmonic hopping of Pb-atoms among their off-centered positions. This maximum is shifted from x = 0.48 at room temperature to 0.52 at 10 K, meaning that the MPB is shifted towards the tetragonal side of the phase diagram at low temperatures.
A new approach for tailoring tunability and permittivity values by using grain size reduction at nanoscale

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The nonlinear dielectric properties of ferroelectrics were intensively studied due to their potentiality for miniaturization of microwave components and integration in microelectronic circuits. Such applications demand a level of tunability of \( n = \frac{\varepsilon(E)}{\varepsilon(0)} > 1.5 \), moderate permittivity below 1000 and losses below 3%. The large majority of publications in the field of tunable materials report the fulfilling of technological requirements by adding to the ferroelectric a low permittivity linear dielectric. We propose a new approach to use the grain size reduction at nanoscale in dense BaTiO\(_3\) - based ceramics for tailoring the dielectric and tunability properties.

The tunable properties of pure and substituted BaTiO\(_3\) - based nanostructured ceramics with grain size of (1 µm - 90 nm) were investigated. A reduced permittivity down to \( \approx 500 \) and almost linear \( \varepsilon(E) \) dependence in a large field range is typical to fine grained nanoceramics. The observed behavior was explained by considering the nanostructured ceramic as a composite formed by ferroelectric grains and low-permittivity non-ferroelectric grain boundaries, whose volume fraction increases when reducing grain size. An original approach was developed to calculate the local field distribution in the nanostructured ceramic with realistic microstructure using a combination of finite element and Monte Carlo models. The experimental data combined with theoretical model show that the reduction of grain size in ferroelectric dense materials can be an effective alternative route to accomplish the tunability applications requirements.

Structural and electrical properties of a new Ba\(_2\)NdTi\(_{2+x}\)Nb\(_{3-x}\)O\(_{15-x/2}\) solid solution with tetragonal tungsten bronze phase

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A ferroelectric tetragonal tungsten bronze (TTB) phases of general formula Ba\(_2\)RETi\(_2\)Nb\(_3\)O\(_{15}\): RE = Nd, Sm, were previously prepared by two low temperature routes, sol-gel synthesis and solvothermal synthesis[1]. The relative permittivity vs temperature data for these samples exhibits two unusual features with ferroelectric materials: first, a significant hysteresis between heating and cooling cycles in their phase transition behaviour, and second, a huge depression in the Curie-Weiss temperature \( T_0 \) which is very different from the behaviour usually observed in first order ferroelectrics. Both effects were attributed to the complex nature of their TTB-related crystal structures.

In this work, based on these studies, a wide range of solid solution of general formula Ba\(_2\)NdTi\(_{2+x}\)Nb\(_{3-x}\)O\(_{15-x/2}\) (BNTN) with TTB phase were prepared by low temperature solvothermal synthesis. Extensive solid solution with oxygen deficiencies forms over the range 0 < x < 1.5. The existence of this BNTN solid solution with oxygen deficiency has not been reported previously. X-ray diffraction (XRD), scanning electron microscopy (SEM) and Powder neutron diffraction (ND) were used to determine the solid solution limit. According impedance measurements, samples were electrically-homogeneous, and highly insulating. The total conductivity increases when the Ti/Nb ratio increases. Besides, the
relative permittivity shows a large dependence on the composition: the $T_c$ and relative permittivity values decrease when $x$ increases.


### Lessons from Bi$_2$Ti$_2$O$_7$: One step closer to finally understanding dielectric relaxation in pyrochlores

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Bismuth titanate with the pyrochlore-like stoichiometry (Bi$_2$Ti$_2$O$_7$) has been the focus of several investigations by various groups around the world. Over the last 40 to 50 years, these investigations have led to several very conflicting and contradicting observations. To help resolve these, here, dense phase-pure Bi$_2$Ti$_2$O$_7$ polycrystalline ceramic pellets were obtained via co-precipitation synthesis methods followed by microwave sintering techniques. Density functional theory was used to model the structure of the pyrochlore, from which the theoretical X-ray diffraction patterns were compared with experimental patterns and confirmed the phase purity in the powder as well as in the pellets. As such, this maiden achievement allowed for primary thermophysical, crystallographic, and dielectric characterization of this ceramic compound. Discrepancies among reports in literature regarding the structure, stability, and supposed ferroelectricity of this material are discussed and clarified. As a result, a modification to the phase diagram of the Bi$_2$O$_3$-TiO$_2$ system is proposed. In addition, and contrary to prior reports, the dielectric characterization of Bi$_2$Ti$_2$O$_7$ reveals a linear dielectric with high permittivity values at room temperature (115 at 500 kHz), and more remarkably, a decrease in permittivity with decreasing temperature unlike the typical dielectric relaxation in ceramics. Based on experimental data and computational simulations, and by contrasting the dielectric response of Bi$_2$Ti$_2$O$_7$ with that of well known bismuth pyrochlore compounds, the necessary and sufficient chemical and crystallographic conditions for dielectric relaxation in pyrochlores will be presented.

### Atomically engineered oxide heterointerfaces: new opportunities for nanoionics and nanoelectronics

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In recent years, the advance in fabrication of oxide heterostructures with atomically engineered interfaces provides new opportunities for both nanoelectronics and nanoionics. Well-defined oxide heterointerfaces, where an oxide is in intimate contact with another, can exhibit exceptional electronic, ionic, optical, and catalytic properties that are remarkably different from those of their bulk counterparts by establishing a new equilibrium of the distribution of electrons or ions across the heterointerface. Here, we will firstly present our efforts in epitaxial growth of atomically flat thin films of oxygen-ions conductors, for example, gadolinia-doped ceria. Secondly, we show that oxygen-redistribution related redox reactions at oxide interfaces can provide an effective way to create two-dimensional electron gases (2DEGs) between two insulating complex oxides, the basis for a new generation of all-oxide electronic devices. By careful oxygen engineering, we obtain 2DEGs with unprecedented mobilities greater than 1.4×10$^5$ cm$^2$V$^{-1}$s$^{-1}$ at these interfaces based on insulating complex oxides.
During the last years, multiferroic materials have received much attention due to possible integration in advanced applications, such as data storage, communications or even energy harvesting. Most of those applications require using thin films and thus, development of multiferroic thin films and related heterostructures has been a hot area of research. Broadly speaking multiferroic thin films activity has focused either on single-phase multiferroic or more complex heterostructures involving materials with distinct ferroic (ferroelectric FE and magnetic M) orders. Whereas in the former an intimate coupling of FE and M orders can be expected and the unavoidable substrate-induced strain can only contribute to modify the magnetoelectric ground state, in the later strain is thought to be the coupling mechanism between FE and M phases.

In this presentation we shall overview the role of substrate and interface-induced strain effects on single phase multiferroic materials (YMnO₃) and on bilayers of ferromagnetic/ferroelectric materials (CoFe₂O₄/BaTiO₃).

Materials are grown by pulsed laser deposition on suitable substrates. It will be shown that YMnO₃ can be grown having a cycloidal magnetic structure that give rise to ferroelectricity with the rare property of its polarization direction being switchable by 90° with appropriate magnetic field. Furthermore, substrate-induced strain dramatically modifies the magnetic order and cancels ferroelectricity, by changing the Mn-O-Mn bond topology.

On the other hand, it will be shown that strain in multilayers plays a dual role. It clamps the film to the substrate but also allows to transmit any film-lattice modifications through the structure. Using this approach, we will show that the dielectric permittivity of BaTiO₃ can be modified by a suitable magnetic field applied to CoFe₂O₄/BaTiO₃ heterostructures. The relevance of CoFe₂O₄/BaTiO₃ stacking order on the observed magnetoelectric coupling will be discussed.
Transition metal oxides display a wide range of physical properties arising from the complex interactions between their spin, charge, orbital and lattice degree of freedom. Rare earth perovskite nickelates are particularly exciting materials as they display a temperature-driven metal-insulator transition, charge disproportionation and a unique antiferromagnetic ordering.

We will demonstrate the ability to control the metal-insulator transition in NdNiO$_3$ using strain, field-effect and light [1,2]. The implications on the underlying mechanisms behind the transition will be discussed.

Then, we will focus on LaNiO$_3$, which is the only nickelate that, in bulk, does not display a metal-insulator transition or any other ordering phenomena. We will show that a metal-insulator transition can be induced as the film thickness is reduced to only a few unit cells [3]. Building on these results, superlattices of ultrathin LaNiO$_3$ and ferromagnetic LaMnO$_3$ were found to display exchange bias, indicating that a complex magnetic order develops in LaNiO$_3$ [4].


SrTiO$_3$ surfaces can host a quasi-2DEG (two dimensional electron gas), with a still, at least partially, obscure origin. The puzzle is complicated by several seemingly contrasting pieces of evidence, indicating that material issues certainly deserve great attention. As a result, different possible mechanisms have been proposed, including electronic reconstruction, doping by oxygen vacancies, effect of defects, etc.

In this context, I will discuss two very different SrTiO$_3$-based systems that host a 2DEG. The first is the bare SrTiO$_3$ surface. I will show scanning tunnelling microscopy/spectroscopy and photoemission data to discuss the properties of the 2DEG. Also according to the thermal treatments adopted to prepare the samples, oxygen vacancies will be shown to play the key role in the 2DEG formation.
The second system is a set of polar/non-polar interfaces, made by depositing LaAlO$_3$, LaGaO$_3$ or NdGaO$_3$ on SrTiO$_3$ surfaces. The similarities of the three systems will be discussed. HRTEM and EELS were used to investigate the interface perfection and the confinement of charges. The origin of the observed 2DEG is again discussed with main reference to the preparation process. By routinely monitoring the optimization process by fast photography and spectroscopy of the ablation plume, we were able to grow conducting samples at very high oxygen pressure (up to $10^{-3}$ mbar). Our data indicate, in this case, that oxygen vacancies formation should be strongly hampered. Moreover, the energy of impinging species is low enough to exclude significant implantation.

An electron gas formed at the interface between two perovskite oxides, an insulating LaAlO$_3$ (LAO) film deposited on top of another insulating TiO$_2$-terminated SrTiO$_3$ (STO) substrate, has been in focus of intensive research since a first report in 2004 [1]. The interface resembles a two-dimensional electron gas in semiconducting heterostructures, where polar or valence discontinuities at the interface give rise to an electronic reconstruction. It is also possible that oxygen vacancies in the STO substrate and/or inter-diffusion of La into the substrate may contribute to the high in-plane conductance of the LAO/STO interface. The conductivity at the LAO/STO interface is observed only when the LAO film thickness is above a critical value of 4 unit cells (uc, 0.39 nm) [2]. The critical thickness effect has been taken as a strong support of charge transfer from the LAO surface to the interface when a polar, built-up potential exceeds the (renormalized) bandgap of LAO [3]. We present an investigation of the electrical transport and microstructure of interfaces between films of various perovskite oxides grown on (001)STO substrates. We show that the electrical properties of NdGaO$_3$/STO and KTaO$_3$/STO interfaces are very similar to the LAO/STO ones. The LaMnO$_3$/STO interfaces remain insulating for all film thicknesses. Surprisingly, the critical film thickness of 4 uc was observed for all conducting interfaces. Medium-energy ion spectroscopy and scanning transmission electron microscopy detected cationic intermixing within several atomic layers from the interface at all studied interfaces. Our results indicate that the electrical reconstruction in the polar oxide interfaces is a complex combination of different mechanisms, and that oxygen vacancies play an important role.

LaTiO$_3$ and LaFeO$_3$ are both antiferromagnetic insulators. However, the arrangement of the Hubbard subbands determines their insulating behavior. LaTiO$_3$ is a Mott-Hubbard insulator; its charge gap ($U$) is determined by the Hubbard splitting of the $3d$ bands of Ti ($U \approx 0.2$ eV). LaFeO$_3$ is a charge transfer insulator; its charge gap ($\Delta$) is determined by the filled $p$ band of oxygen and the unoccupied upper Hubbard band of Fe ($\Delta \approx 2.2$ eV).

In this study, we focus on the charge transfer in LaTiO$_3$/LaFeO$_3$ heterostructures grown on SrTiO$_3$ (001) by pulsed laser deposition. Since LaTiO$_3$ and LaFeO$_3$ share their oxygen octahedra at the interface, we suggest that the oxygen $p$ bands are aligned near the interface. As a result, the empty upper Hubbard band of LaFeO$_3$ becomes lower in energy than the partially filled lower Hubbard band of LaTiO$_3$. Electron transfer from LaTiO$_3$ to LaFeO$_3$ occurs, resulting in the presence of Ti$^{4+}$ and Fe$^{2+}$. The change in valence state is expected to induce variations in the physical properties.

We have studied the proposed charge transfer using in-situ x-ray photoelectron spectroscopy and will show that the Fe is partially reduced from Fe$^{3+}$ to Fe$^{2+}$. Furthermore, we will show that the Fe$^{2+}$/Fe$^{3+}$ ratio strongly depends on the Ti/Fe ratio.

Having the presence of mixed valence Fe, double exchange interactions may be occur, resulting in ferromagnetism. Here, we will discuss the physical properties of LaTiO$_3$/LaFeO$_3$ heterostructures and clarify the results using DFT calculations.

Doped Ga$_{2-x}$Fe$_x$O$_3$ ceramics towards magneto-electric applications

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Magnetoelectric materials are experiencing a renewal of interest in the recent years. This kind of materials can find some applications such as new generation of RAMs. The MeRAMs (Magnetoelectric Random Access Memories), used as data storage applications, can combine the advantages of the magnetic random access memories (MRAMs) in terms of access time and endurance with those of the ferroelectric random access memories (FeRAMs) in terms of writing energy.

Ga$_{2-x}$Fe$_x$O$_3$ (GFO) represents a good alternative to the perovskites usually studied for most of the magnetoelectric materials. Bulk GFO is known to be polar, ferrimagnetic above room temperature for $x \approx 1.3$, and magnetoelectric.

The proposed work is firstly to establish a complete study on the GFO elaboration for Ga$_{2-x}$Fe$_x$O$_3$ with $x$ from 0.6 to 1.4. The ceramic process has been investigated with respect to milling conditions and calcination parameters to optimise each fabrication step in order to obtain pure and high quality materials. Secondly substitutions of Fe with more voluminous species have been envisaged to generate a cell distortion which can enhance the ferroelectric behaviour. A first study has been done with scandium.

X-Ray diffraction has evidenced a single phase material until 10% of scandium substituted with an increase of the cell parameters. The different compounds have been observed by SEM coupled with EDX analyses and the wished Sc values were highlighted. The magnetic
The nonlinear dielectric properties of BiFeO₃ ceramics as a function of temperature were investigated for the first time [Appl. Phys. Lett. 99, 172904 (2011)]. A high dielectric tunability in quite low range of the bias electric fields over a broad temperature interval around the room temperature was observed. The non-linear permittivity-field response results from multiple contributions, whose weights are different at various temperatures and in different field ranges.

A very interesting feature was also observed on the conductivity behavior in the low-frequency range (dc-conductivity). The ac-conductivity vs. temperature shows that, except the low-temperature range, all the values of conductivity at any frequencies lay between the two “master-curves” corresponding to the lowest and highest frequency, respectively, giving rise to the much higher extreme activation energies. The Arrhenius plot of the dc-conductivity determined at the lowest frequency vs. 1/T shows two distinct linear regions separated by the mentioned temperature range of (189 − 244) K, for which the dc conductivity could not be determined from the present data only. A conduction anomaly takes place in this temperature range. Further detailed studies to confirm the presence of such anomaly in ceramics prepared by various routes in order to understand the origin of this conductivity anomaly are under way.

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In multiferroic composites the ferro(piezoelectric and magnetostrictive phases can be electromagnetically coupled via stress mediation (1). In our work we focused on the cosintering of cobalt ferrite (CF) - barium titanate (BT) and cobalt ferrite (CF) - lead zirconate titanate (PZT) composites.

The CF nanoparticles were prepared by hydrothermal synthesis; the PbZr₀.₅₃Tl₀.₄₇O₃ (PZT) powder was synthesized by solid-state synthesis; and the BT nanopowders were commercially obtained. The powder mixtures were pressed into disc-shaped samples, after which they were sintered at different temperatures. The CF-BT and CF-PZT diffusion couples were also investigated. The samples were analyzed with a scanning electron microscope (SEM) and with an electron diffraction spectrometer (EDS). The SEM studies of the samples sintered at 950°C for 4 h revealed the low relative density of the composites and cracks at the interface of the constituent phases. The elemental mapping
showed the distribution of titanium over both constituent phases, while at the same time partial diffusion of the iron and cobalt into the PZT and BT was also detected. The mechanical coupling of two constituent phases is only possible in a composite with a high sintered density and without any interdiffusion or a chemical reaction between the phases. Therefore, we focused on the cosintering of the CF with BT or PZT. A study of the size effect of the constituent powders on the cosintering of the composites will be presented.

response of a dielectric under an applied bias is the role of defect complexes. The kinetics of ‘associated’ oxygen vacancies forming defect complexes with dipole moments can be analyzed using Thermally Stimulated Depolarization Current measurements.

**Results** - Using TSDC measurement data, the effect of applied field on the polarization of defect dipoles in SrTiO$_3$ will be presented. Defect dipoles can be aligned to saturation conditions in accordance with Langevin theory. Data will also be presented on the confirmation of alignment of these defect complexes by monitoring changes in intensity of EPR signals created by the anisotropy of the zero-field splitting parameter.

**Conclusions** - The orientation or dissociation of defect complexes in oxide dielectrics is important in defining the complete picture of the conduction processes of a material and can be understood using TSDC and EPR techniques. We will outline a self-consistent picture of the defect orientation, and space charge development in SrTiO$_3$ using these methodologies.

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**Effects of strain on the soft mode, ferroelectricity and phase transition in BaTiO$_3$/BaZrO$_3$ superlattices: X-ray diffraction, Raman spectroscopy and dielectric measurements**

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We present X-ray diffraction, Raman spectroscopy, and dielectric measurements studies of artificial superlattices (SLs) consisting of ferroelectric BaTiO$_3$ (BT) and paraelectric BaZrO$_3$ (BZ) and compared their properties to the individual thin films BT and BZ. All samples were grown by PLD technique onto (100) MgO substrates buffered with an La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) electrode. The modulation period $\lambda$ of SLs varies between 16 Å and 1056 Å and the thicknesses of all samples are fixed at about 4000 Å. The x-ray results indicate that the polar c-axis of the BT layers lies in the plane of the substrate and BZ layers exhibit enhanced tetragonal distortion which is induced by the mismatch between the alternating BZ and BT layers. The variation of the soft mode as a function of the modulation period shows a partial relaxation at the critical period $\lambda_c$ above which it is energetically more favourable to relax the strain in the SLs due to misfit dislocations. Ferroelectric hysteresis loops measurements, confirmed the x-ray diffraction and Raman results, and revealed a clear ferroelectric behavior for the constrained SLs (32 Å $\leq \lambda \leq$ 256 Å) while a weak ferroelectricity is observed for the large periods ($\lambda=500$ Å to 56 Å). This is attributed to the strain-induced ferroelectricity in BZ layers for the constrained SLs.

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**Oxide ion transport in Ca$_3$Co$_4$O$_{9+\delta}$, a promising SOC electrode**

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Ca$_3$Co$_4$O$_{9+\delta}$ has been evidenced as a promising candidate as air-electrode for solid oxide cells (SOCs). Its structure is built upon the stacking of [Ca$_2$CoO$_3$] rock salt blocks and [CoO$_2$] hexagonal layers of CdI$_2$ type. Ionic conduction is expected in the first layers while the latter displays electronic conductivity. To confirm oxygen diffusion in these materials $^{18}$O/$^{16}$O Isotope Exchange combined with Time-Of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was carried out to derive the oxygen diffusion coefficient ($D^*$,
and the oxygen exchange coefficient \( (k^*, \text{cm.s}^{-1}) \) on dense ceramics. Measurements were performed between 600°C and 750°C. We obtained \( k \) values in the same order of magnitude than that obtained for \( \text{La}_2 \text{Sr}_{x} \text{NiO}_4 \) compounds which are promising materials as cathode for SOFC [2]. Low Energy Ion Scattering Spectroscopy (LEIS) was also carried out on these compounds, in order to characterize the composition of the outermost atomic layer of the ceramic which may strongly affect the oxygen molecule dissociation at the surface, i.e. the \( k \) value. It notably revealed the presence of Calcium at the outermost surface of \( \text{Ca}_3 \text{Co}_4 \text{O}_9 \) showing evidence of the key role played by the ionic layers in the mechanism of oxygen dissociation at surface.

**Impact of sulfur contamination on oxygen transport through BSCF: Relevant issues in the development of capillary and hollow-fiber membranes**

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Fabrication of dense mixed-conducting membranes in the form of capillaries or hollow fibers provides superior surface-area-to-volume ratio compared to conventional planar or tubular membranes, making this geometry attractive for large-scale gas separation applications. For preparation of capillaries and hollow fibers by phase-inversion process, polysulphone or polyethersulphone are commonly used as binders. Formation of sulfates during sintering has, however, a negative impact on membrane performance. Although a possible solution involves adaptation of sulfur-free binders, another strategy to suppress the sulfur contamination impact may include tuning the rate-determining step of permeation process. The present work was focused on comparative analysis of oxygen transport through BSCF membranes.
transport mechanism through sulfur-free and sulfur-containing Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-d}$ (BSCF) membranes. Green capillaries were fabricated by phase-inversion spinning technique using polysulfone and cellulose acetate as binders for sulfur-containing and sulfur-free capillaries, respectively. Dried capillaries were crushed into powders, and disk-shaped BSCF membranes ($d=0.35$-$1.00$mm) were pressed and sintered at 1373 K. Oxygen permeation measurements were performed at 923-1223K under air/(Ar+O$_2$) gradients; the microstructure of membranes before and after experiments was inspected by SEM/EDS. The relative roles of bulk ambipolar transport and surface exchange in the oxygen transport were analyzed. The presence of sulfates was found to decrease the permeation rate, mostly due to the partial blocking of surface oxygen exchange. A possibility to increase the oxygen flux through sulfur-containing BSCF membranes via surface activation up to the level characteristic of sulfur-free membranes was demonstrated.

Bari um titanate (BTO) is used as a high-k dielectric material in multi-layer ceramic capacitors. The minimum BTO thickness that can be achieved commercially is about 0.5 $\mu$m, which implies the use of starting powders with a particle size of ca. 100 nm. Further downscaling requires finer powders and new deposition techniques. Here a novel low-temperature synthesis route towards nano-sized crystalline BTO is presented. The process led, without further calcination steps, directly to crystalline powder (5-15 nm). Barium titanate was synthesized from titanium isopropoxide and barium hydroxide in benzyl alcohol, at temperatures up to 175 °C. As-synthesized powders exhibited a crystalline structure and a narrow size distribution. Electron microscopy and X-ray diffraction indicated that the size of crystallites depended mainly on the amount of water present in the system (contained as crystal water or added externally).

The perovskite phase development from the components was followed by Small Angle X-ray Scattering (SAXS) at $100$ °C and $150$ °C. Solutions containing barium hydroxide octahydrate in benzyl alcohol exhibited a characteristic peak at room temperature that vanished slowly at increasing temperature, and disappeared completely above 78 °C (melting point of barium hydroxide octahydrate). The peak can be attributed to trapping of crystal water and its release. However, the reaction mixture containing barium hydroxide octahydrate and titanium alkoxide at room temperature did not show the presence of the aforementioned peak at any temperature. This indicates that barium hydroxide and titanium alkoxide reacted directly upon mixing.

Among the wide variety of methods available for the preparation of 1 and 2D nanostructures, chemical solution processes and more specifically hydrothermal
preparation stand out as powerful cost-effective, low-energy consuming routes to successfully control the crystallization engineering of ZnO. There is a great variety of procedures that can be used to control the morphology of ZnO during growth, such as the use of surfactants, polymers and different organic additives, as well as the use of substrates.

In the present work the use of low cost, stainless steel substrates and the combination of two soft solution processing techniques, EPD and hydrothermal growth, in order to grow ZnO nanostructures onto them has been studied. The use of ZnO seed layers deposited by EPD as a way to control the morphology of ZnO structures during hydrothermal growth is discussed. Moreover, the nature of the ZnO used during EPD for the seed layer, as a way of tailoring the development (morphology, size, orientation) of nanoarrays instead of using complexing agents or other additives, is analyzed. The deposits obtained from the different cases (without substrate, with unseeded substrate and with seeded substrate) were characterized by FE-SEM.

In recent years, published works about obtaining TiO$_2$ nanoparticles possessing ultra-reactive surfaces have increased exponentially, due to the great interest of their higher reactivity both from a scientific point of view as technological. The unique physical and chemical properties of TiO$_2$ nanoparticles give them a potential application in a wide range of fields such as photocatalysis, dye-sensitive solar cells (DSCs), Li batteries, transparent conductors and so on. These properties depend not only on the crystal phase and particle size but also on the particle shape.

Herein, we report a new approach based on a low temperature technique at atmospheric pressure for the synthesis of nanostructured anatase with high-energy facets. TiO$_2$ particles have been synthesized with different morphologies depending on working conditions: nanostuctured spheres with size of 4-5μm and truncated rhombic nanoparticles of 20-30 nm.

In this work all reactions were carried out at low temperature using Ti(ButO)$_4$ as the starting precursor, due to it slows the process of diffusion and polymerization, respect to other Ti precursors. Except for the obtaining of TiO$_2$ spheres, EtOH 96% provides the water necessary to accelerate the hydrolysis reaction, and oleic acid (OA) and oleylamine (OM) were used as two distinct capping surfactants to control the size and the shape of the products.

In this manner, a new synthetic route has been established, less drastic, more economical and more environmentally friendly to obtain nanostructured particles of anatase TiO$_2$. 

### Synthesis and characterization of nanostructured anatase TiO$_2$ with high-energy facets obtained by a mild method

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BiFeO$_3$ shows multiferroic properties at room temperature. The high phase transition temperatures ($T_N$=640K, and $T_C$=1100K) make it very attractive not only for the fundamental physics but also from application point of view. BiFeO$_3$ epitaxial thin films have been reported to show excellent ferroelectric and magnetic properties. And a BiFeO$_3$ single crystal has also been reported to have a very high polarization, 60$\mu$C/cm$^2$. It has, however, been known that a BiFeO$_3$ ceramic with high resistivity and good ferroelectric properties could hardly be prepared by the conventional solid state reaction due to impurity phases and ionic defects. Recently, a single phase BiFeO$_3$ ceramic with excellent ferroelectric properties has been successfully prepared by a rapid liquid phase sintering at high temperature or sintering a mechano-chemically-activated BiFeO$_3$ powder at low temperature. In this work, BiFeO$_3$ ceramics were prepared by the conventional solid state reaction at various sintering conditions. Sintering a BiFeO$_3$ ceramic at a different temperature and/or with a heating rate produces a different phase evolution, ionic defect concentration and microstructure. And a sintering atmosphere influences the types and concentrations of ionic defects. The phase evolution and microstructure were investigated by using X-ray diffraction and scanning electron micrograph. The insulating resistance, dielectric properties, ferroelectric P-E hysteresis, and S-E characteristics were measured. The effect of sintering condition on the ferroelectric properties will be discussed.

Fabrication and evaluation of anatase titanium dioxide films using aerosol deposition method
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Since the crystal structure of anatase titanium dioxide (TiO$_2$) changes to rutile one above approximately 650°C, it is difficult to deposit film of anatase TiO$_2$ with good quality using conventional deposition methods, such as sputtering, which require high temperature. Thus, anatase TiO$_2$ films were deposited using the aerosol-deposition method (ADM). Using ADM, it is possible to deposit thin film at low temperatures. TiO$_2$ films were fabricated under various conditions to evaluate the relation between thickness and surface morphology. It reveals from X-ray diffraction (XRD) analysis that the crystal structure of the raw particles is maintained in the film. Film thickness increased in proportion to the scan times or the carrier gas flow rate. Film thickness was independent on scanning speed when the both total deposition time and deposition area were fixed. The two type of surface morphology were observed. One was flake-like and was observed for the film thickness of less than 1 $\mu$m. The other was mesh-like and was observed for the film thickness of more than 1 $\mu$m. We also deposited the anatase TiO$_2$ films including aluminum nitride (AlN) nanoparticles in order to fabricate porous films which might be applicable to the electrode in a dye sensitized solar cell. After deposition, the film was immersed into hot water. It was confirmed from XRD analysis that AlN particles could be removed from the film.
Barium Strontium Titanate (BST) thin films are deposited by RF magnetron sputtering and studied with respect to the B/A cation ratio. Stoichiometric ceramic $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ targets are employed for the deposition process followed by an in-situ characterization with XPS. A compositional analysis of a large set of sputtered BST films reveals a broad range of possible titanium contents ($y = \text{Ti}/(\text{Ba}+\text{Sr})$) mainly distributed around two clearly separated values, a nearly stoichiometric and a titanium rich composition with B/A ~1.5. This is also manifested by a chemical shift between the O1s and the Ti2p core level emission of 200 meV. A different crystal structure of the two phases is not yet observed by X-ray diffraction. So far excess titanium in BST was explained by segregation at grain boundaries where in contrast our own results suggest the existence of a new (most likely unstable) phase which is not yet known in the equilibrium phase diagrams of STO and BTO. Dielectric measurements in the MHz range of platinum-BST-platinum (M-I-M structure) thin film varactors reveal lower dielectric losses and tunability for titanium rich BST thin films whereas for the stoichiometric BST high dielectric losses and tunability are observed.

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Despite the large potential of application of rhombohedral perovskite materials as cathodes (i.e. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) and oxygen separation membranes (i.e. of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$) the thermo-mechanical properties of these materials are still not understood properly. Due to chemical gradient and thermal miss-match with electrolyte/support it is important to investigate the thermal and chemical expansion of the materials. The present laboratory has investigated the chemical and thermal expansion of a series of rhombohedral perovskites [1-4]. The anisotropic nature of both the chemical and thermal expansion in such materials will be discussed in detail. Possible implications of slow relaxation of chemically induced stresses at the nanoscale and in epitaxial thin films of these materials will be addressed.

The mechanism of electrostriction in Gd-doped ceria

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Previous studies have shown that at room temperature the structure of Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ deviates locally from fluorite and contains [Ce$_{\text{Ce-VO}}$] complexes, which create a locally anisotropic elastic field. The lability of the cerium-oxygen bond and mobility of the oxygen vacancies suggested that an applied electric field may reorient these complexes, thereby generating a mechanical stress. We investigated electrostriction in strain-free {substrate\ 100nm metal\ 1nm > Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ thin film\ 100nm metal} structures by monitoring mechanical response to application of external electrical bias. We found that field-induced stress in Gd-doped ceria is comparable with that of commercial electromechanically active materials. Low dielectric constant (<28) rules out field compression or relaxor-type electrostriction mechanism. Moreover, it was found that freshly prepared samples undergo poling-like effect that increases significantly the magnitude of electromechanical response. However, the electromechanical response in Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ is proportional to the square of the electric field and, therefore, it cannot be explained by any kind of uniaxial alignment, occurring during poling of ferroelectrics. X-ray Absorption Near Edge Structure (XANES) measurements of Ce-L$_{3}$ and Gd-L$_{3}$ edges clearly identified that external electric field promotes formation of the [Ce$_{\text{Ce-VO}}$] electro-elastic dipoles and thereby increases the electromechanical response. These findings strongly suggest that ionic conductors may be a class of materials that should be seriously investigated for exceptional electromechanical effects.

Influence of synthesis conditions on the electrical properties of the Na$_{0.5}$Bi$_{0.5}$TiO$_3$-KTaO$_3$ ceramics

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Na$_{0.5}$Bi$_{0.5}$TiO$_3$ is a complex perovskite that has attracted increased attention as a base compound for lead-free piezoelectrics. Its structural and electrical characteristics resemble the typical features of relaxors. The composition of Na$_{0.5}$Bi$_{0.5}$TiO$_3$ has often been tailored in order to improve its room-temperature performance. For the preparation of piezoelectric materials mainly K$_{0.5}$Bi$_{0.5}$TiO$_3$ and BaTiO$_3$ have been used. Moreover, we have recently demonstrated that the introduction of NaTaO$_3$ incipient ferroelectrics leads to enhanced voltage-tunable characteristics of the materials prepared. In the present study we investigated the synthesis and structural characteristics of the Na$_{0.5}$Bi$_{0.5}$TiO$_3$-KTaO$_3$ ceramic system which has not previously been investigated. We anticipated that the temperatures of the Na$_{0.5}$Bi$_{0.5}$TiO$_3$ phase transitions might be effectively tailored by the addition of KTaO$_3$ since it has the characteristics of an incipient ferroelectric. The solid-state reactions were followed using XRD, scanning electron microscopy and thermal analysis. We observed that the solid solution exists across the whole concentration range, while numerous firings are required to attain a sufficient level of homogeneity. Meanwhile, considerable weight losses were detected, which can be compensated only by a surplus of selected elements, mainly Bi$_2$O$_3$. We determined that the homogeneity in the Na$_{0.5}$Bi$_{0.5}$TiO$_3$-KTaO$_3$ ceramic system has a significant effect on the dielectric properties, which will be further discussed and correlated to the samples' microstructures during our contribution.
The growth mechanism of (K,Na)NbO₃-based lead-free piezoceramic particles during hydrothermal reaction

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The growth mechanism of (K,Na)NbO₃ (KNN) crystals during a hydrothermal reaction was systematically studied by investigating the effect of KOH:NaOH molar ratio of the starting alkaline solution, reaction time, and reaction temperature on the phase, chemical composition, and morphology of KNN particles. As the starting KOH:NaOH molar ratio was changed from 8.0:2.0 to 7.0:3.0, the phase of KNN particles synthesized by the hydrothermal reaction at 220°C for 24 h was changed from K-rich KNN single phase to Na-rich KNN single phase, via two-phase mixtures consisting of both phases. In the cases of the starting KOH:NaOH molar ratio of between 7.0:3.0 and 7.6:2.4, K-rich KNN crystals firstly nucleated and grew during the hydrothermal reaction at 220°C. As the reaction time increased, K-rich KNN particles became unstable and started to dissolve, and simultaneously the stable Na-rich KNN particles started to precipitate. Therefore, the morphology of KNN crystals was found to be dependent on the progress of the dissolution-precipitation process. Ta-doped KNN particles were also hydrothermally synthesized with the same reaction procedure of pure KNN. The volume fraction of Na-rich KNN phase in the synthesized powders increased with increase of Ta content in the starting solution. This study suggests the growth mechanism of KNN particles during the hydrothermal reaction and demonstrates that the stoichiometry and the morphology of KNN particles can be controlled by changing the chemical composition of the starting alkaline solution or experimental parameters of the hydrothermal reaction.

Lead zirconate titanate-zirconia composites prepared by hetero-agglomeration of constituent particles

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One way how to improve the mechanical properties of lead zirconate titanate (PZT) ceramics, is by introducing the particles of a second phase, such as tetragonal yttria stabilized zirconia (TZ). Furthermore, the zirconia grains should be uniformly distributed within the PZT matrix.

The aim of our work was to find the optimal conditions for a uniform distribution of TZ particles in the powder mixture based on the principle of controlled hetero-agglomeration and keep it throughout the processing. The zeta-potentials (ZP) of the powders were measured as a function of the suspension pH by electrophoretic light scattering. First, the PZT and TZ powders were mixed in water at a high pH, where the ZPs of both components are positive, and thus they repel each other. Therefore no hetero-agglomeration should occur. In the second experiment at a low pH, the TZ powder was pre-milled with 1 wt% of citric acid (CA) and had a negative surface charge, while the PZT is positive. Such conditions should lead to hetero-agglomeration of PZT and TZ-CA. After drying, the powder mixtures were pressed into pellets and sintered at 1275°C for 2 hours. The distribution of zirconia particles within the PZT matrix was evaluated. In the first case (positive ZPs of both PZT and TZ), the composites exhibited a non-homogenous distribution of large zirconia agglomerates in the PZT matrix, while in the second case a higher homogeneity of the composites with smaller TZ agglomerates was achieved.
Perovskite ceramics based on BaO-CoO-Nb2O5 ternary system have found numerous applications in the microwave (MW) engineering as the low-loss dielectric resonator materials. The most studied compounds include B-site ordered cubic perovskite Ba3CoNb2O9 (BCN) as well as layered hexagonal perovskites Ba5Nb4O15 (5L) and Ba8CoNb6O24 (8L) which belong to A\(_n\)B\(_{n-1}\)O\(_3n\) family at \(n = 5\) and \(n = 8\) respectively. The latter one is formed on the tie line Ba3CoNb2O9-Ba5Nb4O15, and demonstrates unusual ordering of Co-layers. Moreover, Ba8CoNb6O24 is often present as secondary phase in the BCN ceramics. However, the effect of 8L crystal phase on the MW properties of a material was not yet clearly examined. Therefore, in our work we studied ceramics with the compositions on the BCN-5L tie line with respect to their phase content, microstructure, and microwave dielectric properties. For the first time, by means of high-resolution phase-contrast electron microscopy we have found the intermediate formation of coherently grown structures Ba3CoNb2O9-Ba5Nb4O15 which further transform to Ba8CoNb6O24. The ceramics composed of these intergrowths displayed noticeably higher values of the MW \(Q\)-factor comparing with those of the separate perovskite phases.

Moreover, processing-driven changes in the phase content of the BCN-5L ceramics allowed a wide-range control of the temperature coefficient of permittivity. The consequent formation of the 8L structure was found to result in a significant deterioration of the \(Q\)-factor due to increasing amount of microstructural defects and accompanying decrease in density.

BiFeO\(_3\) is a widely studied magnetoelectric multiferroic because of its ferroelectric (\(T_C \sim 810 - 830^\circ\text{C}\)) and (anti)ferromagnetic properties (\(T_N \sim 370^\circ\text{C}\))\(^1\). The study and applications of bulk BiFeO\(_3\) is hindered by thermal metastability and overriding electrical conduction due to non-stoichiometry\(^2\). One approach to improve the properties and the stability of the perovskite phase is by substitution of the volatile Bi\(^{3+}\) with rare earths e.g. \(\text{RE} = \text{La}^{3+}, \text{Nd}^{3+}\) (Bi\(_{1-x}\)\(\text{RE}_x\)FeO\(_3\)).

We have carefully prepared electrically insulating samples and investigated structural transitions as a function of temperature and composition using a number of different techniques, including powder neutron diffraction (PND) and electrical impedance spectroscopy. Room temperature data shows a series of transitions from \(R3c\) \((x=0.1) \rightarrow \text{Pbam-like} \ (x=0.15, \ 0.2) \rightarrow \text{Pn}'\text{ma}' \ (x=0.25, \ 0.3)\) within the Nd series; and in the La-doped system \(R3c\) \((x=0.1) \rightarrow \ (x=0.15) \rightarrow \text{Pbam-like} \ (x=0, 0.2) \rightarrow \text{incommensurate} \text{Imma} \ (x=0.3) \rightarrow \text{Imma and Pn}'\text{ma}' \ (x=0.4) \rightarrow \text{Pn}'\text{ma}' \text{and I4/mcm} \ (x=0.5)\).

In particular, PND of La-doped BiFeO\(_3\) \(x = 0.5\) reveals an unusual increasing orthorhombic distortion with temperature (with an anti-phase and increasing in-phase tilt). In addition the octahedra become distorted with temperature and the maximum octahedral distortion correlates with the observed change in the dielectric constant.

SrTiO$_3$ (STO) is a quantum paraelectric with extrapolated ferroelectric transition temperature of $T_c=37$K. At $T_S=105$K STO undergoes an antiferroelectric phase transition from cubic to tetragonal. EuTiO$_3$ (ETO) behaves rather analogous to STO at low temperatures where also quantum paraelectricity exists. In addition, ETO becomes antiferromagnetic at $T_N=5.5$K. Since both compounds have the same lattice constants and the ionic radii of Sr and Eu are comparable, it is challenging to investigate mixed crystals of the end members for possible multiferroic properties.

We have concentrated on the structural instability at $T_S$ which we have recently shown to exist also in ETO. This increases nonlinearly with increasing $x$ in Sr$_{1-x}$Eu$_x$TiO$_3$ to $T_S=280$K for $x=1$. Simultaneously the dynamics change from displacive to order / disorder. However, the structural instability follows for all $x$ mean-field behavior whereas the soft optic mode reveals a boundary between the distinct dynamics of the pure compounds.

The theoretical analysis is complemented by EPR, specific heat, resistivity and mSR measurements.

Possible applications of the layered mixed crystals are addressed where multiferroic properties are suggested to be realized.

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Lead zirconate titanate and barium titanate are important ceramic materials used in contemporary electronic devices. A substantial effort has been made to develop sol-gel methods and appropriate precursors enabling synthesis of sub-200 nm films. In order to understand the differences in crystallization behavior between both materials, a better understanding of microstructure evolution in sols and drying thin films is desired.

We investigated the alkoxide-carboxylate routes for both materials. In the case of amorphous BaTiO$_3$ gels, the system developed into separate TiO$_x$ and Ba-rich phases, as proven by small angle X-ray scattering (SAXS), and EELS mapping in TEM. Depending on the hydrolysis conditions we observed phase-separated domain sizes of 2 to 30 nm. We also performed time-resolved SAXS to study gelation and drying of thin films.

Pb(Zr,Ti)O$_3$ sols evolved in a different manner. It was observed that Pb and Ti components remained homogeneously mixed on the nano-scale, whereas Zr clustered into cylindrical stacks of zirconia tetramers.

Crystalline nano-clusters of zirconia were found embedded in an amorphous matrix containing Pb and Ti in as-dried films, as shown by TEM/EELS. Formation of these crystalline species was suppressed by extensive hydrolysis of sols. In this case the presence of an excess of water was a factor that homogenized the system.
The reduction of the layer thickness below 1 mm for increasing the volume capacitance in MLCCs or embedded capacitance in PCBs led to a high interest for BaTiO₃-based ceramics with grains below 100 nm. The reduction of grain size results in a diminishing of ferroelectric polarisation, permittivity, tunability and other material constants and gives rise to a fundamental question about the stability of the ferroelectric state below a certain size limit (critical size). Preparation of nanocrystalline dense ceramics requires ultra-fine, non-agglomerated powders with a narrow particle size distribution and suitable densification techniques to minimize the grain growth. When reducing grain sizes at nanoscale, interfaces (grain boundaries) and defects play an important extrinsic role on the macroscopic properties, besides the intrinsic size effects. For high volume capacity applications, grain size should be reduced by maintaining as high as possible the permittivity to above 1000, while for tunability devices, the permittivity should be lowered down to few hundreds, while keeping a high tunability and low losses. The present work shows the concept of using the grain size reduction as an additional factor to tune these properties towards the desired range for specific applications. This concept is illustrated with a few results obtained for BaTiO₃-based nanostructured dense ceramics. An effective field model combined with Monte Carlo simulations allowed to determine the local fields in realistic grained structures and the dielectric and ferroelectric response.

The properties of BaTiO₃-based solid solutions are tailored by the substitution level and by controlling their microstructural characteristics. BaSnₓTi₁₋ₓO₃ solid solutions (x=0> 0.20) were investigated by a combined analysis of the field-induced dielectric and ferroelectric properties (tunability, FORC diagram method) and Raman spectroscopy. By increasing the Sn content, a crossover from ferroelectric long-range order towards a relaxor (short-range order) state was found. The short-range order state initiates for low Sn content (down to x=0.05). This tendency expected from the low-field dielectric study was confirmed by the thermo-Raman analysis (large temperature ranges of phase coexistence and the presence of polar nanoregions) and by the FORC study, where a trend of reducing the switchable (non-zero coercivity) contribution with respect to the non-switchable (reversible) one to the ferroelectric polarization with increasing of the Sn content was observed.
While other literature data reported a full relaxor state for higher amounts of Sn (x>0.25) only, the present x=0.20 composition is already found in a predominantly relaxor state. This feature confirms the importance of the synthesis routes and sintering parameters (giving rise to specific microstructural characteristics) on the onset of the relaxor behavior. The existence of such phase superposition is the reason for the unusual macroscopic characteristics. Tailoring the phase coexistence is a very useful method to produce BaTiO$_3$-based solid solutions with optimum functional properties in specific temperature ranges.

**Acknowledgements:** The financial support from ESF-POSDRU 88/1.5/S/47646 and CNCS-UEFISCDI-PN II-ID-3-2011-0745 are highly acknowledged.

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In many piezoelectric actuators the active piezoelectric material is bonded to a variety of passive materials and these bonds may introduce unwanted stresses through thermal expansion mismatch, inhomogeneous manufacturing processes and even through piezoelectric actuation itself. There is some data on the effects of compressive stresses on piezoelectric output, but because applying tensile stresses to these ceramic materials often induces mechanical failure, this regime has been less well studied. In order to design a reliable piezoelectric actuator it is important to know what the allowable stress levels are before actuator performance is compromised.

This work describes a test method to measure the effect of tensile stresses of up to 30MPa, applied perpendicular to the poling direction, on the piezoelectric output in the three orthogonal directions, and describes the results on two soft PZT materials.

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A conventional pulsed laser deposition (PLD) setup was modified to allow for a freely adjustable angle between plasma plume and sample surface. Yttria stabilized zirconia (YSZ) which grows in columns was found to follow this angle with the orientation of its columns as shown by scanning electron microscopy (SEM). Zigzag-structured columns were obtained by additional in-plane rotations during the deposition. Compared to straight columns changes in the thin film properties may be expected. The zigzag-structure is expected to increase the mechanical stability which is crucial for the use of YSZ as free standing membranes in micro solid oxide fuel cells.

The developed thin films were investigated by nanoindentation measurements to determine their hardness and elastic modulus. It was found, that zigzag grown thin films show lower hardness (~15 GPa), and elastic modulus (~240 GPa) than the conventionally grown films by ca. 25%, and 10% respectively. To study the effects of the mechanical response changes with respect to the increase in stability (ductility), thin free standing
YSZ bars are cut from membranes with a focused ion beam. The bending of these bars under external stress is investigated in-situ by an SEM equipped with a nanoindenter. The crystallographic orientation and the in-plane and out-of-plane conductivity were also measured.

### Patterning of LAO/STO interfaces using dry ion beam etching

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<td><strong>Patterning of LAO/STO interfaces using dry ion beam etching</strong></td>
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<td><strong>O.71</strong></td>
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<tr>
<td>Pier Paolo Aurino, Alexey Kalabukhov, Dag Winkler</td>
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<tr>
<td>Department of Microtechnology and Nanoscience – MC2, Chalmers University of Technology, Gothenburg, Sweden</td>
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Several experimental evidences have been reported about the formation of a quasi-two-dimensional electron gas at the interface between the two insulators LaAlO$_3$(LAO) and SrTiO$_3$(STO)[1]. This interface becomes conducting (superconducting and even magnetic) when more than 4u.c. of LAO are epitaxially grown on STO substrate [2,3]. For devices fabrication, the conducting interface should be patterned. In this report, we used Ar$^+$ ion beam etching (IBE) as a possible way to fabricate structures in pulsed laser beam deposited LAO/STO heterostructures. We found that the beam voltage threshold for destroying conductive interface was much smaller as needed for physical etching of the LAO film. In the beginning of the etching process, the resistance of the etched area rose to an insulating state, but longer etching times resulted in a reentrance of the conductivity due to oxygen vacancies produced in the SrTiO$_3$ substrate. The coexistence of these two effects produces a useful etching time interval which depends on the thickness of the LAO film and power of the ion beam. We will present the role of etching parameters on this temporal behavior and discuss the etching mechanism of the conducting interface.

This work is supported by Swedish Research Council and the K. A. Wallenberg foundation.


### Space charge contributions to the sintering of perovskite materials

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<td><strong>Space charge contributions to the sintering of perovskite materials</strong></td>
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<td><strong>O.72</strong></td>
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<tr>
<td>Michael Bäurer, Fabian Lemke, Michael J. Hoffmann</td>
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<tr>
<td>Institute for Applied Materials, Karlsruhe Institute of Technology, Karlsruhe, Germany</td>
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Sintering schedules for perovskite materials are usually developed empirically. Changes in dopant content or raw materials will usually result in an adapted sintering schedule. Defect chemical considerations are usually neglected in designing these schedules. In the model system Strontium titanate a vast amount of defect chemical data is available on defect chemistry in the bulk and at grain boundaries. The defect concentration in the space charge region around those grain boundaries will have a huge impact on material transport during sintering especially in fine grained materials. Based on literature data the impact of defect concentrations on the shrinkage rate during sintering is discussed. Space charge contributions to grain boundary diffusions are included into basic sintering models and the results are compared to experimental data. It can be shown that space charge contributions have a significant impact on sintering of perovskite materials.
The origins of chemical expansion in non-stoichiometric oxides

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Background
Non-stoichiometric oxides are used in many high temperature energy applications such as solid oxide fuel cells, oxygen permeation membranes, and gas conversion/reformation catalysis. Indeed, many high performance SOFC electrodes and electrolytes exhibit significant oxygen stoichiometry fluctuations with changes in atmosphere, temperature, and power demand, resulting, inter alia, in significant mechanical stresses from defect induced lattice parameter changes, also referred to as chemical expansion. While this phenomenon represents an important technological challenge, the governing mechanisms and possible strategies to suppress chemical expansion have not been identified to date.

Methods
Density Functional Theory and Molecular Dynamics Simulations were used for this work. The simulations are validated by/compared to experimental data available from the literature.

Results & Conclusions
In this paper we use computer simulations, validated with experimental data, to elucidate the factors responsible for the chemical expansion observed in several non-stoichiometric oxides, including CeO2, ZrO2 and doped LaGaO3. We find that chemical expansion is the result of two competing processes, the formation of a vacancy (leading to a lattice contraction) and the cation radius change (leading to a lattice expansion). We model the chemical expansion coefficient as the summation of two terms that are proportional to either the cation or oxygen radius change upon reduction. This model introduces one empirical parameter, the oxygen vacancy radius, which we demonstrate can be reliably predicted from computer simulations, as well as from the experimental data. This model can be used to predict compositions of materials that minimize chemical expansion.

Selective conduction through ferroelastic domain walls in epitaxial BiFeO3 thin films

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BiFeO3 (BFO) is a rhombohedrally distorted, ferroelectric and antiferromagnetic perovskite at room temperature. This rare combination makes BFO a good candidate for magneto-electric investigations and promises interesting new spintronics and memory applications. Recent reports on domain walls properties in epitaxially grown BFO thin films reveal appealing properties such as photocurrent generation[1] and conduction through so-called 109° domain walls[2]. We have previously reported that conduction in BFO is not limited to a particular type of domain wall[3]. For clarifying the origin of conductivity in domain/domain walls, conduction mechanisms have been studied using conducting-AFM[3,4]. In the large current regime, Schottky emission from the electrode
turned to be the dominant mechanism. Moreover, migration of oxygen vacancies to the domain walls lowers the Schottky barrier heights at the interface with the metallic AFM-tip compared to that in the domains. This results in the observed conduction enhancement at domain walls. For application purposes, it would be desirable to tune the amount of current by changing the Schottky barrier height. In this work, we investigate the tunability of the conductivity upon changes in the electrode’s work function, as well as the interplay between ferroelectric polarization and conductivity in BFO thin films.


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<th>O.75</th>
<th>Electrical properties in BiFeO₃ based solid solutions</th>
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<td>Fernando Rubio-Marcos¹, Jean-René Duclère², Fabien Remondière², Pascal Marchet²</td>
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<td>¹Departement of Electroceramics, Instituto de Cerámica y Vidrio CSIC, Madrid, Spain, 28049;</td>
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<td>²Centre Européen de la Céramique, Laboratoire de Science des Procédés Céramiques et de Travaux de Surface, UMR 6638 CNRS, Université de Limoges, Limoges, France, 87068</td>
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Multiferroic materials are widely investigated nowadays, because they constitute an exciting challenge in the field of physics and solid state chemistry. Among them, BiFeO₃ (BF) appears actually as one of the most interesting. At room temperature, BF is a rhombohedral perovskite (R3c), presenting both ferroelectricity and an antiferromagnetic order (Tₙ = 640K). But the exact sequence of phase transition of BF is still controversial. An orthorhombic phase (820-925°C) was clearly detected, but the existence of the cubic phase (925-933°C), with metallic behaviour similar to the one induced by pressure, is still discussed because of the closeness of the peritectic decomposition (961°C). Since the formation of solid-solutions can induce a “chemical pressure effect”, similar to the “mechanical pressure effect”, it is interesting to substitute Bi³⁺ or Fe³⁺ by suitable elements in order to obtain a stabilization of such phases. In this work, we focus mainly on the BF-rich range of solid solutions formed with Na₀.₅Bi₀.₅TiO₃ (NBT) and K₀.₅Bi₀.₅TiO₃ (KBT), two lead free ferroelectric materials, corresponding to chemical substitution in both A-site and B-site. The electrical properties of ceramics were studied by impedance spectroscopy and revealed (i) a decrease of the resistivity around two orders of magnitude (350 to 600°C) and (ii) a second change of the conducting behavior (650-700°C). The structural study by temperature programmed X-ray diffraction evidenced that this phenomena corresponds to a structural evolution with the formation of an intermediate phase, leading reversibly to a high temperature cubic phase.

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<th>O.76</th>
<th>Fully ferroelectric/ferroelastic coupled FE model for piezoceramic including the effect of a weak electrical conductivity</th>
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<td>Holger Schwaab¹, Marc Kamlah¹, Marco Deluca², Peter Supancic³</td>
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<td>¹Materialscience, Karlsruhe Institute of Technology, Karlsruhe, Germany; ²MCL, Materials Center Leoben, Forschung GmbH, Leoben, Austria; ³Institut für Struktur- und Funktionskeramik, Montanuniversitaet Leoben, Austria</td>
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Due to the giant piezoelectric effect piezoceramic materials based on lead zirconate/titanate (PZT) are an important class of smart materials for actuators and sensors. In order to obtain macroscopic piezoelectric properties of sintered, polycrystalline PZT material, a so-called poling process has to be applied. Microscopically
a domain switching is induced leading to residual strains, stresses and space charges, which are of relevance for the performance and reliability of piezoelectric devices. In this talk a 3D phenomenological model is presented for the computation of the highly non-linear electro-mechanical behaviour based on fully coupled ferroelectric/ferroelastic properties, including the influence of a weak electrical conductivity. The model has been applied to typical example problems to compare with experimental results.

Structural and functional analysis of newly discovered pyrochlores from Bi$_2$O$_3$-Fe$_2$O$_3$-TeO$_3$ system

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Pyrochlore structure, represented by the general formula A$_2$B$_2$O$_7$ or A$_2$O' B$_2$O$_6$ can accommodate a wide range of different chemical constituents and structural defects, which makes functional properties of pyrochlores adaptable and interesting for technology. A new pyrochlore homogeneity field in Bi$_2$O$_3$–Fe$_2$O$_3$–TeO$_3$ system is presented here with respect to its compositional range and phase relations. The highly polarizable Bi$^{3+}$ cation in combination with a magnetic Fe$^{3+}$ cation can produce a stable pyrochlore phase when introducing the high valence Te$^{6+}$ cation. This results in a spin-glass formation and interesting (di)electric properties. Furthermore, due to the high concentration of Fe ions the band gap of this new pyrochlore is the lowest (<2eV) among all Bi-pyrochlore, which makes them interesting for solar light driven photocatalytic applications.

Here we report on the synthesis and structural characterization of these newly discovered pyrochlore. We will discuss the results obtained with X-ray and neutron diffraction analysis as well as Raman spectroscopy. We will review their (di)electric and magnetic properties, which show some unusual behaviour at cryogenic temperatures due to the geometrically frustrated behaviour. The focus will be on the details of the electron conductivity and related conductive mechanism.

Nucleation and growth of an exotic ferroelectric domain structure in PZT close the morphotropic phase boundary

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Self-organization and evolution of phase-transition-induced topological defects: vortices, solitons and domain walls is the fascinating problem of condensed matter physics. In ferroelectricity, such defects are usually presented by domain structures where polarization periodically alternates to minimize the global electrostatic or/and elastic energy of the sample. However the recent ab-initio study of polarization distribution in finite-size nano-scale ferroelectrics clearly demonstrated the existence of unconventional buckling textures [Naumov I., PRL. 98, 077603, (2007)], known as polarization vortex rings, toroidal vortices. Formation of such patterns can be qualitatively understood on the purely electrostatic basis. As the working material we consider the multi-axial cubic perovskite-like displacive ferroelectric with weak polarization anisotropy, like, e.g. the PZT close to the morphotropic phase boundary. Our analytical modeling was based on the Ginzburg-Laudau theory, coupled with Maxwell equations in a finite cylindrical sample. The dynamics of non-uniform polarization structures is accounted for by Lifshitz-
Khalatnikov dissipation formalism. We describe, the formation of an exotic polarization texture in nanoferroelectrics, known as chiral skyrmion in magnetism. Moreover we found that the critical field required for this defect formation is lower than thermodynamical coercive field, that could explain, at least partially explain the Landauer paradox [JAP 28, 227, (1957)].

With the enactment of the ROHS-Directive within the EU in 2006, the limitation of heavy-metal content in electrical and electronic equipment became valid. Despite the still existing exception for piezoelectric ceramic materials, this legislation, together with growing worldwide concerns about environmental impacts, increases the research activities on lead-free piezoelectric ceramics drastically.

The most popular candidates for lead-free piezoelectric ceramics are BNT and KNN based systems. Although all these systems show promising piezoelectric properties, there are still efforts necessary in order to replace the well-established PZT adequately. All lead-free piezoelectric materials still cannot match the unique properties of PZT ceramics. BNT based ceramics are characterized by a depolarization temperature well below the Curie temperature. Therefore, their range of operation is limited to temperatures below 200°C (BNT). In contrast, KNN based ceramics exhibit high Curie temperatures but have additional polymorphic phase transitions.

Hence, for replacing PZT ceramics by lead-free piezoelectric materials successfully, optimized lead-free formulations as well as suitable processing routes have to be developed. Furthermore, an adaptation of the electronic devices and the mechanical interfaces will be necessary for the replacement of PZT based materials in industrial applications.

Since 2004 PI Ceramic is investigating lead-free piezoceramic materials as well as the required technologies. The current status and the tasks for the future will be discussed from a point of view of the industry.

Bismuth containing ceramics with perovskite-related structures attract much attention due to prospects of their applications at high temperatures. In this work, dielectric and piezoelectric properties on complex oxides based on CaBi$_4$Ti$_4$O$_{15}$ and BiScO$_3$ were studied. Ceramic samples Ca(Bi$_{1-x}$Pb$_x$)$_4$(Ti,B)$_4$O$_{15}$ and (Bi,Pb)(Sc,Ti)O$_3$ were prepared by the solid state reaction method. Phase composition, structure and microstructure, ferroelectric phase transitions and piezoelectric properties were studied using different physico-chemical methods (X-ray Diffraction and Scanning Electron Microscopy methods, DTA/DSC and dielectric spectroscopy). Piezoelectric parameters were determined using $d_{33}$ meter, electromechanical coupling coefficients measured by a standard resonance – antiresonance method.
The optimal conditions of preparation of dense ceramics were determined. In compositions additionally doped by additives (Ni$_2$O$_3$, MnO$_2$, Bi$_2$O$_3$ and Cr$_2$O$_3$) marked orientation of grains was revealed. Changes in the unit cell parameters corresponding to the substitution of A and B cations were observed. The 1st order ferroelectric phase transitions are marked by peaks at temperatures higher than 1000 K in $e(t)$ and $\tan\delta(t)$ dependences. Effects of dielectric relaxation related to the presence of oxygen vacancies in anion sublattice were observed in some ceramics. High piezoelectric coefficients $d_{33}$ up to 400 pC/N and electromechanical coupling coefficient $k_t$ up to 0.6 were measured in modified ceramics. Enhancement of piezoelectric properties will be discussed in relation to the preparation conditions optimization, types and contents of dopants and additives, concentration of oxygen vacancies in anion sublattice.

The work is supported by the Russian Fund for Basic Research (Grant 12-03-00388).

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<th>The electro-mechanical properties of BNT based multilayer actuators</th>
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<tr>
<td><strong>Klaus Reichmann</strong>$^1$, Denis Schuetz$^1$, Marco Deluca$^{2,3}$, Werner Krauss$^1$, Peter Supancic$^2$</td>
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<td>$^1$Christian-Doppler-Laboratory for Advanced Ferroic Oxides, Graz University of Technology, Graz, Austria, 8010; $^2$Institut fuer Struktur- und Funktionskeramik, Montanuniversitaet Leoben, Austria, 8700; $^3$Forschung, Materials Center Leoben Forschung GmbH, Leoben, Austria, 8700</td>
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BNT-based solid solutions have been subject to a flurry of research interest recently. We have manufactured a prototype multilayer actuator$^1$ encompassing 50 active layers, with extended strain, based upon the BNT-BKT system, which experiences less than 10% variation in strain between 25°C and 150°C (avg. strain 0.22% @7kV /mm). Mechanical measurements under preload conditions revealed that the actuator is able to exert force under a preload exceeding 60 MPa. The strain was reduced by app. 50% under high load conditions, putting it firmly within the range of a conventional PZT actuator.


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<th>In situ ferroelectric domain structure by confocal Raman microscopy coupled with atomic force microscopy</th>
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<td><strong>Fernando Rubio-Marcos, Ángel Adolfo Del Campo García, Juan J. Romero, José F. Fernández</strong></td>
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In order to investigate the structure and distribution of ferroelectric domains, a number of techniques have been usually applied, among them, scanning probe microscopy, optical microscopy, transmission electron microscopy, scanning force microscopy and lately, scanning electron microscopy in the backscattered mode. In contrast to spectroscopy methods, the above mentioned methods yield no or very limited chemical information. For complex domain structure, the purely topographic information is not sufficient to understand the distribution of all domains within a ceramic material.

Different attempts have been made to combine the high spatial resolution of scanning probe microscopy with chemical information provided by spectroscopic techniques. Methods based on micro Raman spectroscopy give the possibility to study at a local scale the structural deformations of perovskites, which are induced both by the tilting of BO$_6$ octahedra and by the cationic displacements.
In this contribution we highlight some practical aspects in the study of different ferroelectric domains structures, with special attention to some relevant results obtained in different lead-free piezoceramics, such as (K,Na)NbO₃ and Bi₄Ti₃O₁₂, and in single crystals (BaTiO₃). This work presents and discusses the ferroelectric domain structure existing in different systems studied by Confocal Raman Microscopy (CRM) coupled with Atomic Force Microscopy. The study of ferroelectric domains distribution by CRM permits us a comprehension of the domain formation mechanism and the stress reduction processes in piezoelectric materials.

O.83
Temperature-dependent Raman spectroscopy of unmodified, Fe- and Ba-modified sodium bismuth titanate lead-free ferroelectric ceramics
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Sodium bismuth titanate (Na₀.₅Bi₀.₅TiO₃−NBT) and its solid solutions are considered promising lead-free materials for actuator applications due to their large field-induced strains. Modification of NBT by doping, or forming a solid solution (which induces a morphotropic phase boundary−MPB) enhances many properties and has recently been the focus of much research. In these materials, the phase constitution and the sequence of structural changes between the room-temperature ferroelectric phase (reported in the literature as either rhombohedral or monoclinic) and the high-temperature cubic phase (i.e. the changes occurring at the depolarisation temperature, T_d) are unclear. The presence of either an antiferroelectric/ferrielectric phase or a diffuse transition involving polar clusters has been suggested.

In this work, temperature-dependent Raman spectroscopy has been used to support the interpretation of results obtained from depoling measurements and synchrotron X-ray diffraction (XRD) in unmodified, Fe-modified and Ba-modified NBT (i.e., NBT-BaTiO₃ or NBT-BT solid solutions). Changes in T_d due to Fe substitution were detected by Raman, and interpreted in terms of the nucleation of nanosized clusters. In NBT-BT, Raman analyses helped identify the compositional range in which the MPB appears, also highlighting differences induced by changing the processing method.

The access to short-range phenomena provided by Raman is a decisive supplement to results obtained with long-range sensitive techniques such as XRD. This study confirms the role of Raman spectroscopy as a complementary tool to interpreting the complex micro- and macroscopic behaviour of lead-free ferroelectrics.

O.84
Lone-pair induced covalency as the cause for the extended strain in BNT based solid solutions
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The underlying physical and chemical mechanisms for the extraordinarily high strain levels in BNT related compounds in the vicinity of the depolarization temperature (T_d) are still poorly understood. We propose a comprehensive explanation combining the short-range chemical and structural sensitivity of in-situ Raman spectroscopy (under applied electric field and temperature) with macroscopic electrical measurements both obtained
through the use of a prototype multilayer. Our results clarify the causes for extended strain as well as the peculiar temperature dependent properties encountered in this system. The underlying cause is determined to be mediated by the complex-like bonding of the octahedra at the centre of the perovskite. Namely, a loss of hybridisation of the 6s² Bismuth lone pair interacting with oxygen p-orbitals occurs, which triggers both the field-induced phase transition and the loss of ferroelectric order at the depolarisation temperature.

O.85 Poling field dependence of Young’s modulus and Poisson’s ratio in lead-free piezoelectric ceramics
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Lead-free piezoelectric ceramics have been studied by many researchers, because of replacing Pb(Zr,Ti)O₃ (PZT) ceramics. While relatively high piezoelectricity of 70% in PZT ceramics is realized in alkali niobate: the piezoelectric strain d₃₃ constant is 307 pC/N in 0.95(Na,K,Li,Ba)(Nb₀.₉Ta₀.₁)O₃-0.05SrZrO₃ with a small amount of MnO [1], and low piezoelectricity with low dielectric constant and high electromechanical quality factor are obtained in alkali bismuth titanate. Improving the piezoelectricity, a study on domain alignment by DC poling field is important that how to realize higher piezoelectricity in lead-free ceramics.

Ferroelectric domain structures were evaluated in piezoelectric ceramics composed of alkali bismuth niobate and alkali bismuth titanate. Ferroelectric domain switching and domain rotation could be explained by DC poling field dependence of dielectric and piezoelectric properties. In addition, Young’s modulus and Poisson’s ratio toward poling field in lead-free ceramics were investigated by measuring longitudinal and transverse acoustic wave velocities to clarify the relationships between high piezoelectricity and the values. Basically, increasing domain alignment by applying DC poling field, the Young’s modulus decreased and Poisson ratio increase.

This work was partially supported by a Grant-in-Aid for Scientific Research C (No. 21560340) and a Grant of Strategic Research Foundation Grant-aided Project for Private Universities (No. S1001032) from the Ministry of Education, Culture, Sports, Science and Technology.


O.86 Epitaxial growth and properties of lead-free ferroelectric Na₀.₅Bi₀.₅TiO₃ thin films on various single crystal substrates
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The epitaxial growth of lead-free ferroelectric Na₀.₅Bi₀.₅TiO₃ (NBT) thin films on various single crystal substrates was successfully achieved, using the pulsed laser deposition technique. This work is divided in two parts, focused on:
- the growth of NBT layers on c- and r-sapphire (Al₂O₃) substrates, with and without introducing a CeO₂ buffer layer.
- the growth of NBT layers on (001)SrTiO3 substrates, with and without introducing a LaNiO3 layer.

In the first part, it was shown that the introduction of a CeO2 buffer layer completely modifies the out-of-plane growth orientation of the NBT films, as well as their microstructure. Indeed, as revealed by X-Ray Diffraction (XRD) measurements, it turns out that (001)NBT films epitaxially grow only on r-Al2O3 substrates buffered with epitaxial (001)CeO2 layers. On the other hand, growing simply NBT on bare c- or r-Al2O3 substrates, or on CeO2/c-Al2O3 heterostructures leads to polycrystalline or textured films. Some linear optical properties are also presented. Finally, the introduction of CeO2, as a potential layer serving for blocking the diffusion of the substrate elements, is currently under investigation.

In the second part, detailed XRD investigations demonstrate that (001)-oriented NBT layers deposited on either bare (001)SrTiO3 or (001)SrTiO3 substrates covered with (001)LaNiO3 are systematically epitaxially grown. Furthermore, the aspect of the microstructure is again strongly affected by the introduction of the LaNiO3 layer. Its potentiality to be used as a bottom electrode for future electrical measurements is not discussed.

An increasing interest is observed in the development of lead-free ferro-piezoelectric materials to substitute the well known Pb(Zr, Ti)O3 (PZT). This would avoid the lead emission and cross-contamination during the electronic manufacturing. In addition, the fabrication of these materials in thin film form is demanded for their integration in microelectronic devices.

Solid solutions of bismuth sodium titanate (Bi0.5Na0.5)TiO3 and barium titanate BaTiO3 are considered good alternative lead-free materials. These have a rhombohedral–tetragonal MPB, where bulk ceramics show enhanced dielectric, ferroelectric and piezoelectric properties.

(Bi0.5Na0.5)xBa1-xTiO3 (BNBT) thin films are prepared with different compositions (x=0.050, 0.650, 0.800, 0.100 and 0.150) onto Pt/TiO2/SiO2/(100)Si substrates, by a hybrid solution route. Stoichiometric solutions and others containing Na(I) and Bi(III) excesses have been prepared. The crystalline phases developed in the BNBT films and in the corresponding powders have been monitored by X-Ray Diffraction (XRD). From the analysis of the results we conclude that the position of the MPB depends on the Na and Bi excess added to the solution. Besides, the MPB in the BNBT thin films does not appear in the same range of compositions than that reported for bulk ceramics. Dielectric and ferroelectric measurements indicate an improvement of the properties of these films for a composition with x=0.10, where the MPB has been identified previously by XRD.

These results are discussed based on the potential and reliability of these lead-free thin films integrated in microelectronic devices.
Ba$_5$Nb$_4$O$_{15}$ is a good candidate for type I multilayer capacitors, thanks to its dielectric properties (dielectric constant close to 40 with a resistivity above $10^{12}$ ohm.cm and dielectric losses lower to $10^{-3}$). The study we present here consists in different commercial mixed glass frit powders addition with the goal of lowering its sintering temperature and, thus, the use of silver electrodes for multilayer capacitors making. The sintering behaviours of each glass frit additive were studied by thermometric analysis (TMA). Some of them permit the densification of Ba$_5$Nb$_4$O$_{15}$ at 900°C. We have studied the influence of these additions on the electric and dielectric properties of sintered ceramic pellets. The dielectric properties have been studied in the range -30°C to +145°C. The results show a type I dielectric behaviour and are close to the one of pure Ba$_5$Nb$_4$O$_{15}$. Then co-sintering with Ag was tested on the different compositions and Ag diffusion in ceramic investigated.

The essential concept underlying varistor action in ZnO-based polycrystalline ceramics is that electron transport across charged grain boundaries is voltage dependent. In normal use varistors are subject to a voltage below their characteristic switch voltage, almost no electrons overcome the electrostatic barriers at those grain boundaries, and only a leakage current pass through the material. However these currents may entail a considerable energy loss, especially for high voltage applications, so in order to obtain high-performance devices the leakage current flow must be reduced to a minimum. In the present contribution we face this goal by acting over the microstructure of the ceramic material. More specifically we have introduced intended modifications on the skeleton of secondary phases, which actually represents the conduction path for the leakage current to flow. As a consequence, an increased control of the varistor functional microstructure is achieved which eventually resulted in a drastic reduction of the measured leakage currents.

Composites of electroceramic particles in a polymer matrix are valued for easy, low temperature processing and good mechanical properties. However, the electronic properties generally suffer due to limited connectivity of the electroceramic particles, especially at low ceramic volume fraction. Composites with enhanced properties compared to composites with randomly dispersed particles can be obtained by dielectrophoretic alignment of the particles during curing of the polymer matrix.
As an example, piezoelectric composites processed using dielectrophoresis achieve higher permittivity and piezoelectric constants in the poling direction. The enhancement effect depends on particle shape and orientation. The particle orientation depends on processing parameters such as the amplitude and frequency of the applied electric field and the viscosity of the matrix.

In this presentation new possible electroceramic composites will be discussed. Examples will be presented for oriented composites based on Negative Temperature Coefficient (NTC) materials, Pyroelectric and lead free piezoelectric materials.

### Design of a piezoelectric rotation actuator

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In order to facilitate active damping within a linear motion system, a self-sensing piezoelectric rotation actuator has been designed. The rotation actuator consists of two piezoelectric stacks that function as linear actuators, embedded in a mechanical interface with several elastic elements, thus allowing for an efficient transformation of linear deformation into rotational motion. Each stack consists of a $d_{33}$ ceramic multilayer actuator and a $d_{33}$ ceramic single layer sensor.

Key issues in the design are:

- the trade-off between strength and stiffness of the elastic elements on the one hand and actuator stroke at the other hand
- appropriate integration of piezoelectric force sensors so as to allow for active damping based on collocated control
- practical mechanical considerations —e.g. gluing, preloading, stroke limitation —so as to ensure correct loading of the piezoelectric actuators

The rotation actuator as such comprises many of the typical design trade-offs as encountered when using piezoelectric elements in a mechatronic application.

### Starbugs: Piezoelectric robots for exploring the universe

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Starbugs are miniature piezoelectric 'walking' robots developed to position large numbers of optical fibres within some of the world's largest telescopes. Their simple design incorporates two PZT piezoceramic tubes to form a pair of concentric 'legs' capable of taking individual steps of less than a micron, yet with the capacity to move a payload several millimetres per second. The robots are able to walk in orthogonal $x$-$y$ directions and also rotate about their centre, providing a flexible platform for positioning many types of payload. The Australian Astronomical Observatory has developed this novel use of piezoelectric actuator to create an entirely parallel positioning system and thus overcome the inherent limitations of existing fibre positioning technology in telescopes, most significantly that reconfiguration times become high for large numbers of fibres. We present an overview of the piezo-driven Starbug project and its potential scientific impact in the astronomical community. We also discuss some of the challenges encountered when designing a system with over one thousand PZT elements, all of which require high voltage drive signals.
There is a growing interest in sensors inside tires measuring pressure, temperature and accelerations, enabling to determine the tire and road status. These sensors need to be small and the energy will be provided by energy harvesting. In this paper, we will discuss the feasibility of using resonant piezoelectric energy harvesters and how requirements translate into piezoelectric properties. Inside car tires, repetitive high amplitude shocks occur every rotation. The seismic mass of the harvester will be excited by these shocks after which the mass will “ring-down” at its natural resonance frequency. During the ring-down period (which increases with increasing quality factor) part of the mechanical energy is harvested. The package of the MEMS energy harvesters is essential both for reliability, in preventing excessive displacements, as well for preventing air damping by the use of vacuum. Therefore, the released MEMS structures are vacuum packaged with a 6-inch wafer level process, using two glass substrates with a cavity depth of 600 μm. The high quality factor harvesters enable continuous power generation of a few tens of μW, sufficient to power a wireless sensor. Using sinusoidal excitation, a power of up to 489 μW has been obtained. An important parameter when choosing either AlN or PZT is the figure of Merit ($e_{31}^2/\tau_{33}^{\prime\prime}$) as it correlates to the harvesters power output. Progress in development of sputtering PZT thin films and its implementation in device fabrication and its characterization will be discussed.
### P.01 The stability of bi-based ZnO varistors

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ZnO varistor ceramics show grossly non-linear I-V characteristics. Bi-based ZnO varistors have been prepared by the mixed oxide route; ceramics were sintered at temperatures in the range 950°C to 1250°C. The oxides of Sb, Co, and Mn were added to improve the non-linear behaviour. The products were characterised in terms of microstructure, current-voltage (I-V), and DC degradation behaviour. Materials were typically 94-98% dense. X-ray diffraction spectra showed the presence of three phases, dominated by ZnO. EDX analysis confirmed the additives were concentrated in or near the grain boundaries. SEM micrographs demonstrate the presence of inversion boundaries in the ZnO grains. The average grain sizes are in the range of 3-55μm. Current-voltage characteristics indicate that the nonlinear coefficients ($\alpha$) are in the range 3-50; the leakage currents ($I_L$) are in the range 6-85μA. Degradation tests revealed that the specimens sintered at 950°C-1150°C survived for 24 h or more whereas ones sintered at 1250°C tended to degrade during the 24-h test. Reasons for differences in the degradation behaviour will be discussed.

### P.02 Structural and magnetic studies of Co$_2$MnO$_4$ and Bi$_x$Co$_{2-x}$MnO$_4$ spinel oxides

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Study and design of new multiferroic materials have been performed because of their technological interest. Structural characterization of Bi-substituted Co$_2$MnO$_4$ systems (Bi$_x$Co$_{2-x}$MnO$_4$, $x$ varying between 0.0 and 0.3) has been done; physical properties are enhanced when Bi$^{3+}$occupies the Co positions and Co$^{3+}$and Co$^{2+}$ ions are distributed over both octahedral and tetrahedral sites, respectively [1]. In Bi$_x$Co$_{2-x}$MnO$_4$, Bi$^{3+}$distorts the oxygen octahedron introducing ferroelectricity and altering the magnetic properties due to the fluctuating valence states of both Co and Mn (Co$^{2+}$/Co$^{3+}$, Mn$^{2+}$/Mn$^{3+}$/Mn$^{4+}$) [2]. We show herein results on samples obtained by a polymeric precursors method and characterized by XRD with Rietveld refinement, SEM-EDX and magnetic studies. Results indicate a cubic spinel structure (Fd3m) with tiny inclusions of magnetic oxides. The zero-field-cooled (ZFC) and field-cooled (FC) modes and the M-versus-H hysteresis loops showed a ferrimagnetic transition which is optimized at the $x = 0.3$ content, with Curie temperatures varying from $T_C = 171K$ ($x=0.0$) to $T_C = 178K$ ($x=0.3$). The M(H) loops performed at various temperatures below the $T_C$ showed a larger loop area when decreasing the temperature, indicating an increased magnetization. These results allow a deeper understanding of the electronic structure and the exchange interactions in oxide spinels, necessary to design multiferroic materials with interesting properties.
The characteristics of composite thin films of molybdenum disilicide $\text{MoSi}_2$ and Si, $\text{MoSiX}$ ($X=2.0-2.2$) have been intensively investigated by the authors because their excellent resistance to oxidation makes them highly suitable for application to heating elements. For $X=2.0-2.2$, the resistivity of the films exhibited a highly linear temperature dependence above approximately 150 K, and was independent of temperatures below this. However, the conduction mechanism has not yet been clarified. Therefore, in this study, the temperature dependence of the resistivity was investigated. Composite $\text{MoSiX}$ ($X=2.0-2.5$) thin films were deposited on sapphire substrates (c-plane) by radio frequency magnetron sputtering. The true resistivity was measured in the range 110-473 K using the four-probe method, the crystal structure was analyzed using X-ray diffraction, and the Hall coefficient was measured at room temperature. The temperature dependence of the measured resistivity values for $X=2.0-2.2$ could be well explained using a combination of the Grueneisen-Bloch formula considering scattering due to phonons and a temperature-independent resistivity component due to scattering by impurities and defects based on Matthiessen's rule. The Debye temperatures were determined to be approximately 1000, 800, and 1300 K for $X=2.0$, 2.1 and 2.2, respectively. A $T^3$ type temperature dependence was substituted for the temperature independent resistivity for $X>2.33$ because the metallic temperature dependence disappeared and the temperature coefficient of resistivity was negative. The Hall coefficient measurements revealed that the main carriers were electron holes for $X=2.0-2.2$, so that the effective mass of electrons was negative.

Electrical properties and Parallel connection of PNN-PMN-PZT step-down transformers

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Electrical properties and parallel operation of step-down PNN-PMN-PZT ceramics transformers is presented in this paper. An important factor affecting the parallel operation of piezoelectric transformer was the resonance frequency, and a small difference in resonance frequencies was obtained with transformers having the same dimensions and fabricating processes. The piezoelectric transformers were found to operate in first radial mode at a frequency of 68 kHz. An equivalent circuit was used to investigate parallel driving of piezoelectric transformers and then to compare the result with experimental observations. The electrical properties, including the output voltage, output power and efficient were measured at a matching resistive load. Effects of frequency on the step-down ratio and of the input voltage on the power properties in the simulation were similar to the experimental results. The output power of the parallel operation was 35 W at a load of 50 and an input voltage of 100 V; the temperature rise was 30°C.
Microstructures and electrical properties of Al$_2$O$_3$ films deposited by aerosol deposition method (ADM) were investigated. The advantages of ADM are room-temperature process, maintenance of raw material’s crystal structure, and a high deposition rate. Heat-dried-Al$_2$O$_3$ sub-micrometer sized particles were mixed with N$_2$ carrier gas, and formed a colloiding aerosol. The Al$_2$O$_3$ particles, which were accelerated to several hundred m/s, were crushed against the substrate, and deposited as a film by scanning the substrate. Film thickness increased in proportion to the scan times or carrier gas flow rate (GFR). The surface roughness of the film increased as the GFR increased. Furthermore, the surface roughness showed a tendency to asymptotically approach a value of approximately 23 nm with increasing the film thickness. It is also confirmed that the center of distribution of deposited particle size shifted from 12 nm to 4 nm, and the width of them became narrow as the GFR increased. The nanometer-sized particles induced that the films had high optical transparency in visible spectrum region. The breakdown electric field for the Al$_2$O$_3$ films deposited using ADM was approximately 66 kV/mm, about 3 times larger than that for bulk Al$_2$O$_3$ produced by sintering. Additionally, no leakage current was observed in all samples with the thickness between 0.25 to 2.8 mm. It means that Al$_2$O$_3$ film deposited by ADM could be low defects, no pin-hole and high-density formation was achieved.

In order to obtain the low varistor voltage for Bi-based ZnO varistors, addition of Ba is effective. The reduction of varistor voltage by addition of Ba is due to promotion of ZnO grain growth. However, the resistance to electrical degradation is poor due to both the abnormal grain growth of ZnO grain and the formation of Ba$_2$Mn$_3$O$_8$. It is expected that the addition of Si improves the uniformity of the grain growth due to the reduction in the surface free energy of grain boundaries of ZnO. In the present study, samples added Bi (0.5 mol%) –Mn (0.5 mol%) –Co (0.6 mol%) –Ba (0.5 mol%) –Si (0–2.0 mol%) to ZnO are fabricated and the correlation between the resistance to electrical degradation and the distribution of impurities on the surface of a ZnO grain is investigated by changing both the amount of added Si and the thermal treatment conditions. The resistance to electrical degradation for the sample added 0.15 mol% Si was improved the most due to the disappearance of Ba$_2$Mn$_3$O$_8$. Two types of deposits were observed on fractured surfaces of ZnO grains for all samples: spot-like and sheet-like deposits. The spot-like deposits mainly contain Bi. The thickness of the sheet-like deposits became thin with increasing the amount of Si. After annealing, the form of deposits changed and varistor voltage might become drastically small. This result suggests that double Schottky-barriers disappeared on annealing.
Besides other metal chalcogenides, the mixed conducting Ag$_2$S is a fascinating prototype material for cation-based switching devices usable for resistive memories. Formation of highly conducting channels can be achieved by polarization voltages applied to thin films. Reversible switching simply occurs by reversing the sign of the voltage. This contribution concerns the electrochemical mechanism during reversible switching based on experiments with newer scanning probe techniques.

Resistive switching was mainly investigated by means of scanning tunneling techniques (STM). Atomic force microscopy (AFM) was hardly used up to now. AFM has the edge over STM, as it does not rely on dc-voltages for imaging which interfere with voltage-induced Ag diffusion and deposition of Ag metal.

In our studies, a substrate with sputtered Ag film on an YSZ wafer was used. A thin layer of Ag$_{2}$S was deposited on this using pulsed laser deposition. Using the novel Scanning Microwave Microscopy (SMM), the contrast between conducting and less conducting domains could be enhanced while studying changes at the sample during and after polarization. The main mechanism for the formation of structures is supposed to be Ag metal deposition which causes the appearance of conducting channels. This is mainly coupled to a preceding supersaturation of Ag in Ag$_{2+x}$S. The present question is whether the Ag needles as conducting channels are the only factor contributing to formation of high conductivity channels. Results of AFM-based measurements with SMM and Kelvin Force Microscopy are presented in this context.

Barium titanate based PTC-material shows an exponential increase of the resistance in a certain temperature range related to the ferroelectric-paraelectric phase transition. As a consequence PTC-based devices can be used as self-regulated heating elements with a reversible switching behaviour.

Until now the geometries of such heaters have been simple cuboids or disks, clamped next to the location to be heated up. Nowadays, owing to the ceramic injection moulding (CIM) technology, free shaped self-regulated heaters can be produced. The advantage of CIM is the production of heaters with appropriate geometric designs to raise the efficiency of the heating process and to reduce energy losses.

In order to find the appropriate design the use of a theoretical model to describe the highly non-linear material properties (e.g. thermistor and varistor effects) and the solid-fluid-heat transfer is mandatory.

In this work, we present some sophisticated product designs for self-regulated heaters as well as some results from theoretical studies. Calculations were done with the Finite-Element-Analysis Software ANSYS and an additional, self-programmed user-routine to take into account the non-linear temperature dependent material properties. Different
geometries were examined theoretically in order to improve the heating properties (e.g. heating rate, heat yield, etc.) and to reduce the electrical voltage. Experimental investigations confirm the results found in the theoretical studies. This study shows that the geometry (e.g. wall thickness, contact designs, etc.) has an essential influence on the efficiency of the heating process.

### Investigation of the conduction processes on the PZT/BaFe12O19 multiferroic system

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Research on materials exhibiting multiferroic properties has attracted the attention of the scientific community in the last decade because of its high potential to be used in the manufacture of electronic devices such as sensors, transducers and storage memories. In particular, composite materials containing both ferroelectric and ferrimagnetic phases can be explored where new properties of great interest can be investigated. In this work the ferroelectric, dielectric and conductive properties were investigated on a multiferroic ceramic system based on the Pb(Zr1-yTiy)O3 (ferroelectric phase) and BaFe12O19 (magnetic phase) systems, obtained from the conventional sintering method. The Pb(Zr0.65Ti0.35)O3 (PZT) and BaFe12O19 (BaM) systems have been synthesized separately and then stoichiometrically mixed in order to obtain the PZT−xBaM multiferroic ceramic samples. Preliminary measurements, based on the structural and thermal properties, were performed in order to confirm the corresponding phases of the pure PZT and BaM systems and the composites. Four series of the composite PZT−xBaM multiferroic composite were stoichiometrically prepared according to the relation x=0, 0.03, 0.04 and 0.05. In addition, a pure BaM sample was included in the analysis in order to get information on the conductive processes and its direct influence on the dielectric properties of the four previous compositions. The dielectric and conductive properties were investigated over a wide frequency and temperature range for all the cases. The results were discussed according to the current theories previously reported in the literature.

### Ba₃Co₀.₇Zn₀.₃Nb₂O₉ microwave dielectric properties optimization by powders synthesis and ceramic heat treatments

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Ba₃Co₀.₇Zn₀.₃Nb₂O₉ ceramics are known for their good microwave dielectric properties (εᵣ = 33.5, Qf = 71 500 GHz @ 6.5 GHz, and θf = 0ppm/°C) and as substitute material of tantalum-based perovskites (BZT). We present a study concerning the three main steps of the ceramic solid route elaboration in order to improve the dielectric properties: starting powders (ZnO, Co₃O₄, BaCO₃, Nb₂O₅) mixing, calcined powders grinding and sintering/annealing heat treatments. Starting powders mixing is optimized by rheological and zeta potential measurements as function of pH and/or surfactant addings. Calcined powders are grinding with a DYNOMill© high energy attrition mill and can reach a specific surface area of 13m²/g. Sintering is studied with temperatures ranging from 1350°C to 1450°C and annealing post-treatments ranging from 1250°C to 1350°C. Structure and microstructure are performed
by XRD analysis and SEM observations. All ceramics are monophased in bulk, but secondary phases can be observed at the surface. The best properties reached $r_\sigma = 34$, $Q_f = 100,000 \text{ GHz @ 6 GHz}$, and $f = 0 \text{ppm/°C}$.

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### Effects of particle size in the titanium dioxide films deposited by electrophoresis on efficiency of dye-sensitized solar cells

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The long diffusion length of an electron in TiO$_2$ thin films as a negative-electrode is one of the critical factors for obtaining the high power-conversion-efficiency (PCE) when TiO$_2$ thin films are used as cathodes in dye-sensitized solar cells (DSSCs). It is possible to lengthen the conduction path of electrons formed by junction of the crystalline lattice between TiO$_2$-particles. However, it is difficult to realize it using the conventional TiO$_2$-particles, such as P25. The TiO$_2$-nanoparticles used in this study can smoothly transport electrons between nanoparticles by junction of crystal lattices due to the oriented attachment mechanism. We have employed electrophoresis to realize it and improve PCE of DSSC. Electrophoresis is an inexpensive process and is possible to uniformly deposit the TiO$_2$ thin film with the desired thickness. However, at this stage, it is difficult to deposit thick films above approximately 2 $\mu$m. This is because the film exfoliates from a substrate in the middle of deposition or drying in air. On the other hand, it is possible to deposit TiO$_2$ thin films with the thickness of more than approximately 10 $\mu$m. Thus, in this study, we examine the deposition of thick TiO$_2$ thin films using simultaneous electrophoresis of TiO$_2$-nanoparticles with small size by classification and P25 by filling up with TiO$_2$-nanoparticles into the matrix formed by P25. The mixture ratio was variously changed. The optical transparency and the PCE of DSSCs increased.

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### TiN/AlN ceramic substrates for high temperature power electronics applications

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Wide band gap semiconductors like SiC, GaN and diamond will constitute a real breakthrough in Power Electronics in the near future. Their unique properties will allow the development of high switching speed, high voltage and high temperature application in harsh environments mainly in “on board applications" like automobile, aircraft, space exploration. Nevertheless, the opportunities given by these components may be reduced since their packages are inadequate as regards insulation, interconnection and thermal management under high-temperature operations and environments. In a classic approach, ceramic substrates as DBC (Direct bonded copper) manage thermal exchange with the environment, assure the electrical insulation and support the electrical conductor that feeds the semiconductor. Metal-ceramic assemblies have a reliability issues at high temperatures, thus we propose a ceramic-only substrate technology, which integrates both conducting and insulating functions. The proposed structure consists of TiN/AlN co-fired ceramics. TiN is well known to be a conductive material and AlN an insulating one, the proposed structure can be used in a very large temperature range (up
to 500°C). The co-firing is realized thanks to a Spark Plasma Sintering (SPS) in a short sintering cycle, that ensures both the quality of the interface and the compatibility of the materials. Electrical properties of the assembly show that these new ceramic substrates can be used for high temperature applications.

Deposition of yttria stabilized zirconia thin films for solid oxide fuel cells by high power impulse magnetron sputtering

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High power impulse magnetron sputtering (HiPIMS) is an emerging technique for thin film deposition. Inherent for this technique is a high fraction of ionization of the sputtered material. This favors the growth of dense films which is of the highest importance in the production of thin film electrolytes for solid oxide fuel cells (SOFC).

In this work, we have deposited yttria stabilized zirconia (YSZ) thin films by HiPIMS and pulsed direct current magnetron sputtering (DCMS) on NiO-YSZ anodes. In both cases, the thin films were deposited by reactive sputtering from a Zr0.82Y0.18 alloy target in an Ar-O2 atmosphere. Films deposited by the two techniques were characterized by scanning electron microscopy, X-ray diffraction, and impedance spectroscopy. Films deposited by pulsed DCMS were found to be columnar and <220> textured irrespective of the value of the applied negative substrate bias. In contrast, films deposited by HiPIMS were columnar and <220> textured at floating potential but as the negative substrate bias was increased to -70 V the films became dense and featureless with no texture. To test the properties of the much denser HiPIMS coatings as SOFC electrolytes, samples will be prepared for cell testing in a fuel cell setup.

Ni-CGO anodes obtained by one-step synthesis: Microstructure and performance

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Anodes for Solid Oxide Fuel Cells usually consist of cermets including one metal (Ni) and one oxide-ion conductor. The microstructural optimization of these cermets is still a critical issue. In this study, a novel one-step sol-gel synthesis method (resins obtained from polymeric precursors are thermally treated to directly produce the cermet powder) is used to prepare nanocomposite Ni-Ce0.9Gd0.1O1.95 (Ni-CGO) cermets. These anodes were screen-printed on dense CGO substrates, fired for adherence and afterwards reduced. Anodes of the same composition prepared from commercial powders are used as reference. The anodes performance is studied by polarization and impedance spectroscopy in the temperature range 650-750°C, in flowing humidified 10% H2+90% N2 gas mixtures, using a three-electrode configuration cell, and by Scanning Electron Microscopy (SEM). The impedance spectra of all anodes reveal two major contributions at high and low frequency, with the overall electrode resistance being dominated by the low frequency impedance. One-step anodes sintered at 1450°C showed an area specific resistance of 0.42 ohm.cm² at 750°C under open circuit conditions. The reference
conventional anodes sintered at 1400 and 1450°C show values far higher under identical experimental conditions. The enhanced electrochemical performance of one-step cermet anodes is mainly attributed to unique microstructural features, namely small particle size (lower than 600 nm) and homogeneous phase distribution, which extends the triple-phase boundary region. These results demonstrate the potential of the one-step synthesis process to manipulate the anode performance by microstructural design.

The influence of indium on the performances of SOFCs based on proton-conducting BaCe_{1-x}In_xO_3-δ

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The influence of amount of indium on the microstructural and electrical properties of proton-conducting electrolyte BaCe_{1-x}In_xO_3-δ (BCIx) was investigated. In-doped BaCeO_3 showed improved sinterability and high chemical resistivity during the testing in CO_2 atmosphere comparing to rare earth doped BaCeO_3. The conductivity measurements revealed higher grain boundary and lower bulk conductivities comparing to rare earth doped BaCeO_3. The anode supported BCIx membranes reached high densities after sintering at 1200°C for 5 h. The mixture of BCIx and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3-δ was used as a cathode during fabrication of solid oxide fuel cells stacks. Fuel cell tests and impedance measurements were performed and the influence of In amount on fuel cells performances were discussed. Fuel cells based on BCIx have maximum power densities more than 200 mW/cm² at 600°C and good stability during long-term stability tests in the working conditions.

Role of gas-phase on the electrical transport properties of ceria-carbonate composite electrolytes

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Ceria-based composites including alkali-metal carbonates emerged as potential electrolytes for low/intermediate temperature fuel cells and selective carbon dioxide separation membranes due to a unique mixed oxide- and carbonate-ion conductivity. However, these composites must perform under various environments, preserving their stability and ionic conductivity, a subject so far deserving little attention. This is the central theme of this work.

Composites based on 50:50 vol% mixtures of cerium oxide and binary alkaline carbonate mixtures (Na_2CO_3/Li_2CO_3, molar ratio of 2:1) were ground by high-energy milling, uniaxially pressed into pellets and sintered at 690°C for 1 h. Composite samples were afterwards (Au) electroded for impedance spectroscopy measurements under pure carbon dioxide and oxygen, also under hydrogen (10 vol%, diluted in N_2), from 300 to 580 °C. Samples were also characterized by X-ray diffraction and Fourier Transform Infrared Spectroscopy to evaluate the impact of exposure to such different environmental conditions. As a general tendency, the conductivity of all samples followed the sequence CO_2>O_2>H_2. This compelling evidence for changes in the concentration and/or nature of charge carriers is discussed based on the positive identification of hydrogen-containing
species after exposure to the latter gas mixture, confirming a complex chemical interaction with the gas-phase.

Recently, intermediate temperature fuel cells (ITFCs), which are operated in the temperature range of 120-300°, have been attracted to researchers because of their higher CO tolerance, faster electrochemical reaction kinetics, etc. Thus, anhydrous proton conductors have been investigated as the electrolytes for ITFCs, such as CSHSO₄ and SnP₂O₇. Then, in this study, the Al- and/or Bi-doped MP₂O₇(M=Zr and Ti) ceramics have been synthesized and characterized by the X-ray powder diffraction (XRPD), fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). The XRPD profiles of the Al-doped ZrP₂O₇ ceramics showed the similar profiles to that of pure ZrP₂O₇ up to 15 mol-% Al-doping whereas the secondary phase was detected when doping 20 mol-% Al. FT-IR measurement revealed that the effects of doping on the proton conductivity could be attributed to an increase in the proton concentration in the bulk. Conductivities of MP₂O₇(M=Zr and Ti) with different Al and/or Bi doping were studied in the temperature range from 100 to 300° in un-humidified air. The conductivity of 15 mol-% Al-doped ZrP₂O₇ was approximately 6.73×10⁻³ S/cm at 140°.

Dielectrically structured pyroelectric composites

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Pyroelectric materials generate a voltage upon a small change of temperature. These materials find wide application in infra red detectors and are generally based on lead zirconium titanate ceramics. The pyroelectric figure of merit (FOM) is proportional to the pyroelectric coefficient, p(T), and inversely proportional to the relative dielectric permittivity, epsilon.

Recently, an unstructured pyroelectric composite made of calcium modified lead titanate ceramic granulate polymer and polyether-ether-ketone (PEEK) high performance polymer has been obtained by hot pressing the ceramic/polymer mixture into the desired composition (Estevam and Washington, RSI (2011)). After polarization with a suitable electric field, a ceramic 60% volume composite film exhibiting a pyroelectric figure of merit three times higher than that of a monolytic lead zirconium titanate ceramic was obtained.

In this work we explored a new method (dielectricphoretic structuring) to create a structured polymer composite. In this pyroelectric granulate composite the particles are oriented into chains. As in the case of polymer-PZT composites, the structuring leads to a significant improvement in performance with respect to unstructured composites. The observed improvements are supported by a physical model.
Nanomaterials have attracted the attention of researchers in the last decade due to their interesting properties. Moreover, there is a wide applicability of these materials in several areas of knowledge, for example, chemicals sensors, solar cells and microelectronic devices, and tests have showed that the use of nanomaterials can make devices faster, more sensitive and consume less energy. In this way we have synthesized tin oxide (SnO) nanobelts using carbothermal reduction process and belts characterization showed they are single-crystalline one-dimensional materials with flat surface and homogeneous size along the growth direction. In this work we have measured the sensor response (electrical response changes) of this material for a reducing gas (H₂) in different temperatures (200-400°C) and with different amount of analyte gas concentration (10 to 500 ppm) using synthetic air as the flow gas. Results showed that sensor signal of SnO sample decreases as the temperature increases, which is related to thermal desorption of analyte from sample surface, jeopardizing the sensor sensitivity. So, for this system, the best temperature for the sensor signal obtained was 200°C. Moreover, it was found that the response time decreases as the amount of analyte increases following an inversely exponential equation, which is related to the amount of analyte molecules in contact with material surface. For this system, the best response time obtained was about 1 minute.

Temperature dependent in-plane impedance spectroscopy measurements were carried out in order to analyze the charge transport properties of functional oxide NiMn₂O₄ negative temperature coefficient (NTC) thermistor films deposited via aerosol deposition techniques onto glass and Al₂O₃ substrates. The in-plane resistivity (R) versus temperature (T) curves of all films were uniform over a large temperature range (180 K to 500 K) and showed the typical exponential power-law behavior associated with variable-range hopping. The R-T dependences of annealed and as-deposited films exhibited power-law exponents p of about 0.6 and thermistor constants B in the range of 3500 K to 5000 K. As-deposited films showed higher p values as compared to annealed films. As-deposited films exhibited also increased B values, leading to increased sensitivity of the resistance to temperature changes, whereas annealed films deposited on Al₂O₃ showed the lowest scatter in differentiated R-T data and might display superior reliability for temperature sensing applications. In plane ac impedance measurements in NMO films proved to enable more precise resistivity determination over a wider temperature range as compared to conventional dc measurements. Therefore, the read-out of the resistivity values from film type NTC thermistor temperature sensors in industrial applications might be performed preferably by inplane low frequency ac fields.
Optimal matching and interfacing of piezoelectric actuators within mechatronic applications

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Successful use of piezoelectric actuators in mechatronic applications depends on three key factors in the conceptual design stage. First of all appropriate quantitative requirements need to be derived. Secondly, the piezoelectric actuator needs to be chosen to appropriately match the performance requirements, within both the available space and the allowed cost budget. Thirdly, the mechanical interface should be designed so as to ensure correct loading of the piezoelectric actuator. The impact of the mechanical interface often necessitates reconsideration of the quantitative requirements and thus leads to iterations in the search for the optimal piezoelectric actuator.

In order to facilitate the iterative analysis and design process, the quantitative requirements can appropriately be expressed as characteristic lines and points in the so-called force-stroke diagram. This diagram allows for a transparent analysis of the key factors in the design problem, and as such for an optimal choice for the piezoelectric actuator in terms of e.g. design space, cost, and energy consumption.

This iterative design approach, with a central role for the force-stroke diagram analysis, will be illustrated for two mechatronic applications:
- a piezoelectric actuated valve, based on a d\textsubscript{31} ceramic multilayer bender
- a piezoelectric stepping device., based on a d\textsubscript{33} ceramic multilayer stack actuator

Development and electrical characterization of conductive Ti —Magneli phases for sensing applications

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This research aims to understand the electrical properties of conductive titanium based Magneli phases (Ti\textsubscript{n}O\textsubscript{2n-1}, 3 <n< 10) fibres and determine the processing factors that influence their properties. TiO\textsubscript{2} powder (99.5%, 0.3 \textmu m) was initially processed in order to obtain green bodies in both tablet and fibre form. The tablets were formed by uniaxial pressing with an average diameter of 10 mm and for the fibres a ram extruder was used with a die of 300 \textmu m. Sintering conditions were optimized to achieve high sintered density and control the grain size and the electrical properties. To produce the reduced Magneli phase, the sintered TiO\textsubscript{2} was subsequently subjected to a carbothermal treatment under an argon flow (typically at 1300°C for 6h). Various reduction conditions were investigated to prevent grain growth during the reduction treatment and observe changes in the electrical properties. The average density of the Magneli phases was 97% of theoretical.

The ac conductivity and permittivity were determined over a broad range of temperature (up to 1000°C for TiO\textsubscript{2} and 375°C for Ti\textsubscript{6}O\textsubscript{11}) and frequencies using impedance spectroscopy. For the electrical measurements platinum, aluminium and silver electrodes were evaluated in order to achieve an optimum electrical contact. The characterization and development of highly conductive Magneli phases materials will enable the production of fine scale, robust devices for novel sensing applications.
Oxygen deficiency and grain boundary-related giant relaxation in Ba(Zr,Ti)O₃ ceramics
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The influence of the oxygen vacancies on the dielectric response of BaZr₀.₁₀Ti₀.₉₀O₃ ceramics prepared by solid-state reaction and sintered at 1400°C for 2 h was investigated. The as-sintered ceramic exhibits a giant relaxation with a shift of the transition temperature from ~85°C to above 170°C in the frequency ranges of 1 Hz to 100 kHz, with high losses above unity and two components in the complex impedance plot. A complex dielectric relaxation response, with at least two thermally activated defect mechanisms with activation energies of ~0.2 eV below the transition temperature and ~0.7 eV for higher temperatures in the range of 85°C-170°C was determined. The observed giant relaxation is an extrinsic effect related to the oxygen deficiency, inhomogeneous distributed in the ceramic grain and not to the relaxor behavior of this system. After a post-annealing treatment at 1000°C for 50 h, the dielectric response is completely changed: the permittivity vs. temperature dependences present maxima located at around T_m=90°C, with almost no frequency dispersion. The conductivity spectra remained almost unchanged after the annealing, showing that the level of oxygen deficiency in this case is related to dielectric relaxations and not to the ac-conductivity dispersion. Two thermally activated dielectric relaxation processes were still identified, below the transition temperature and for higher temperatures in the range of 85°C-170°C. The high frequency relaxation process is almost suppressed by the reoxidation and its activation energy increased with more than one order in magnitude.

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Large electrostriction in Gd-doped ceria
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Doped cerium oxide is one of the most important and extensively studied oxygen ion conductors for solid oxide fuel cell or sensor applications. Recent investigations of the microscopic origin of the elastic anomalies in 20% Gd-doped ceria (Kossoy, Adv. Mat. 2009) indicates that in presence of oxygen vacancies, oxygen ions shifts towards Ce Ce ions. As a result Ce Ce-VO distance becomes much larger than Ce Ce-O bond and the lattice undergoes local distortion. Due to this local lattice distortion [Ce Ce -VO] complex behaves as an elastic dipole and as an electric dipole as well. Therefore, it was expected to reorient under external electric field.

We investigated electrostriction in strain-free {substrate\metal\1μm > Ce₀.₅Gd₀.₅O₁.₉ \thin film\metal} structures by monitoring mechanical response to application of external electrical bias. We found that field-induced stress in Gd-doped ceria is comparable with that of commercial electrostrictors. Low dielectric constant (~24) rules out field compression or relaxor-type electrostriction mechanism. In this view, low relaxation frequency (~180 Hz) and Debye-type relaxation behavior suggests that the electrostriction in doped ceria originates in reorientation of the electro-elastic dipoles.

Proton conducting solid oxide fuel cells provide an option for reducing the operating temperature. Thus, the oxygen reduction at the cathode maintains as the most limiting part of the fuel cell because the overpotential is strongly increased at low temperatures. Therefore, we are investigating the mechanism of the oxygen reaction at well-defined thin film microelectrodes on proton conducting Y-doped BaZrO₃.

Dense, polycrystalline BaZrO₃ substrates with 15% Y-content are used as electrolyte. Thin, dense, polycrystalline films of Ba₀.₅Sr₀.₅Co₀.₈Fe₀.₂O₃₋d and Ba₀.₅Sr₀.₅Fe₀.₈Zn₀.₂O₃₋d are applied by pulse laser deposition (PLD) ranging from 30 to 300 nm thickness. Circular microelectrodes with diameters from 20 to 100 micrometers are obtained by photolithography. Impedance spectroscopy is used to characterize the oxygen exchange kinetics at different temperatures, oxygen and water partial pressures and DC bias.

In general, three contributions are found in the impedance spectra fitted as high (h), medium (m) and low (l) frequency \( RQ \) pairs in series. \( R_hQ_h \) and its intercept are assigned to the bulk and grain boundary feature of the electrolyte. According to their high capacity and strong \( p_{O_2} \)-dependence \( R_mQ_m \) and \( R_lQ_l \) must be related to electrode and electrode-electrolyte interface processes. The \( p_{H_2O} \)-dependence is counterintuitive and not understood yet. In summary, oxygen exchange reaction is more complex on proton conducting electrolytes than on oxide ion conductors because three possible charge carriers must be considered. Determination of the mechanism remains a challenge so far.

\( \beta \)-Ga\(_2\)O\(_3\) has recently attracted renewed attention due to its potential application as a transparent conductive oxide (TCO) in photovoltaics due to its ability to transmit UV-light [1] and as the active material in non-volatile memories due to a pronounced resistivity difference between amorphous and crystalline phase [2]. In both cases, knowledge of the point defect chemistry is critical for optimization of the respective phenomena, but little is known.

In this study we investigated defect behavior of \( \beta \)-Ga\(_2\)O\(_3\) by means of “double oxidation” experiments of the intermetallic compound CoGa. (Oxidation of CoGa results in the preferential formation of \( \beta \)-Ga\(_2\)O\(_3\).) In a “double oxidation” experiment, a sample is first oxidized in natural oxygen and afterwards in an \(^{18}\text{O}\)-enriched atmosphere; subsequently the sample is analysed by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Analysis of the profiles yields information on the dominant point defects and their preferred diffusion path.

The oxygen exchange surface reaction is of interest from a fundamental point of view (mechanistic understanding of an important gas-solid reaction) as well as for applications (performance of SOFC cathodes). While (Ba,Sr)(Co,Fe)O$_3$-d exhibits the highest exchange rates reported so far for perovskites, this material suffers from a detrimental transformation to hexagonal perovskites as well as carbonate formation.

Studies on (Ba,Sr)(Co,Fe)O$_3$-d [1] indicated that not only a high concentration but also a high mobility of oxygen vacancies is beneficial for fast surface exchange. Thus we investigate (Bi,Sr)(Co,Fe)O$_3$-d (BiSCF) perovskites [2], where a high vacancy mobility is expected owing to the large polarizability of Bi$^{3+}$ (and carbonate formation / hexagonal perovskites are absent).

Dense BiSCF films were deposited by PLD on single-crystalline YSZ. This allows to compare the surface exchange kinetics for different cation compositions without interference from varying film morphology (which is expected in case of porous films). Effective rate constants of the oxygen surface reaction are extracted from impedance spectra measured under various pO$_2$ and T. The obtained values for BiSCF are higher than for the respective (La,Sr)(Co,Fe)O$_3$-d perovskites with comparable Sr and Co content. Correlations with bulk properties such as ionic conductivity will be discussed.

the models generally overestimate the actual electromechanical properties of such composites. We have developed a numerical model which is capable of taking into account quantified imperfection parameters for PCMs yielding more accurate predictions of PCM’s properties than the currently available models.

**The ionic conductivity of yttria stabilized zirconia at lower temperatures:**

**Effects of microstructure and local inhomogeneities**

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**Purpose:**

Due to its excellent ionic conductivity, yttria stabilized zirconia (YSZ) is widely used in high technology applications such as SOFCs, SOECs or oxygen sensors. The conductivity of YSZ and its influencing parameters have been extensively investigated at temperatures above 600°C. The lower temperature regime, however, is not that well characterized and literature values partly differ by almost one order of magnitude. The goal of this contribution is the investigation of the influences of microstructural parameters and local inhomogeneities on the ionic conductivity of YSZ at lower temperatures (200-500°C).

**Methods:**

Ionic conductivities were measured at temperatures between 200 and 900°C using impedance spectroscopy. Several monocristalline and polycristalline YSZ samples of comparable doping level were analyzed in a conventional “macroscopic” setup with symmetric, extended electrodes. In addition, on polycrstalline samples spatially resolved conductivity measurements were done by means of micro-electrodes.

**Results and Conclusion:**

At lower temperatures (250°C-400°C) the samples significantly differ in terms of their ionic conductivity despite comparable dopant concentrations. Effects of the thermal pre-treatment on the conductivity will be considered. Moreover, at temperatures about 300°C the capacitive response of the bulk material changes. In case of micro electrode measurements between single grains, resistive and capacitive information on grain boundaries was obtained. Both resistive and capacitive properties are discussed in terms of microstructure and local inhomogeneities.

**The investigation of thickness guided evolution in sol-gel fabricated BiFeO3-PbTiO3 films**

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During the first decade of 21st century, bismuth ferrite (BiFeO3, BFO) must be one of the most favorable research topics because of its unique multiferroic property. Massive BFO derivative materials have been accordingly developed. In our previous work, we have reported the electrical and optical properties of xBiFeO3-(1-x)PbTiO3 (BF-PT) thin films prepared by sol-gel technique [1, 2]. The thickness of these films is between ~200 nm and ~400 nm. Although cheap and convenient, it is not easy to controllably obtain very thin (~10 nm) and thick (~1 mm) BF-PT films with active ferroelectric behavior by normal sol-gel technique. The motivation of this work is to acquire the thinnest ferroelectric effective BF-PT film via sol-gel process and investigate the film evolution with increasing the thickness. With an appropriately adjusted sol recipe, 0.7BF-0.3PT films with thickness
ranging from 30 nm to 1 mm have been fabricated. The variations of morphology, electric and ferroelectric properties of the films along with thickness change are going to be presented in this report. Additionally, phonon dynamics of the BF-PT films is studied by Raman scattering technique to sketch a picture of thickness guided long/short range interaction in the films.


Anisotropy effects on the dc-tunability characteristics of porous ferroelectric ceramics
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The nonlinear dielectric characteristics of ferroelectrics drive them as possible candidates for voltage tunable microwave devices (tunable oscillators, phase shifters, varactors), in which permittivity of hundreds is desired. For preserving high tunability combined with moderate permittivity and low losses, two approaches were proposed: (i) doping with different ions, (ii) forming composites with low-permittivity non-ferroelectrics. Although a desired “dilution” of permittivity resulted in such composites, it was accompanied also by a reduction of tunability. Another method was to produce porous ceramics, for which an interesting “discrepancy” was noticed: a reasonable high tunability was still present, while permittivity was reduced by comparison with dense material. There is still a lack of understanding the correlation between dielectric tunability and porosity characteristics of ferroelectric ceramics.

The dc-tunability properties of anisotropic PZT porous ceramics (with elongated pores) and various porosity levels (10, 20, and 40%) were investigated at room temperature in parallel and perpendicular electrode configurations (relative to the pores orientation). To explain the observed properties, an original model was developed, which takes into account realistic pores microstructures (porosity degree and pore orientation) to determine the local field and the field-induced permittivity, by a combination between finite element method and Monte Carlo model. This approach properly explains the effect of porosity anisotropy on the non-linear dielectric properties in porous ferroelectric ceramics and it has a high degree of generality and applicability to describe nonlinear properties of realistic ceramic microstructures.

Computer simulation studies of the phase stability of the Sr_{n+1}Ti_nO_{3n+1} Ruddlesden-Popper phases
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Atomistic simulation techniques using different sets of empirical potentials are used to examine the stability of phases in the pseudo-binary SrO-TiO_2 system, specifically the perovskite oxide, SrTiO_3, and Ruddlesden-Popper (RP) phases of the general composition Sr_{n+1}Ti_nO_{3n+2}. The different potentials are used to determine the formation energies of the RP phases according to different reaction schemes. The results obtained from the
Simulations are then compared to results of similar simulations from literature as well as with experimental data. As the RP compounds are known to show intergrowths, simulations have been conducted in order to investigate the stability of intergrowths with respect to the pure RP compounds. The SrO partial Schottky disorder energy for strontium titanate is also examined and compared with data from literature.

**Ab initio calculation of cation migration energies in SrTiO<sub>3</sub>**

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SrTiO<sub>3</sub> is a prototypical ABO<sub>3</sub> perovskite-type oxide and often serves as a model system for this broad class of materials. There have been numerous theoretical and experimental investigations aimed at a detailed understanding of the defect chemistry and defect migration. These studies have focussed predominantly on the migration of oxygen ions and protons; in contrast the migration of cation defects has received little attention. The latter plays a key role in the synthesis, preparation and conditioning of perovskite oxides, and also governs the long term behaviour of perovskite samples, such as deformation under applied stress (creep) and degradation under electrochemical potential gradients (e.g. kinetic demixing, interdiffusion). In addition, understanding cation defect migration is essential for determining the suitability of perovskite oxides as hosts for nuclear waste. In this study we performed Nudged-Elastic-Band (NEB) calculations with the plane-wave DFT-code VASP, employing both GGA and GGA+U functionals, to determine the migration energies for cations on the A-site and B-site in strontium titanate. We investigated the migration of the native cations (Sr, Ti) as well as foreign cations (impurities / dopants). Furthermore we examined the effects of defect charge on the migration energetics. The behaviour is rationalised in terms of the valence states and ionic radii of the migrating species.

**The influence of zinc oxide in ceria ceramics on the electronic conductivity**

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**Introduction**

Doped ceria is a material which is already widely used for different applications, such as electrolyte membranes in SOFCs, gas sensor materials and catalytic additives. The influence of doping with transition metals like Co, Fe, and Mn especially on the sinterability of these ceramics has already been studied intensely, as well as their influence on the conductivity. The influence of zinc, in contrast, has not yet been investigated thoroughly, although ZnO is cheaper and mixtures of ZnO and CeO<sub>2</sub> are already used as UV-absorber in sunscreen. A ZnO electron percolation path in the ceria matrix could make a composite material interesting for application as gas separation membrane.

**Experimental**

Ceria-ZnO composite pellets with the composition Ce<sub>1-x</sub>Zn<sub>x</sub>O<sub>2</sub> (x=0.1, 0.2, 0.3) were produced and investigated using a modified Hebb-Wagner method. This technique allows the solitary measurement of electronic conductivity in dependence of the oxygen partial pressure using a platinum micro contact, which is encapsuled with glass paste to prevent ionic movement.
Results
XRD measurements and ion probe investigations showed, that only a small amount of ZnO is incorporated into the fluorite lattice. An increasing electronic conductivity in the n-range with increasing amount of Zn$^{2+}$ has been found. Based on four hypothetical border cases, the theoretical background of the doping effect is explained and compared to actual measurements.

| P.35 | Influence of Zn$^{2+}$ and Co$^{3+}$ addition on the electronic conductivity of doped ceria
| Kerstin Schmale, Sebastian Koops, Mariano Grünbaum, Hans-Dieter Wiemhöfer
| Institute for Inorganic and Analytical Chemistry, University of Munster, Germany, 48149 |

Background
Doped ceria has received much attention in the last years due to its good ionic conductivity at low temperature. To receive dense membranes, doped ceria normally has to be sintered at high temperatures. The improvement of the sinterability by the addition of transition metals has already successfully been tested and it additionally showed only small influence on the total conductivity while the electronic conductivity was significantly increased.

Unlike cobalt, the influence of zinc on the electronic conductivity of doped ceria has not yet been thoroughly tested. In contrast to the small Co$^{3+}$ cation, a certain amount of Zn$^{2+}$ fits into the ceria lattice, leading to acceptor doping of the material and therefore possibly to a reduction of the electronic conductivity while increasing the ionic conductivity. Additionally, Zn$^{2+}$ normally is not prone to redox processes, while Co$^{3+}$ can change its valence in a reducing environment, leading to changes in the electronic conductivity of the material over a range of $p(O_2)$.

Experimental and Results
The electronic conductivity the different samples was measured using a modified Hebb-Wagner method, which allows electronic conductivity measurements at a range of $p(O_2)$. The electronic conductivity of $\text{Ce}_{1-x}\text{Gd}_x\text{O}_2$ and $\text{Ce}_{1-x-y}\text{Gd}_y\text{Pr}_y\text{O}_2$ with and without the addition of 2 cat% of Co$^{3+}$ and Zn$^{2+}$ has been measured and subsequently compared. The influence of the transition metal cations is discussed in terms of a defect model.

| P.36 | Redox and electrochemical behavior of Ce- and Pr-substituted strontium titanates for SOFC anodes
| Aleksey Yaremchenko$^1$, Mikhail Patrakeev$^2$, Oleg Merkulov$^2$, Sónia Patrício$^1$, Jorge Frade$^1$
| $^1$Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, Portugal, 3810-193; $^2$Institute of Solid State Chemistry, Ural Division of RAS, Ekaterinburg, Russian Federation, 620219 |

Stability in a wide range of oxygen partial pressures, moderate thermal expansion and significant level of electrical conductivity under reducing conditions make donor-doped strontium titanates a possible alternative to conventional Ni-based cermets for solid oxide fuel cells (SOFCs). The present work was focused on the evaluation of Ce- and Pr-doped SrTiO$_3$ as components of SOFC anodes with emphasis on the electrochemical activity of porous anode layers and properties relevant for fuel cell applications. Dense ceramic samples of $\text{Sr}_{0.90-x}\text{A}_x\text{O}_{3.10}\text{TiO}_3$ (A = Ce, Pr; x = 0-0.10) with cubic perovskite-like structure were prepared in oxidizing and reducing conditions at 1500-1700°C. XPS studies indicated that cerium and praseodymium substitute into strontium sublattice in mixed
3+/4+ oxidation state. All prepared ceramics exhibit moderate, nearly p(O₂)-independent, thermal expansion (TEC = 11.5-12.0 × 10⁻⁶ K⁻¹) and rather negligible dimensional changes on reduction. Sintering or high-temperature treatment in reducing atmospheres results in significant level of n-type electronic conductivity, which increases with introduction of cation vacancies into Sr sublattice and depends on thermal pre-history of ceramics. At temperatures characteristic for SOFC operation, the transition between oxidized and reduced forms is kinetically stagnated, as indicated by thermogravimetric and electrical measurements, and associated, most likely, with a slow reconstruction of perovskite-related lattice. Submicron powders for anode fabrication were synthesized by Pechini method. The electrochemical activity of porous Sr(Fe,Pr)TiO₃ and Sr(Fe,Pr)TiO₃+Ce₀.₉Gd₀.₁O₂₋d layers in contact with LSGM solid electrolyte was evaluated in atmosphere of diluted wet hydrogen at 600-900°C.

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<th>P.37</th>
<th>Ni/oxide catalyst composites for oxygen reduction electrodes in alkaline media</th>
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<td>Jose F. Monteiro, Andrei V. Kovalevsky, Aleksey A. Yaremchenko, João C. Waerenborgh, Jorge R. Frade</td>
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<td>Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, Portugal, 3810-193</td>
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The electrochemical oxygen evolution reaction (OER) in alkaline solutions is especially important in water electrolyzers, secondary metal-air batteries and chloralkali cells. The electrocatalytic performance of common nickel electrodes is known to diminish with time, raising a challenge for innovative concepts of oxygen electrodes, which may provide lower overpotential, combined with long term physical and chemical stability, at reasonable costs. A potential approach includes the mechanical alloying of composites based on metal matrixes (e.g., Ni) with inclusions of nanostructured electrocatalysts based on transition metal oxides.

In the present work, electrocatalysts were “mechanically activated” in the presence of Ni powders, compacted and annealed at low temperatures in conditions to promote plastic deformation of the metal phase. This method combines advantages of uniform distribution of electrocatalysts within a metallic matrix, with simplicity and low manufacturing costs. The electrocatalysts chosen were mixed-conducting SrFeO₃₋δ- and Ln₂NiO₄₊δ-based materials, owing to their ability to undergo significant oxygen nonstoichiometry changes. Oxygen vacancies and magnetic environment in SrFeO₃₋δ-based samples were analyzed by Mössbauer spectroscopy. Ni/oxide composites containing Sr₀.₁K₀.₉FeO₃₋δ and Pr₂NiO₄₊δ electrocatalysts showed higher OER performance than commercial Ni plates. For Sr₀.₁K₀.₉FeO₃₋δ the overpotential was found to increase with time due to partial leaching of the electrode surface. The influence of electrolyte bath composition on the stability of prepared composite anodes was studied in various conditions.

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<th>P.38</th>
<th>Assessment of electrodes for composite ceria-based carbon dioxide separation membranes</th>
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<td>João R.S. Pereira, Rajesh S. Nair, Filipe M.L. Figueiredo, Fernando M.B. Marques</td>
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<td>CICECO/Ceramic Eng. Dept., University of Aveiro, Portugal, 3810-193</td>
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Selective CO₂ separation from gas mixtures, at 500-600 °C, can be achieved if O²⁻ and CO₃²⁻ ions move in counter flow. Composite membranes, including one ceramic oxide-ion conductor and one mixture of alkaline carbonates, provide the required pathways to
reach this goal. Also, surface reactions between the gaseous species and the ionic species in the membrane can be influenced by the presence of appropriate catalysts or electrodes. In this work, selected materials are tested as membrane electrodes. Composites consisting of mixtures of 50 vol% Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ and Li and Na carbonates were used as reference mixed ionic conducting membrane. Several electrode materials with general formula (La,Sr)MnO$_3$, (La,Sr)CoO$_3$ and (La,Sr)(Fe,Co)O$_3$ were mixed with the composite electrolyte and fired at 600-650 °C to test their relative chemical stability by X-Ray Diffraction. These experiments showed the general superior chemical inertness of materials containing Co. Symmetrical cells prepared with these electrode materials were studied by impedance spectroscopy under variable temperature and in different atmospheres, namely carbon dioxide, air and oxygen. This study was complemented by Scanning Electron Microscopy combined with Energy Dispersive X-Ray Spectroscopy. Results show that LaCoO$_3$-type electrodes have the best electrochemical performance but are not fully stable in CO$_2$ rich atmospheres. (La,Sr)(Fe,Co)O$_3$ electrodes have higher polarization resistance, but are stable under the same conditions. The performance of both ceramic electrodes is much better than that of reference gold electrodes, suggesting their potential for further optimization for the envisaged application.

In the context of our systematic study of grain boundary effects on the electrical conductivity ceria thin films with different doping content, including also donor doped ceria, were grown on various substrates with pulsed laser deposition. Depending on substrate, deposition conditions and dopant the thin films exhibit different microstructures, which were investigated with transmission electron microscopy. The electrical conductivity, its activation energy and oxygen partial pressure dependence, were measured with impedance spectroscopy.

The grain boundary effects were found to dominate the conductivity. As expected, for the acceptor doped samples the conductivity variations are in agreement with a depletion of oxygen vacancies and an enrichment of electrons due to a positive space charge potential. Nanocrystalline samples, consisting of ultra small grains, show drastically enhanced grain boundary effects. These include not only changes in the conductivity by many orders of magnitude but also other unusual effects, such as a switch from ionic to electronic conductivity upon temperature decrease. Notably, depending on the substrate certain samples with a high grain boundary density show a rather high ionic conductivity. In these samples the space charge potential was found to be relatively low, most likely due to changes in the microstructure. As opposed to the results for acceptor doped ceria, in the donor doped material the grain boundaries were found to block the electronic conductivity. Possible origins of the mentioned effects (space charge layer and strain) are discussed.

Bismuth oxide has five known crystalline phases: alpha, beta, gamma, delta and omega, with distinct properties and stability domains. The delta phase exhibits ionic conductivity 1-2 orders of magnitude higher than YSZ (widely used in solid oxide fuel cells) but is stable
only in 750-825°C interval. Outside this temperature range, other phases are stable but their conductivities are up to three orders of magnitude lower. The stability of the delta phase can be extended to lower temperatures by doping, but this process yields a severe reduction in ionic conductivity.

In present work we synthesized Bi₂O₃ films by RF reactive magnetron sputtering using a Bismuth target. We investigate how film's structure is influenced by substrate temperature, source power and oxygen/total gas flow rate ratio. Deposition at ambient temperature yields amorphous films while higher temperature yields crystalline films. Different stoichiometric compositions were obtained by varying the source power and the oxygen flow rate ratio. By tuning all these parameters we obtained cubic Bi₂O₃, with thickness of hundreds of nanometers. XRD shows crystalline films with peaks corresponding to (111) and (222) planes for cubic structure. For these peaks diffractions rings were observed near phi of 70 degree, corresponding to the angle between (111) and (11-1) planes in a cubic structure, consistent with the delta phase. SEM showed columnar structure and a good uniformity. Electrical and optical measurements performed yield a 2.5 eV bandgap and optical constants n ~ 2.5 and k ~ 0.5 for UV-Vis wavelengths interval.

(Ba,Sr)(Co,Fe)O₃-δ perovskites exhibit a high concentration and mobility of oxygen vacancies, which makes them interesting as materials for oxygen permeation membranes and SOFC cathodes. DFT calculations (VASP) were performed for several cation compositions (Ba and Co content) and cation configurations within the cubic supercells to identify the quantities which are responsible for the low oxygen migration barrier [1]. The obtained barriers range from 0.44 eV for Ba₀.₅Sr₀.₅Co₀.₇₅Fe₀.₂₅O₂.₈₇₅ to 0.7 eV for Ba₀.₅Sr₀.₅FeO₂.₈₇₅, in good agreement with experiments [2]. The migration barrier is influenced by geometrical constraints such as the distance between migrating O and the neighboring two A-site and one B-site cations in the transition state (yielding higher barriers for jumps with two Ba neighbors compared to Ba,Sr and Sr,Sr configurations). Interestingly, the decrease of the barriers in the series Ba₀.₅Sr₀.₅CoₓFe₁₋ₓO₂.₈₇₅ with increasing Co content appears to be correlated to the decreasing oxygen vacancy formation energy. This can be interpreted such that a certain transfer of electron density occurs from the oxygen to the B cation in the transition state, decreasing the effective size of the migrating O. The energy of vacancy formation (which also involves electron transfer to the B cations) is then a measure for the energetic cost of this transfer.


Lead zirconate titanate (PZT) is known to suffer from different kinds of degradation including fatigue, aging and loss of insulation resistance. All these degradation
phenomena include complex kinetic processes and are not completely understood yet. Particularly resistance degradation seems to be an effect that could be caused by different, possibly independent processes. In this contribution, we present results on the resistance degradation of donor doped PZT taking place at temperatures between 400 and 550°C. Several methods were employed to analyze location and nature of current paths appearing upon fields of about 100 kV/m after tens or hundreds of minutes. Mechanical removal of near-surface layers revealed the depth distribution of the paths in dependence of temperature, time and field. Conductive mode AFM measurements were employed to further specify and monitor the local distribution of the paths and their relation to grain boundaries. Correlation of the paths with simultaneously appearing precipitates on the surface will also be discussed.

Complex Lithium-oxide compounds are considered good candidates for the breeding blanket (BB) material of controlled thermonuclear reactors. Knowing that the functions of BBs are tritium breeding and energy extraction, the effect of long-term irradiation on tritium release behavior and microstructural changes are of special concern for their design.

The macroscopic conducting behavior by electronic impedance spectroscopy (EIS) and the surface microstructure by scanning electron microscopy (SEM) were analyzed on as-received sintered samples (AR) with different lithium contents (Li$_2$SiO$_3$, Li$_2$Si$_2$O$_5$, Li$_3$SiO$_4$,Li$_6$SiO$_5$) and different matrix (Li$_2$TiO$_3$). The electrical conductivity and the activation energy ($E_a$) were calculated as a function of temperature (297K–1073K) on as prepared and $\gamma$-rays irradiated pellets up to $15*10^6$Gy. At about 600K silica-based samples show a change in slope of AC conductivity in the case of AR and irradiated pellets. Moreover, the $E_a$ values as a function of Li-content changes from 2.56 eV and 7 eV in the AR samples. The effect of a prolonged $\gamma$-irradiation implies the decrease of the $E_a$ and an increase on the permanent electrical conductivity in all samples. These variations are attributed to Li$^+$ ions as the main mobile charge carriers generated by induced microstructural changes and defective status leading to a prevalence of grain boundary resistance over the grain one.

Considering the existing correlation behavior of lithium and tritium diffusion, to better simulate the radiation-induced defects under reactor conditions, EIS is a simple and brief technique that should be performed in an in situ condition under radiation.
shows the increase of electrocatalytic activity with the x=1.5-3.0 mole% addition. The DC conductivity and AC impedance analyses indicate the enhancement of anode function. The obtained MIEC composite anodes are further treated in air and in strongly reducing atmosphere at different sintering temperatures to characterize the Ce-diffusion and substitution in lanthalum doped strontium titanates (LST) lattice to clarify the reduction and oxidation (redox) behavior of Ce$^{3+}$ and Ce$^{4+}$ in the composite anode. The roles CeO$_2$ or reacted compound from CeO$_2$ and LST are identified to the effects on the electrochemical properties of composite anode. The power densities are measured with the prepared composite anode on CeO$_2$-based electrolyte. This half cell exhibits a promising electrochemical characteristics at 700°C.

### Electronic transport properties of (Ba,Sr)TiO$_3$ thin films with blocking and injecting electrodes

Thorsten J.M. Bayer, Shunyi Li, Jan Morasch, Cosmina Ghinea, Andreas Klein

Department of Materials and Earth Science, Technische Universität Darmstadt, Germany, 64287

The interface formation of (Ba,Sr)TiO$_3$ thin films with different materials can be studied by photoelectron spectroscopy with in situ sample preparation via RF magnetron sputtering. The studied energy level alignment of the BST/electrode interface has revealed that the investigated materials can be divided in two groups depending on the barrier height. Besides Platinum which owns a high barrier for electrons there are materials like Indium Tin Oxide (ITO) and Tantalum which are characterized by a negligible barrier height.

This work aims to compare different Pt/BST/electrode systems paying attention to the charge transport through the BST film by means of current-voltage and impedance measurements. There is a variety of differences influenced by the different barrier height. A change in injection mechanism from thermionic Schottky emission (Pt) to ohmic behavior with space-charge limited current (SCLC) (ITO) can be identified by IV measurements. The latter allows studies to determine the carrier mobility of BST thin films. In impedance spectroscopy the low frequency regime is closely linked to the current-voltage characteristics and the space charge leads to a relaxation in the frequency dependence of the dielectric response. The voltage dependence of the impedance reveals a symmetric behavior with Pt whereas an injecting electrode causes an asymmetry which is particularly pronounced at lower frequencies.

### Broad-band dielectric spectroscopy of some dielectric-carbon nanofiber composites

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$^1$Department of Dielectrics, Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic, 18221; $^2$Consejo superior de Investigaciones Científicas, Centro de Investigación en Nanomateriales y Nanotecnología, Llanera, Spain, 33428

Nanocomposite systems based on dielectric and conductor components of sufficiently high contrast in the electromagnetic properties are good candidates for applications due to possibility of tuning their properties. The study of the conductivity and dielectric properties near the percolation threshold is of our primary interest.

Two sets of dielectric-conductor nanocomposites: (Ni,Zn)Fe$_2$O$_4$-carbon nanofibres (CNF) and Al$_2$O$_3$-CNF were prepared by mechanosynthesis using spark plasma sintering in the range of 1-9 vol.% CNF content. Field Emission Scanning Electron Microscopy and X-ray diffraction were used for basic characterization. After that dielectric response in a broad
frequency range $10^{-2}$-$10^{14}$ Hz using standard low-frequency dielectric measurements, microwave open-end coaxial technique, time-domain THz transmission and infrared reflectivity spectroscopy was studied. We found several features which seem to be general for such type of compounds. The increase of the conductivity with CNF content was revealed at all frequencies. Above the percolation threshold all samples display conductivity plateau at low frequencies and this plateau is broadening to higher frequencies with the increase of CNF content. But some irregularities around the percolation threshold in the dielectric/conductivity behavior were also observed and will be discussed.

Low-temperature sintering of NTC thick films and multilayer thermistors

Timmy Reimann, Jörg Töpfer
SciTec, Univ. Applied Sciences Jena, Germany, 07745

NTC thermistors based on NiMn2O4 and substituted spinels are frequently used for temperature control in hybrid circuits. The use of spinel oxides for low-temperature sintering of thermistors requires high sintering activity of the powder and stability of the spinel phase at $T_s \geq 900^\circ$C. We report on NTC thermistor materials for printed thick film NTC thermistors, multilayer devices and integrated LTCC modules. To guarantee densification at $900^\circ$C the shrinkage behavior of the thermistor has to be adjusted by the addition of proper sintering additives. NiMn2O4 is stable from 700°C to 970°C only and readily interacts with sintering additives. As alternative, we investigated the spinel system ZnxNi0.5Co0.5Mn2-xO4 and found cubic spinels between $0.6 \leq x \leq 0.9$ which are stable at low temperature. Addition of liquid phase sintering additives results in complete densification at 900°C. The effect of Cu-substitution into the spinel was also investigated. Dense samples with room temperature resistivities of $80 \Omega \cdot cm$ and a thermistor constant of $B = 2900$ K were obtained. Functional NTC pastes were printed on alumina substrates and post-fired at 900°C. The printed NTC thermistor films have a sheet resistivity of about 280 kΩ/sq and a $B = 3350$ K. Monolithic multilayer devices with NTC behaviour were sintered at 900°C. The cofiring behavior, microstructure formation and electric properties of NTC multilayers will be reported. Moreover, NTC thermistors were embedded in LTCC moduls.

Partial conductivities and chemical diffusion in donor-doped lead zirconate titanate (PZT)

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Institute of Chemical Technologies and Analytics, TU Vienna, Austria

Even in case of donor doping, lead zirconate titanate may exhibit a significant oxygen vacancy concentration. This can be attributed to the only partially controllable loss of lead oxide during preparation. Accordingly, many questions are still to be solved regarding oxygen chemical diffusion and partial conductivities of ions and electrons in PZT. In this contribution, we present results of an impedance spectroscopic study on Nd-doped PZT. Temperature and oxygen partial pressure were varied and corresponding time-dependent and steady state measurements allowed conclusions on the nature of the conducting charge carriers (electrons, holes, oxygen vacancies) and the chemical diffusion coefficients. It will be shown that substantial oxide ion conduction sets in at temperatures above ca. 600 °C and leads to additional features in impedance spectra.
These electrical studies are complemented by 18O tracer diffusion experiments, analyzed by SIMS (secondary ion mass spectrometry). From those we were able to deduce additional information on the ionic conductivity and they also revealed how far grain boundaries are involved in the ionic charge transport.

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<th>P.49</th>
<th>Defect ordering and the conductivity maximum in doped fluorite conductors</th>
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<td>Dario Marrocchelli$^1$, Mario Burbano$^1$, Graeme W. Watson$^1$, Stefan T. Norberg$^2$, Sten Erikson$^3$, Stephen Hull$^3$, Paul A. Madden$^4$</td>
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<td>$^1$School of Chemistry, Trinity College, Dublin, Ireland; $^2$Department of Chemical and Environmental Engineering, Chalmers University of Technology, Gothenburg, Sweden; $^3$Rutherford Appleton Laboratory, The ISIS Facility, Didcot, United Kingdom; $^4$Department of Materials, University of Oxford, United Kingdom</td>
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**Background**

Doped CeO$_2$ and ZrO$_2$ are the most common electrolyte materials for solid oxide fuel cells applications. A typical feature of these materials is that when they are doped with a lower valent cation, their conductivity first increases as a function of the dopant concentration, but then drops sharply for concentrations above 10-15%. The causes of this well known maximum in the conductivity are still under debate. In this presentation, I will review the results of recent experimental and computational investigations that clearly tie this phenomenon to vacancy-vacancy ordering effects.

**Methods**

In this work we combined neutron diffraction and impedance spectroscopy experiments with ab-initio-based molecular dynamics calculations.

**Results & Conclusions**

We found that two defect ordering processes strongly affect the vacancy mobility in these fluorite-structured materials, namely the interaction between a vacancy and a specific cation (cation-vacancy) and that between a vacancy and another vacancy (vacancy-vacancy). These interactions were studied by means of molecular dynamics simulations and we were able to identify the position of each vacancy in the studied system and to isolate the effects of these two interactions on the conduction mechanism. The most striking finding of our investigation is that, contrary to what is generally believed, it is vacancy-vacancy interactions that are responsible for the observed maximum in conductivity and therefore ultimately limit the conductivity of these materials. The consequences of this finding are discussed.

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<th>P.50</th>
<th>Order-disorder phase transformations in heavily doped ceria: Implications for doping strategies</th>
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<td>Juan C. Nino</td>
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<td>Materials Science and Engineering, University of Florida, Gainesville, FL, USA, 32611</td>
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Doped ceria materials are excellent electrolyte candidates for solid oxide fuel cells (SOFC) operating in the intermediate temperature range (400 - 700°C). In order to enhance the ionic conductivity, higher dopant concentrations are routinely used to increase the oxygen vacancy concentration. However, it is known that higher dopant concentrations eventually lead to a decrease in conductivity as a result to defect association that hinders the diffusion of oxygen vacancies. We have shown that a co-doping strategy based on the indifferent dopant concept can eliminate defect association and enhance ionic conductivity thereby opening the door for utilizing higher dopant concentrations. Nonetheless, our recent diffraction experiments have revealed that highly doped ceria exhibits an disorder-order transition at approximately 40% dopant concentration, where
the crystal structure of the highly defective fluorite stabilizes into a C-type rare earth oxide structure with an associated doubling of the unit cell. We show that the transition is mediated by large changes in the shortest O-O distance (e.g., in Nd doped ceria, the distance declines from 2.747 Å to 2.548 Å). By contrasting the Arrhenius behavior of the conductivity (activation energy and pre-exponential values) across the disorder-order phase transformation in the cases of Sm$_x$Ce$_{1-x}$O$_2$δ (0.05 ≤ x ≤ 0.55) and Nd$_x$Ce$_{1-x}$O$_2$δ (0.05 ≤ x ≤ 0.55), we will present a promising crystallochemical criteria for selecting promising co-dopant compositions in ceria based electrolytes.

Several mixed ionic-electronic conducting (MIEC) oxide materials exhibit very good oxygen-ionic and electronic transport properties. In recent years the perovskite Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (BSCF5582) in its cubic phase has been reported by many groups to have outstanding oxygen permeability and selectivity for oxygen/air separation. This makes it a very promising candidate for, e.g., high-performance ceramic oxygen-transport membranes (OTMs) to be used for oxygen production in oxyfuel combustion processes in the absence of carbon dioxide.

The oxygen flux through such a membrane can be increased by decreasing its thickness. However, upon reducing the thickness below a certain “characteristic” membrane thickness, oxygen surface transfer becomes rate-determining. Therefore, a further decrease of membrane thickness results in no substantial increase in the oxygen flux. Hence, oxygen surface exchange has to be enhanced by nanostructuring the gas/membrane interface. This yields a substantial enlargement of the electrochemically active surface area available for oxygen reduction.

To this end, dense BSCF5582 thin film layers were prepared on NdGaO$_3$ single crystal substrates by PVD techniques. Subsequently, a nanoporous MIEC activation layer was added by means of a sol-gel process. The resulting structure has been characterized by transmission electron microscopy (TEM) with regard to microstructure, phase composition, and interdiffusion processes. The effect of surface activation on oxygen exchange kinetics was investigated by conductivity relaxation measurements in the frequency domain, yielding oxygen surface exchange coefficients $k_δ$.

Mixed ionic electronic conductivity (MIEC) in single phase oxides has been shown to decrease electrode resistance in solid oxide fuel cells (SOFCs), especially at lower operating temperatures (~600 °C). MIEC is achieved through the use of non-stoichiometric oxides, where loss or addition of oxygen, with changes in oxygen pressure
and temperature, is charged balanced by formation of electrons or holes, respectively. Changes in stoichiometry under operating conditions not only lead to changes in electrode performance, but are also accompanied by mechanical dilation, termed chemical expansion. Typically, when reducing a non-stoichiometric oxide, it expands, for example, Pr$_{0.1}$Ce$_{0.9}$O$_2$$\times$0.8, a potential SOFC cathode material, exhibits a >200% increase in the effective thermal expansion coefficient upon heating in air. Under the chemical potential gradient of an SOFC, a gradient in non-stoichiometry throughout an oxide membrane and/or electrode can exist resulting in a variation in strain, partially compensated by the generation of stress. As shown in this presentation, large stresses (>500 MPa), derived with the aid of a point defect based model, can develop in a bulk non-stoichiometric oxide upon cooling (or heating) in air. The model is further applied to demonstrate the ability to reduce stresses by appropriate selection of cooling rate and oxygen pressure. Additionally, applying recent atomistic understanding of the origin of chemical expansion in non-stoichiometric oxides, new experimental evidence, based on a doping approach for reducing the chemical expansion coefficient will be presented.

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<th>P.53</th>
<th>Pyroelectricity and mechanisms of conductivity in niobium modified lead zirconate titanate ferroelectric ceramics</th>
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<td>A. C. García-Wong, Aimé Peláiz-Barranco, Yuslín González-Abreu, José de los Santos Guerra</td>
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<td>1Facultad de Física-Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana, Plaza, La Habana, Cuba, 10400; 2Instituto de Física, Universidade Federal de Uberlândia, Minas Gerais, Brazil, 38400902</td>
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Ferroelectric materials, well isolators for their nature, exhibit a temperature dependence of the polarization. When the sample is heating the polarization changes and an electrical current is produced which should disappear at the paraelectric-ferroelectric transition temperature. This behavior is rather evident in the real experimental conditions because of the temperature activates all processes in the materials such as the conductive mechanisms, which can overlap with the pyroelectric response in the i-T dependence. Therefore, is very important a detailed analysis of this phenomenon in the ferroelectric materials in order to separate the different components to the electrical current during the heating of the material. The modified lead zirconate titanate (PZT) is an important system widely used for piezoelectric and pyroelectric devices. PZT systems show a p-type conductivity, where major defects are related to the lead and oxygen vacancies. According to the ionic radius of the modified ions, the substitutions in the A- and/or B-sites should provide lead and/or oxygen vacancies, respectively, in order to maintain the electroneutrality of the unit cell. The present work shows the analysis of the thermally activated processes in niobium modified PZT ferroelectric ceramics, from room temperature up to the ferroelectric-paraelectric phase transition temperature. A theoretical model has been considered to evaluate the i-T experimental data. The results associated to the pyroelectric current and the electrical conduction mechanisms related to the oxygen vacancies are analyzed.
Fabrication of long lanthanum tungstate-based tubes by thermoplastic extrusion for protonic ceramic membrane reactors

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Proton conductors will become a key element of future energy systems—from coal to natural gas and solar energy. In order to develop new manufacturing technology for protonic ceramics to be used in catalytic membrane reactors for synthetic fuel from gas-to-liquid (GTL) processes, long lanthanum tungstate-based tubes was fabricated and characterized by a cost-effective solid-state synthesis and thermoplastic extrusion process. Green powders of La₅.₆WO₁₂₋δ (LWO₅₆), La₅.₄WO₁₂₋δ (LWO₅₄) and La₅.₄W₀.₇Mo₀.₃O₁₂₋δ (LWMO₅₄) were prepared by solid state reaction method using oxide precursors, and the particle size could be easily controlled about for 1 μm by adjusting the time of ball milling. The structure and the average crystalline grain sizes were determined by X-ray powder diffraction and scanning electron microscopy measurements. Tubes with an outer diameter of 10 mm and thickness of 1 mm were produced with carbon black as pore former. The influences of burnout and sintering temperatures on the microstructure, porosity, shrinkage and thermal expansion were investigated in detail. This work indicates that proton-conducting lanthanum tungstates are potential materials and thermoplastic extrusion is a promising technique in producing high quality tubes for catalytic membrane reactors.

Preliminary studies of the manufacture of MAX phase ceramics

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MAX phase ceramics are a novel class of ductile material with the general formula Mn+1AXn-1 (n = 1, 2 or 3), where M is a transition metal, A is an element often of IIIA or IVA subgroup of the periodic table and X is either nitrogen or carbon. These ceramic are attracting significant interest since they are inherently nano-laminated ternary nitrides or carbides and to date there are up to sixty known phases. Their initial discovery and crystallographic analysis was carried by Nowotony in 1960’s but it is only in recent year that they have found major recognition [1]. Academic and industrial interest in MAX phase ceramics increased when MAX phase Ti₂SiC₂ exhibited an unusual combination of both ceramic and metallic character in the mechanical and electrical properties. Recent research has resulted in the discovery of other ternary compounds such as Ti₂AlC and Ti₃AlC₂ which are known to be low density, high electrical conductivity and oxidation resistant compounds in their category [2]. These novel Ti-Al-C systems can be generally prepared by sintering or combustion synthesis. The sintering methods currently employed are pressure-less sintering, electropulse sintering and hot isostatic pressing [3]. This poster will provide an overview of MAX phase ceramics with an emphasis on the synthesis of Ti-Al-C based MAX phase ceramics using reactive processing methods such as combustion synthesis, also known as self-propagating high temperature synthesis (SHS). This work also includes the first analysis of the thermodynamics involved in the synthesis of Ti2AlC Max-phase by establishing a thermodynamic model to calculate the adiabatic combustion temperature (Tad) in the combustion synthesis of MAX-phase material.
Complex oxide heterostructures have attracted a lot of interest recently, while they can be prepared with atomic precision. Using Pulsed Laser Deposition (PLD), one can essentially build artificial crystal structures bottom up, for example, by the depositing heterostructures, where either A, B or both cations are periodically varied in an ABO$_3$ crystal structure. These heterostructure consisting of alternating sheets of material, are typically grown on singly terminated substrates; TiO$_2$ terminated SrTiO$_3$ or ScO$_2$ terminated DyScO$_3$. Surfaces of the mixed variant, showing ordered areas of both AO and BO$_2$ surface termination, are shown in literature to be templates for nanostructured PLD growth of epitaxial SrRuO$_3$ thin film structures of several nanometers in height.

Here we study this growth mechanism, which drives the formation of the epitaxial nanostructures, by employing a kinetic Monte Carlo model. A mixed terminated substrate is simulated by locally adjusting the activation energy for diffusion. Unit cell blocks are allowed to hop on a three dimensional grid, where there hopping probability depends on the number and type of neighboring cells. SrRuO$_3$ is known to be able to grow in a step-flow-like growth mode. Here we show that this high SrRuO$_3$ diffusivity will lead to an enhanced sensitivity to different surface areas. Furthermore the model is used to study and tune the evolution of a variation of different kinetically derived nanostructures.

The room temperature multiferroic material bismuth ferrite (BiFeO$_3$) has attracted a great deal of attention due to the fascinating fundamental physics and potential application for novel magnetoelectric devices. Furthermore, BiFeO$_3$ can be used as photocatalytic material due to its small band-gap. BiFeO$_3$ shows antiferromagnetic ($T_N$ = 370°C) and ferroelectric ($T_c$ = 830°C) ordering and coupling between the two ferroics properties.

We report the synthesis and characterisation of BiFeO$_3$ nanoparticles and the investigation of its magnetic and dielectric properties. Single phase material with the rhombohedral perowskite structure was synthesized via a wet chemical route using bismuth nitrate and iron nitrate as starting materials. The composition and the structure of the BiFeO$_3$ nanopowders have been investigated by powder X-ray diffraction, DSC/ TG and scanning electron microscopy (SEM). Magnetic property tests of the nanoparticles will be shown.
Investigation of the composition-dependent properties of BaTi$_{1-x}$Zr$_x$O$_3$ ceramics prepared via Pechini method

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In this work, BaTi$_{1-x}$Zr$_x$O$_3$ ($x = 0; 0.10; 0.15$ and $0.20$) nanopowders were prepared by the modified Pechini method from titanium isopropoxide, zirconium propoxide and barium carbonate using citric acid as a chelating agent and ethylene glycol as an esterification agent. X-ray diffraction data show the formation of single phase Ba(Ti,Zr)O$_3$ solid solutions, when the polymeric precursors were thermally treated in air at $850^\circ$C/2 hours. As the zirconium content, $x$, increases, the tetragonality degree decreases, so that the unit cell symmetry changes from a tetragonal one, specific to the pure BaTiO$_3$ powder, towards a cubic form, for powder with $x = 0.20$. Dense and microstructurally homogeneous ceramic samples were obtained from the powders after classical sintering at temperatures ranged between $1300^\circ$C − $1400^\circ$C. The impedance spectroscopy analysis performed in the range of temperature $30^\circ$C − $150^\circ$C indicates specific features related to the composition and size effects. A shift towards lower values of the Curie temperature with increasing Zr addition and with reducing grain size was observed. A strong dipolar relaxation is observed for $x = 0.15$ at 105-106 Hz, which can be explained by considering the composition-induced ferroelectric-relaxor transition at room temperature which makes the composition $x = 0.15$ close to the relaxor state, for which non-Debye relaxation in kHz range occurs. The high-field tunability data show that by increasing the Zr addition, multiple polarization components with various weights are responsible for the dielectric and ferroelectric properties.

Characteristics of BaTi$_{1-x}$Sn$_x$O$_3$ solid solutions prepared by the polymeric precursor method

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BaTi$_{1-x}$Sn$_x$O$_3$ ($x = 0; 0.10; 0.15$ and $0.20$) nanopowders were prepared by the modified Pechini method from titanium isopropoxide, tin isopropoxide and barium carbonate using citric acid as a chelating agent and ethylene glycol as an esterification agent. X-ray diffraction data show the formation of Ba(Ti,Sn)O$_3$ solid solutions, free from secondary phases as BaCO$_3$ or Ti-rich oxides, when the polymeric precursors were thermally treated in air at $900^\circ$C for 2 hours. As the Sn content, $x$, increases, the tetragonality degree decreases, so that the unit cell symmetry changes from a tetragonal one, specific to the pure BaTiO$_3$ powder towards a cubic form, for powder with $x=0.15$. The particle average size of the as-prepared powders decreases from 44 nm, for pure BaTiO$_3$, to 22 - 26 nm for the BaTi$_{1-x}$Sn$_x$O$_3$ solid solutions. The microstructural features (density, porosity, grain size and grain size distribution) of the ceramic pellets obtained after shaping and classical sintering at $1300^\circ$C/4 hours, $1300^\circ$C/8 hours and $1400^\circ$C/4 hours, obviously varied as a
function of the sintering strategy. The dielectric and ferroelectric properties of the BaTi$_1-x$Sn$_x$O$_3$ ceramics are strongly dependent on the Sn addition and on the grain size. A ferroelectric-relaxor crossover is induced when increasing the Sn concentration.

Synthesis and properties of weakly agglomerated nanoparticles of M type BHF
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Nanoscale M-type barium hexaferrite (BHF) attracts increasing attention, which is caused by the creation of a novel generation of multifunctional materials. Particularly, nanoscale M-type BHF is promising for high-density data recording and storage systems, MW devices, multiferroics, biomedical applications.

The ability to control the shape anisotropy, weak interaction between particles and high values of magnetic characteristics are the main requirements to BHF nanoparticles. It is known that fractal aggregates of nanoparticles affects on their agglomeration and properties.

The aim of this work is to study the effect of fractal structure on ferrite formation, particles morphology and magnetic properties of nanoscale M-type BHF.

Precipitation from solutions and sol-gel technique were used for samples preparation. Small-angle X-ray scattering, X-ray diffraction, transmission electron microscopy and magnetic measurements were used.

The obtained precipitates are characterized by the presence of mass and surface fractals. In this case, a significant decrease in the temperature of single-phase BHF synthesis (down to 1223 K) and production of weakly agglomerated, monodisperse nanoparticles (d = 60 nm) with plate-like shape anisotropy and good magnetic characteristics ($M_s = 68.7$ emu/g and $H_c = 432.9$ kA/m) were observed.

The sol-gel samples are characterized by the presence of surface fractals. The ratio of gel-forming components (citric acid and ethylene glycol) affects the on sample fractal structure. The nanoparticles of BHF were shown can to be prepared with plate-like ($d_{av} = 65$ nm) and rod-like ($d_{av} = 30$ nm, $l_{av} = 70$ nm) shape anisotropy.

Blue light excited nanophosphors synthesized by soft wet methods
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Solvothermal is a feasible method to synthesize nanophosphors with various morphologies and well crystallization. The blue light excited yttrium oxides nanophosphors were prepared by microemulsion combined isopropanol-solvothermal (MIS) process. The morphologies were determined by the added surfactant, pH value and centrifugation runs. The well-crystallized Y$_2$O$_3$; 9 mol% Eu nanophosphors were obtained from 180C/24 h along with 500C/2 h heat treatment. The 611 nm red emission was excited by 466 nm blue light to show high photoluminescence (PL). Furthermore, the more iso-morphological yttrium oxides were obtained by the urea-hydro-deposition (UHD) method. Those hydrolyzed nanophosphors possessed nearly isotropic particles after 80C water bath heating for 2 h. Such nanophosphors prepared processing might keep the small phosphor particles about 80 nm without much growth even post-heat treatment upto temperature of 1000C. Combine the MIS and UHS processes, the well crystallized and isolated red and green yttrium oxides nanophosphors could be achieved.
with high photoluminescence excited by blue light for applications in LED and LCD industries.

We have investigated the processing of Pb(Zr0.53Ti0.47)O3 (PZT) thick film structures by piezoelectric ink-jet printing. To perform jettablety of the ink particles must be well dispersed in a solvent and particle size must be 50 times smaller than cartridges' nozzle size. For particular ink-jet printer the viscosity and surface tension of the ink must be 10 mPas and 30 mN/m, respectively.

Micrometer sized PZT powder was stabilized in water with polyacrylic acid (PAA). To reduce the particle size we milled the suspensions in a colloidal mill at pH 10. The influence of milling conditions on particle size and stability of the suspension will be reported. Suspensions containing 15 vol. % PZT and optimal amount of PAA milled for 10 h exhibited d50 of 210 nm and d100 of 580 nm what is appropriate for printing. The viscosity, surface tension and drying of the ink were optimised by PZT solid load, addition of non-ionic amphiphiles and binders.

The successful jettability of PZT water-based ink was demonstrated on Pt-electroded Si/SiO2 and Au-electroded Al2O3 substrates. The influence of jetting amplitude and temperature on the drop formation will be discussed. The sintering procedure of samples deposited on alumina substrate was optimised with regard to sintering temperature and time. The structural, microstructural and functional response of sintered PZT thick-film structure will be reported.

Double perovskite Sr2FeMoO6 was prepared by various methods including sol-gel technique, solid-state reaction method and coprecipitation method. The resulting powders from gels and precipitate precursor showed microstructures consisting of nano-sized grains and a crystalline perovskite structure. The structural and microstructural properties of the double perovskite powders prepared by different routes ware compared. Targets for pulsed laser deposition (PLD) deposition were prepared from these powders and characterized.

Recently there has been great interest in fabrication of flexible piezoelectric MEMS-based devices. New technologies are enabled by the availability of flexible, irregularly shaped, or very large MEMS (sensor skins covering an airplane wing, an energy generator implanted into a shoe, adaptive texture surfaces, phased array pressure sensors, etc.). In this work, two approaches are taken to integrate Pb(Zr1-xTix)O3 (PZT) thin films on flexible metallic substrates. First, ion beam assisted deposition (IBAD) is used to deposit a biaxially
textured MgO template upon a 100 µm thick metal ribbon. 300-500 nm thick PZT is epitaxially integrated with this substrate using chemical solution deposition and pulsed laser deposition (lattice matched conductive oxides are used as a bottom electrodes). The PZT exhibits in-plane FWHM values of ~4.1° and out-of-plane FWHM of ~1.8°. A fine grained morphology is seen, with very square hysteresis response having remanent polarization up to 40 µC/cm². Switching Spectroscopy Piezoresponse Force Microscopy (SSPFM) showed definitive switching behavior with d33 up to 80 pm/V. The second approach directly integrates polycrystalline PZT onto 50-100 µm thick Cu foil substrates. PZT is rf-magnetron sputtered at room temperature and subsequently crystallized in controlled oxygen partial pressure. This crystallizes the PZT while preventing Cu oxidation. Typical 500 nm thick PZT films on Cu display remanent polarization and coercive fields of ~30 µC/cm² and ~75 kV/cm. The dielectric constant and loss were typically 700-800 and 5-6%. Initial SSPFM measurements indicate definitive switching behavior.

A barium titanate ceramic was prepared using a conventional solid-state reaction method. The conductivity of the ceramic samples was achieved by a high-temperature treatment in a reducing atmosphere. A positive temperature coefficient of the electrical resistivity (PTCR) of five orders of magnitude was obtained in a composite ceramic composed of highly Mn-doped BaTiO₃ grains and pure BaTiO₃ grains. The sintering temperature, the amount of manganese in the doped BaTiO₃ grains and the composition of the composite were optimized in order to obtain a composite ceramic with a remarkable anomaly in the electrical resistivity at the Curie temperature. Dielectric measurements, impedance measurements, microstructural analyses, scanning electron microscopy, XRD powder diffraction, dilatometry and electrical measurements were used to characterize the materials that showed the PTCR effect.

Piezoelectric materials have attained significant attention in recent years, especially with regard to the development of lead-free piezoceramics intended to replace the state of the art PbZrₓTi₁₋ₓO₃ materials. One of the most investigated materials is the perovskite BiₓA₁₋ₓTiO₃ (A = K, Na, Li) with various dopants on A- and B-site.¹ The work described herein comprise the synthesis and characterization of the system Bi₀.₅(NaₓK₁₋ₓ)₀.₅(ZrₓTi₁₋ₓ)O₃. The materials were synthesized by the solid state reaction method. The phase purity and crystal structure were investigated by X-ray diffraction (XRD), and phase transition in the system was investigated by a combination of differential thermal analysis (DTA) and high temperature XRD. The materials were also characterized with respect to dielectric/ferroelectric properties by dielectric spectroscopy and ferroelectric measurements.

Degradation analysis of the SnO₂ and ZnO- based varistors using electrostatic force microscopy

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The degradation phenomena of ZnO and SnO₂- based varistors were investigated using continuous tension with temperature increments and degradation with pulsed currents 8/20 μs (lightning type). The degradation was monitored by means of electrical behavior (I vs V), structural aspects by X-Ray Diffraction and microstructural aspects by scanning electron microscopy. Electrostatic Force Microscopy was used to analyze the surface charge accumulated at grain boundary region before and after degradation. Before the degradation process the SnO₂ system has 85% of effective barriers and ZnO system 30%. Both systems showed changes in the electrical behavior when degraded with pulses. In the case of the ZnO system, the behavior after the degradation with pulses was essentially Ohmic due to the destruction of the barriers (about 99% of the interfaces are conductive) generated by phase changes, diffusion of metastable defects and presence of macrostructural failures (cracking and/or puncture). After the degradation with pulsed current the SnO₂ system still present non-Ohmic behavior with a decrease in the quantity of effective barriers (from 85% to 5%), however, when the degradation is accomplished with continuous current, SnO₂ system exhibit minimum variation. This result indicates the existence of metastable defects of low concentration and/or low diffusion in the SnO₂ system. High energy necessary to activate diffusion processes that generate the degradation of the potential barrier due to defect annihilation in SnO₂ system.

Low-temperature sintered MgO ceramic with low-dielectric loss and near-zero temperature coefficient of resonant frequency

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The low-temperature sintered microwave dielectric ceramics is considered to be one of the essential materials for the application to the multilayer integrate circuit components. Thus, many attempts have been carried out to reduce the sintering temperatures of the dielectric ceramics by the addition of sintering aids. Thus, a variety of the microwave dielectric properties of low-temperature co-fired ceramics (LTCCs) have been reported to date. In addition to the reduction of the sintering temperature of the dielectric ceramics, the LTCCs which have a low dielectric constant and a high quality factor may be suitable for the application to the high-frequency devices. In order to reduce the sintering temperature of MgO, the addition of LiF addition as a sintering was performed and the microwave dielectric properties of the (1-x)MgO-xLiF ceramics were characterized in this study. The (1-x)MgO-xLiF ceramics (x=0.01-0.25) were synthesized by the conventional solid-state reaction method and sintered at 925-1100° for 4h in covered crucible. The (1-x)MgO-xLiF ceramics were successfully sintered at 950°; therefore, the ε, and Qf values of 0.95MgO-0.05LiF ceramic were 9.7 and 115,000 GHz, respectively. From the refinement of the crystal structure of LiF-added MgO ceramic, it was found that the small
amounts of Mg\(^{2+}\) cation in MgO lattice were replaced by Li\(^{+}\) cation. The Q\(_f\) values of the ceramics were extremely improved by heat treatment at 900\(^\circ\)C (Q\(_f\) = 228,000 GHz).

The ceramic-polymer composites have been demonstrated lighter, more flexible and more mechanically robust than bulk ceramics. Lead zirconate titanate (PZT) ceramic powders combining boric acid and polyvinyl alcohol (PVA) were extruded by a pressured syringe to form piezoelectric fibers through the condensation of boric acid and PVA. The PZT fibers were obtained at the sintering temperatures of 1200-1250\(^\circ\)C under the PbO protected atmosphere. The 1-3 type composite fibers were made by the prepared and sintered PZT fibers along with passive polymers under curing. The dielectric constant of 1-3 composite increased with the PZT fibers volume percentage in the polymer matrix, such as K\(_{2300}\) at 1 kHz after poling for 78 vol% PZT fibers, typically. However, the dielectric constant varied not so much for different diameter of fibers in the composite. The remnant polarization and saturation polarization decreased with the volume content of PZT fibers but the coercive fields changed slightly for different PZT fibers volume percentage in composite. If the composite precursor only contained PZT powders and PVA without boric acid then was extruded and pulled through boric acid solution, the obtained composite fibers might enhance their mechanical strength and circular degree. Those boric acid solution strengthened fibers then increased the workability. The modified 1-3 composite fibers are a promising actuator such as a panel speaker.

Barium tantalate-based perovskite ceramics were prepared by conventional solid-state reaction method. The Ba\((X\frac{1}{3}Ta\frac{2}{3})O_3\) (X=Mg, Zn) samples were sintered in air at temperatures of 1550\(^\circ\)C, 1600\(^\circ\)C, and 1650\(^\circ\)C for 4h. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were employed for morphological and structural characterization of Ba\((X\frac{1}{3}Ta\frac{2}{3})O_3\) (BXT) sample. The broadband frequency behavior of the complex dielectric constant was investigated in the 1 Hz - 5 THz range through 4 measurement techniques. The low frequency dielectric spectra were carried out on BXT parallel-plate capacitors by using a Novocontrol Alpha Analyzer and an Agilent E4991A RF Impedance Analyzer. Microwave dielectric parameters of BXT resonators were obtained by means of the Hakki-Coleman method. An Agilent E8361A PNA Network Analyzer was employed for microwave measurements. Millimeter wave and terahertz transmission spectra were measured with an Aispec pulse IRS-2000 Pro time-domain spectrometer. The frequency dispersion of dielectric constant is rather small from 1 Hz to about 100 GHz. However, around 1 THz, the permittivity of both types of BXT samples rapidly increases with the increase of the frequency. The microwave dielectric constant of the resonators was 24 for Ba(Mg\(_{\frac{1}{3}}\)Ta\(_{\frac{2}{3}}\)O\(_3\)) and 28 for Ba(Zn\(_{\frac{1}{3}}\)Ta\(_{\frac{2}{3}}\)O\(_3\)) samples. The temperature coefficient of the resonance frequency (0 < \(\tau_f\) < 6 ppm/\(^\circ\)C) measured in
microwave domain was in a good agreement with the value estimated from temperature
dependence of the capacitance at low frequency.
Abstracts poster presentations  
Tuesday, June 26 (16.00-18.00h)

P.71  
Sintering and properties of ceria-based electrolytes with Zn as sintering aid  
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Ceria-based electrolytes are amongst the most promising oxide-ion conductors for SOFC, due to their high ionic conductivity with respect to traditional zirconia-based electrolytes. Sintering of ceria-based solid solutions usually requires high temperatures, which justified a large attention to alternative processing or compositional approaches to avoid this problem. In this work we report the impact of Zn additions to gadolinium doped ceria (CGO). Starting materials included three commercially available CGO powders. In all cases, 0.4 mol% ZnO was introduced as sintering aid. The ceramic samples were shaped both by powder pressing and slip-casting, and afterwards sintered following a two-step profile. Samples were studied by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Impedance Spectroscopy (IS) in air. XRD and SEM provided no evidence for the presence of secondary phases, which might be inconclusive given the low dopant amount. The impact of Zn-additions on densification was significant allowing peak sintering temperatures in the order of 1000°C to reach densifications in excess of 95%. IS data showed the usual characteristics, with significant grain boundary impedances but still lower than the bulk impedances even at low temperature (250°C). Overall conductivity results, including low temperature activation energies in the range 0.8 to 0.9 eV, match the corresponding values for Zn-free samples. This suggests that Zn-additions have a positive role on sintering without the formation of ion-blocking grain boundaries, thus resembling Co-doped CGO rather than materials based on other sintering additives like Ga.

P.72  
Searching for better nano-piezoelectrics by combined strain and composition tuning  
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We have investigated thin films of the ferroelectric PbTiO₃. Substituting Pb⁺⁺ by Sr⁺⁺ cations allows us to tune the lattice parameter of the films and thus the strain induced by the substrate. Theoretical predictions of the PbTiO₃-SrTiO₃ solid solution grown under strain on single-crystal (110)-oriented DyScO₃ substrates show a phase transition as a function of composition[1]. Boundaries between different crystal phases are expected to show enhanced piezoelectric properties, similar to the well-known piezoelectric PZT. Commercially available DyScO₃ substrates are good candidates for these experiments, as the PbTiO₃ and DyScO₃ lattices match perfectly at the growth temperature. We have studied the combined influence of epitaxial strain, compositional variation, film-to-substrate clamping and size effects on the properties of these ferroelectric films.

A series of thin films with various compositions of Pb₅Sr₄₋ₓTiO₉ have been grown by Pulsed Laser Deposition on (110)-DyScO₃ atomically flat surfaces[2]. To maintain the films fully strained, the film thickness is chosen to be ~12nm. In order to measure piezo-
response of the ultra-thin films, the clamping of the film to the substrate has been limited by reducing the lateral size. Electron Beam Lithography was utilized to prepare series of capacitors. Finally, piezo-AFM was used to measure the local piezoelectric response of the capacitors and its size-dependence.


Investigation of Zr-doped BSCF perovskite membranes for oxygen separation in the intermediate temperature range
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One of the most promising mixed ionic electronic conducting materials (MIEC) for oxygen separation is the cubic perovskite (Ba$_{0.5}$Sr$_{0.5}$)(Co$_{0.8}$Fe$_{0.2}$)O$_3$-δ (BSCF), because it exhibits a good phase stability next to excellent oxygen permeabilities at temperatures above 900 °C. Nevertheless, at intermediate temperatures (500-800 °C) the oxygen flux decreases dramatically which is caused by phase transformations of the cubic perovskite structure. To improve the phase stability of the cubic structure, the B site was doped with zirconium cations. A series of (Ba$_{0.5}$Sr$_{0.5}$)(Co$_{0.8}$Fe$_{0.2}$)$_{1-x}$Zr$_x$O$_3$-δ perovskite-type materials with $x = 0.01$-0.09 (BSCFZ) was successfully synthesized by a combined ethylenediaminetetraacetic acid and citric acid method. X-ray diffraction and transmission electron microscopy investigations indicate the formation of single phase BSCFZ cubic structure with $x \leq 0.03$. With a higher Zr-content the formation of Zr-rich phases in the grain boundaries and in the grains itself was observed. A long-term oxygen permeation experiment at 750 °C for 180 h has shown a slight improvement of oxygen flux for BSCFZ membranes with $x \leq 0.03$. The cross-sections of BSCFZ membranes before and after the long-term oxygen permeation measurements were analyzed by different scanning electron microscopy techniques, and a decrease of cubic phase transformation was observed. The XRD analysis of the oxygen supply (feed) and oxygen release (permeate) side of BSCFZ membranes signals an affected formation of hexagonal and trigonal phases under oxidizing conditions.

Synthesis and ferroelectric properties of M (M=Fe, Cr, Mn, Co and Ni)-doped KNbO$_3$-based lead-free ceramics
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The $M$ (M= Fe, Cr, Mn, Co and Ni)-doped KNbO$_3$-based lead-free ceramics were synthesized and the effects of the $M$ additions (0.1-0.9 mol%) on the crystal structure and the ferroelectric properties of KNbO$_3$-based lead-free ceramics were systematically investigated in this study. The $x$ mol% Fe-doped ($K_{0.474}Na_{0.474}Li_{0.052}$(Nb$_{0.948}$Sb$_{0.052})$O$_3$ (KNLNS) ceramics were synthesized by the conventional solid state reaction method, using high purity K$_2$CO$_3$, Na$_2$CO$_3$, Li$_2$CO$_3$, Nb$_2$O$_5$, Sb$_2$O$_3$ and Fe$_2$O$_3$ powders. These ceramics were sintered at the temperatures ranging from 1070 to 1095 °C for 3h in air. The crystalline phase and microstructure of the ceramics were investigated by using the X-ray powder diffraction (XRPD) and the field emission scanning electron microscopy (FE-SEM), respectively. The $P$-$E$ hysteresis loop and the temperature dependence of dielectric constant at 1MHz were also evaluated in terms of the AxiaCCT TF-2000 analyzer and LCR
meter, respectively. The XRPD profiles of KNLNS ceramics sintered at 1070° showed a single phase, whereas the secondary phase was detected at the compositions higher than x=0.1. As for the ferroelectric properties of Fe-doped KNLNS ceramics, the $P_r$ values of the ceramics were enhanced by a small amount of Fe-doping, ranging from 13 to 26 C/cm$^2$, whereas the coercive field of the ceramics decreased from 14 to 11 kV/cm. As a result, a well-saturated $P-E$ hysteresis loop of Fe-doped KNLNS ceramics was obtained at x=0.5 and the $P_r$ value was 28 C/cm$^2$ at the applied electric field of 50 kV/cm.

A relation is established between the domain fraction, the domain inclination and the substrate-induced strain of epitaxial PZT thin films, in the tetragonal phase towards the morphotropic phase boundary (Zr-content 1-x=0.2, 0.4, 0.45). The substrate-induced strain is controlled through thermal expansion coefficient mismatch between film and the silicon, KTaO3, DyScO3 and SrTiO3 substrates. A poly domain structure is found by reciprocal space mapping and piezo force microscopy, for which the domain fraction depends strongly on strain, while the lattice strain remains constant. The concept of the effective substrate and a new model based on geometrical arguments is used to derive the volume fraction directly from the lattice parameters. A fit to the x-ray diffraction intensity data is found. Next to the tilted a and b-domains, we observe c-domains which are tilted in both the a and b-direction. The same geometrical model describes this simultaneous buckling of in-plane and out-of-plane domains as function of strain. Furthermore, indications for an increase of the domain-wall width as function of Zr-content have been obtained.

Enhanced Phase Miscibility and Luminescence of Ce$_{1-x}$Eu$_x$O$_{2-\delta}$ by excess oxygen vacancies

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Cerium oxide (CeO$_2$) has many practical applications, such as an electrolyte in SOFC, catalyst for exhaust gas treatment, and oxygen gas sensors. Recently, there has been a strong interest in understanding phenomena associated with the nanostructured ceria because of a potential to be used in new frontiers such as catalyst for hydrogen production and biomedical applications as radical scavenging antioxidants and biological labels. Nanostructured CeO$_2$ has been prepared by various methods such as sol-gel synthesis, chemical precipitation technique and electrochemical deposition. This work reports a novel manufacturing process that can provide the same unique effects arising from the nanostructured particles such as the increase of solubility limit, production of oxygen vacancies, and the increase of Ce$^{3+}$/Ce$^{4+}$ ratio in a form of bulk Ce$_{1-x}$Eu$_x$O$_{2-\delta}$ powder. This process can not only enhance the luminescence efficiency of Ce$_{1-x}$Eu$_x$O$_{2-\delta}$ drastically and but also expand the solubility limit of Eu$^{3+}$ to x = 0.7. Hence the complete miscibility between CeO$_2$ (Fm3m) and Eu$_2$O$_3$ (Ia-3) can be obtained by this process. This wide miscibility ceramic can enhance the functions of cerium oxide in a wide
range of applications such as an electrolyte in SOFC, catalyst for exhaust gas treatment, and biomedical labels.

For LED lighting systems thermal management is one of important issues especially for the packages using high power LEDs. Most LED failures originate from elevated junction temperature; light-output decreases with temperature, CRI shift with temperature, and LED chip degradation. For heat dissipation capability of LED package either heat slug or heat sink are commonly being used. Several types of TIM are in usages such as metal core PCB, Al metal substrate, and ceramics (AlN). Diamond has the highest thermal conductivity (20 W/cmK) among the materials present in the world. Aluminum and copper have also relatively high thermal conductivity (2.4 ~ 4.0 W/cmK). Aluminum has a low specific density (2.64, Al) than metal Cu or the ceramics such as AlN and Al2O3. In this study the composite materials of diamond and metals such as Cu and Al are manufactured and the thermal properties such as thermal conductivity and diffusivity were characterized by using Laser Flash Method. The thermal conductivity of the diamond-aluminum composites were calculated by using thermal analysis software-tools, i.e., STAR-CD and ANSYS. The simulated results and the experimentally measured properties will be presented.

CaMnO3 is one of the main compounds studied nowadays as an electron-doped thermoelectric (TE) oxide materials. The CaMnO3 compared to other oxides offer the possibility to prepare the fine particle size. In addition this compound is suitable for high temperature applications because his chemical and thermal stability and oxidation resistant in air.

The solid solution Ca1-x(RE)xMnO3 ( where rare earth, RE= Bi, Dy, Sm and Yb) perovskite structure, highlights a n-type behavior and exhibits the interesting thermoelectric properties. But the challenge remains to reduce the thermal conductivity, which can be done by nanoparticles synthesis, grain growth control. Basically, we focused our work on the synthesis of calcium manganite by flash combustion route. The wet chemical combustion methods of preparing ceramic nanopowders offer an alternate route to overcome the drawbacks of chemical methods. The advantage of this synthesis method is the possibility to obtain reactive powders in shorter time with better purity, homogeneous, fine particle size and low temperature sinterability.

In this work, we report a study of such rare-earth doped CaMnO3. The microstructure and the chemical composition of all samples were examined using a scanning electron microscopy (SEM) coupled to an X-ray energy dispersion detector (EDX) for composition analysis. The X-ray diffraction method was used to analyse the phase and crystallographic
structure of the samples. The temperature dependence of thermoelectric properties was measured from 300 to 973 K and the RE-dopant effects were investigated.

An impedance spectroscopy method, by using an Agilent E4991A RF Impedance/Material Analyzer, was employed for the determination of radiofrequency and microwaves electric characteristics of high permittivity ceramics such as BaTiO₃, Pb(Zr,Ti)O₃-based single phase, and PZT-ferrite composites. Resonances were observed experimentally in the frequency range of 100 MHz – 1 GHz. So, the ceramic samples were considered as dielectric cylindrical resonators characterized by fundamental TM₁₁₀ and by the TM₂₁₀ resonance modes. The specified material analyzer is designed to work properly in certain permittivity - frequency domains, for samples having the dimensions closed to the measuring head’s electrodes diameter. Getting out from these requirements, as for higher than 500 relative permittivity materials and for frequencies higher than 100 MHz, induces big errors on the directly measured values of the permittivity and permeability. Evaluating the resonance frequencies of high permittivity ceramic samples considered as dielectric resonant cavities is very useful in determination of the “true” value of the effective complex permittivity of a given material, in measurements as Impedance Spectroscopy, Frequency Domain Reflectometry FDR and Time Domain Reflectometry TDR. The work also presents a detailed model for calculating the needed corrections, starting with the high frequencies data obtained by using the specified Impedance/Material Analyzer and the low frequencies data obtained by using the SOLATRON 1260A system, the condition of continuity at 1 MHz and the high frequencies resonances of the measured high permittivity ceramic samples.

Acknowledgements: This work was financial supported by the Projects: POSDRU FSE-POSDRU 89/1.5/S/49944 and CNCS-UEFISCDI Project No. PN-II-ID-PCE-2011-3-0745.
effect of sintering temperature on relative density and the temperature dependence of dielectric properties are further investigated.

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<th>P.81</th>
<th>Evaluation of the polarization state of embedded piezoceramics by charge monitoring during periodic heating</th>
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<td>Agnes Eydam, Gunnar Suchaneck, Gerald Gerlach</td>
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<td>Solid State Electronics Lab, Technische Universität Dresden, Germany, 01062</td>
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The pyroelectric coefficient depth profile (or polarization distribution) of ferroelectrics is usually determined by thermal wave methods (TWM) analyzing the pyroelectric current spectrum. A serious limitation of TWM is the lack of broadband preamplifiers for current signals in the order of 1 nA provided by piezoelectric samples representing capacitive loads of up to a few 10 nF. A smart solution for this problem is the use of a charge amplifier which transfers the input charge to another reference capacitor and produces an output voltage equal to the voltage across the reference capacitor.

In this work, we derive the basic equations of TWM for the case of charge-to-voltage conversion and we analyze the polarization state of Pb(Zr,Ti)O₃ (PZT) plates embedded into a low-temperature-cofired ceramics (LTCC) packaging and of PZT rods forming a Macro-Fiber-Composite (MFC) piezoelectric actuator. Transient thermal analysis of the MFC actuator was performed using the finite element modelling package ANSYS 11.0.

For PZT plates electroded at the top and the bottom, nearly constant heating and cooling rates were obtained up to 800 Hz. In the case of embedded piezoceramics of sensor-actuator modules, higher harmonics of a square wave disappear during travelling of the thermal wave through the embedding material due to its thermal conductivity and the thermal wave gradually becomes sinusoidal. Here, the module is described by a harmonically heated piezoelectric plate exhibiting heat losses to the environment characterized by a single thermal relaxation time.

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<th>P.82</th>
<th>Searching for new multiferroics: Ba₁₂Fe₂₈Ti₁₅O₈₄ intergrowth layered ferrite</th>
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<td>Lavinia Curecheriu, Ioana Veronica Ciuchi, Alexandra Neagu, Geanina Apachitei, Leontin Paduraru, Maria Teresa Buscaglia, Giovanna Canu, Catalin Harnagea, Liliana Mitoseriu, Vincenzo Buscaglia</td>
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<td>¹Physics, Alexandru Ioan Cuza University, Iasi, Romania, 700506; ²Electroceramics, Institute of Energetics and Interphases IENI-CNR, Genova, Italy, 16149; ³IRIS-Energie, Matériaux et Télécommunications, University of Québec, Canada</td>
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The BaO-Fe₂O₃-TiO₂ system has rich crystal chemistry and the existence of at least 16 different quaternary compounds was reported. These materials are nowadays attracting considerable interest for the production of permanent magnets and microwave devices, especially due to their high permittivity. Recently, ceramic quaternary ferrites Ba₁₂Fe₂₈Ti₁₅O₈₄ were prepared for the first time. Ba₁₂Fe₂₈Ti₁₅O₈₄ possesses a natural superlattice structure (monoclinic C2/m), constituted by perovskite/spinel-like layers. The aim of the present study is to investigate the magnetic properties, the possible ferroelectric behaviour and to explain theoretically the observed properties.

The magnetic study determined a ferro/ferrimagnetic order similar to that of spinel ferrites with a main magnetic transition at ~415 K and the disappearance of magnetization above 500 K. The dielectric properties are influenced by polaron hopping conductivity associated to the Fe²⁺/Fe³⁺ valence state variations and to the electrical heterogeneity of the ceramics (semiconducting grains, insulating grain boundaries). The local ferroelectricity tested by AFM-piezoresponse experiments revealed local incomplete poling and switching with clockwise loops in various positions. On the basis of a Monte
Carlo model built for a ferroelectric/nonferroelectric layered system, local incomplete poling and switching with abnormal clockwise loops were obtained in specific positions close to the interfaces. Although a typical ferroelectric behavior was not clearly demonstrated, the observed properties might result from a combination of BaTiO$_3$-like ferroelectric order within perovskite layers with non-ferroelectric behavior of the spinel layers and charge defect-associated effects.

Effect of combined thermo-mechanical loading on the domain texture and the fracture resistance of lead zirconate titanate ceramics

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Lead zirconate titanate (PZT) is nowadays the most important piezoceramic for commercial high-performance actuators. In order to improve the design of existing devices it is mandatory to study the effect of combined thermo-mechanical loadings on their structural integrity. This is influenced by the in-service propagation of cracks introduced during poling. Crack propagation in PZT is intimately related with the microscopic domain structure. Ferroelastic switching of domains in front of an advancing crack consumes elastic energy, thus producing an extrinsic toughening effect. The investigation of the crack growth resistance (CGR) and the domain texture in dependence of combined thermo-mechanical loads is thus extremely important to provide guidelines to improve the toughness of piezo-actuators.

In the present work, poled and unpoled bulk PZT specimens were subjected to several compressive loads at 25°C, 150°C, 300°C and above the Curie temperature in an universal testing machine equipped with a temperature chamber. This procedure changes the pre-existing domain texture in the material, thus influencing the CGR (measured here with the indentation fracture method) in several directions. Polarised Raman spectroscopy was used to measure semi-quantitatively the texture of ferroelectric domains in dependence of the combined loading, upon assumption of suitable texture models for the domain orientation distribution. This allowed us to correlate the differences in the CGR with the sample history and the resulting domain configuration, thus highlighting domain texture’s crucial role for crack propagation in PZT.

Domain engineering in ferroelectric thins films by nanopatterened bottom electrodes

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Ferroelectric thin films are used in a wide range of device applications from MEMS sensors and actuators to non-volatile random access memories. The wide range of applications is due to several attractive properties of ferroelectrics such as high dielectric permittivities and reversible spontaneous polarization. The domain structure of a ferroelectric film has a large influence on the properties of the film and therefore controlling the domain structure is essential to optimize their properties and performance. Furthermore, different applications of ferroelectric thin films need different domain structures for optimum performance. Domain engineering has been achieved by control of the misfit strain through epitaxial growth on substrates with different lattice
constants. However, this method only influences the relative domain populations and does not allow specific control over the domain structure. Here we report domain engineering in ferroelectric thin films by using a nanopatterened bottom electrode. Pulsed laser deposition epitaxial grown ferroelectric thin films of PbTiO3 and BiFeO3 have been grown on self assembled SrRuO3 nanopatterns 5nm thick and with lateral dimensions of 100-200nm. The patterned SrRuO3 changes the mechanical boundary conditions of the ferroelectric film and as a result new domain structures are obtained with features corresponding to the SrRuO3 patterns. This technique allows nanometer control of the domain structure in ferroelectric films that has not previously been achieved.

The most commonly used piezoelectric materials for transducer and sensor applications are monolithic Lead Zirconate Titanate (PZT) ceramics. However their brittle nature, high stiffness as well as limited shapeability makes them unsuitable for applications such as vibration or impact sensors. The fabrication of a composite material combining the advantage of the high piezoelectric sensitivity and dielectric constant of PZT together with the low density and high flexibility of polymers matrix will be of great interest for such applications. Conventional processing techniques for fabricating 1-3 PZT fibre-polymer composites are rather complex and expensive if a high degree of fibre alignment is required to obtain good sensing properties. In this study a dielectrophoresis technique was used to fabricate structured quasi 1-3 PZT-epoxy based composites using granular PZT powder. With this process, manufacturing simplicity remains comparable to 0-3 composites and production costs can be kept low. Piezoelectric and mechanical properties of the composites as a function of PZT volume fraction were investigated and compared with the corresponding unstructured 0-3 composites. Moreover, the effect of poling voltage on piezoelectric properties of the composite has been studied for different volume fractions of PZT. The experimentally observed piezoelectric and dielectric properties have been compared with recent theoretical models from which the interparticle distance can be deduced and such results are compared with experimentally obtained data from SEM micrographs.

Large-scale applications of ferrites have promoted the development of various chemical methods for preparation and an increased interest in understanding their functional characteristics. Among different types of ferrites, MgFe2O4 enjoys a special attention because of its vast applications in high-density recording media, heterogeneous catalysis, adsorption, sensors and magnetic technologies, while NiFe2O4 are one of the most important ferrites with reversed spinel structure. From this point of view, it is highly
interesting to perform a systematic study of the effect of the Mg substitution on to the Ni-ferrite. Electrical conductivity and dielectric measurements have been performed for Ni$_1-x$MgxFe$_2$O$_4$ ($x=0; 0.17; 0.34; 0.5; 0.64; 0.83; 1$) sintered at 1200°C/2h. The activation energy for the grain and grain boundary conduction and its variation with the Mg degree of substitution has been investigated. The conduction mechanism was found to be due to the hopping of both electrons and holes. The high-temperature dependence of conductivity shows a change of slope that is attributed to the hole hopping in tetrahedral sites of ferrite. Since the activation energy for the dielectric relaxation is almost equal to that of dc-conductivity, the mechanisms of electrical conduction and of the dielectric polarization are similar. The anomalous frequency dependence of the real part of permittivity can be explained on the basis of hopping of both electrons and holes. The electrical modulus analysis shows the non-Debye nature of the Mg-doped Ni ferrites.

**Acknowledgments:** The financial support from grant POSDRU/CPP 107/DMI 1.5/S/78342 and CNCS-UEFISCDI-PN II-ID-3-2011-0745 are highly acknowledged.

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**Electrophysical properties of high-Tc (1-x)BaTiO$_3$-x(Na,K)$_0.5$Bi$_0.5$TiO$_3$ ceramics**

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Positive temperature coefficient of resistance (PTCR) effect occurs in semiconducting barium titanate in the temperature range above the Curie temperature ($T_C = 120°C$). Substitution of Ba$^{2+}$ ions with Pb$^{2+}$ leads to an increase in Curie temperature. However lead-containing materials are toxic. It is important to develop lead-free PTCR materials with high $T_C (>120°C)$. It is known that the addition of (Na,K)$_0.5$Bi$_0.5$TiO$_3$ to BaTiO$_3$ materials shifts $T_C$ towards higher temperature. Therefore the purpose of this work is to study the electrophysical properties of (1-x)BaTiO$_3$-x(Na,K)$_0.5$Bi$_0.5$TiO$_3$ solid solutions.

Samples of (1-x)BaTiO$_3$-x(Na,K)$_0.5$Bi$_0.5$TiO$_3$ system were prepared by the solid-state reaction technique. Phase composition and crystal structure were investigated by X-ray powder diffractometry. The permittivity and dielectric loss tangent were investigated in wide frequency and temperature ranges. An investigation of the influence of grain regions on the PTCR effect using impedance spectroscopy in (1-x)BaTiO$_3$-x(Na,K)$_0.5$Bi$_0.5$TiO$_3$ was carried out. It has been found that in (1-x)BaTiO$_3$-x(Na,K)$_0.5$Bi$_0.5$TiO$_3$ system the grain boundary and the outer layer region make a contribution to the PTCR effect. With increasing x, the values of $P_{max}$ and $P_{min}$ were observed to increase due to the growth of potential barrier at grain boundaries. The resistance of potassium-containing samples is higher as compared with lead-containing ones. The resistance and PTCR jump in sodium-containing system are similar to those in lead-containing system, and these materials can be used in practice as current limiters and temperature controllers.

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**Hydroxyapatite nanostructure’s dielectric and piezoelectric properties**

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Hydroxyapatite (HAP) is the main mineral component of tooth enamel and bone. Special interest is connected with the physical properties of the nanosized HAP, because it grows as nanosized platelets at nucleation sites on a protein template. Recently, it were shown that HAP dielectric properties provides the large surface charge storage, that is important
for living cells proliferations, and could reveals the piezoelectric properties, which arise in its noncentrosymmetric monoclinic phase P21. The hexagonal crystal structure of HAP with P63/m symmetry is centrosymmetric and not manifested piezoelectricity. Here we report the computational studies of the structural, dielectric, elastic and piezoelectric properties for both HAP crystal structures symmetries. The first principles calculations, modeling and computer simulations were made using as semi-empirical PM3 method as well ab initio and DFT calculations (from HyperChem 8.0 and AIMPRO codes). These computational studies show that HAP crystal cell parameters are different for two symmetries and phases along the main c-axis, that provide the varieties of HAP nano-films widths in this direction (which could be revealed experimentally, e.g. by atomic force microscopy). The calculated values of elastic constants are close to known experimental data for both HAP group symmetries and confirm the existence of piezoelectricity for P21. The calculated small total energy difference for P63/m and P21 leads to opportunity of coexistence for both phases.

### Electric and piezoelectric properties of the lead-free solid solution

**Ba0.85Ca0.15Ti1-xZrxO3 (0.1 ≤ x ≤ 0.2)**

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Lead zirconate-titanate ceramics (PZT) are the most widely used piezoelectric materials to date, because of their high piezoelectric response, large scale production capability and the tailoring of their properties through composition. Nevertheless, the PZT is now restricted by the toxicity of the Pb, and therefore, there is an urgent need to develop lead-free piezoceramics. Very recently, a high-performance Pb-free piezoelectric system Ba0.85Ca0.15Ti1-xZrxO3 (BCTZ), has been reported, showing a very high d33 of 50-600 pC/N. It is also important the synthesis method selected, because of its influence on the grain size and then on the sintering conditions in order to obtain high density, homogeneous ceramics. In the present work the synthesis of Ba0.85Ca0.15Ti1-xZrxO3 (0.1 ≤ x ≤ 0.2) ceramics was performed by Pechini method; the crystalline powders were obtained after calcinations at 600° C, 700° C, 750° C, and 800° C. The powders were sintered at several temperatures and their electric properties have been measured by impedance spectroscopy. The piezoelectric properties have been evaluated using an iterative method of analysis of the resonance. Improved values of piezoelectric parameters as well as permittivity and dielectric losses are presented.

### Advance engineered piezoelectric materials for energy harvesting devices

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Piezoelectric materials offer a number of advantages in energy harvesting systems, by transforming ambient vibration into electrical energy, which can be stored and power other devices. To improve energy harvesting device performance, the figure of merit (e312 / ϵ) is vital to achieve a higher piezoelectric voltage and maximum the power output.
In this study, Pb(Zr\(_{1-x}\)Ti\(_x\))O\(_3\) (PZT) was chosen for its prime piezoelectric properties, such as their high piezoelectric coefficients, high power output density and relatively low epsilon. Epitaxial PZT thin films with controlled orientations are achieved on silicon substrates by pulsed laser deposition (PLD). Pb(Zr\(_{1-x}\)Ti\(_x\))O\(_3\) thin films with variety of dielectric constant (\(\varepsilon\)) and piezoelectric coefficient (\(e_{31}\), \(d_{33}\)), were studied and compared with each other. We found very large figure of merit values within these engineered piezoelectric thin films. Using optimized composition, crystal orientation and strain, maximum values of 20.4 \(\pm\)3 C/m\(^2\) were found. A shift of morphotropic phase boundary (MPB) is observed in the perovskite thin film structure, which is due to the residual strain caused by the different thermal expansion coefficients between PZT thin films and silicon substrates. These results show that for epitaxial PZT thin films, the composition of the PZT should be optimized to compensate the strain state. Besides the characterization of material properties, energy harvesting devices are also being fabricated and will be discussed in the contribution.

**Electro-optical piezoelectric fibres based on PLZT compositions: Synthesis and characterisation**

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Lantanium doped PZT is well known as an electro-optical material. In the 70\(^{th}\) such material was developed for anti-flash goggles. For future application this materials, in form of fibres will be very interesting for transducer application. Enhanced functionality of electro-optic devices are proposed by implementing piezoelectric micro fibers into composite construction. In this study different doped PLZT fiber with a diameter of around 300 micron were produced by thermoplastic processing method and disks were pressed by conventional uniaxial dry pressing method. The materials where sintered in PbO and PbZrO3/ZrO2 atmospheres to avoid lead loss in the material at different temperatures and dwell times. Finally the microstructural properties of fiber and pressed bulk materials were investigated by SEM analysis. Additionally from all materials phase analysis by XRD was investigated. As expected, the microstructure (grain size and porosity) and phase composition are influenced by the sintering conditions. To investigate the electro-optical properties fibre with the lowest porosity 0.5% and a grain size of 3.7 micrometer was used. The phase purity was investigated by the XRD pattern and Rietveld analysis. The light-induced impedance and piezoelectric coefficient was investigated at relatively low light intensity (below 50 mW/cm\(^2\)). By applying a UV LED, a piezoelectric change constant of 219 C/N could be observed.

**Grain size effects on dielectric and piezoelectric properties of piezoceramics under compressive stress**

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In many applications, piezoceramics operate under compression stress. When these materials are subjected to usual prestress of designed devices, functional properties display significant changes. Moreover it is well known that grain size reduction notably affect piezoceramic properties by dropping their functionality. Exploring grain size effects on properties of piezoceramics under prestress should contribute to improve design of
microdevices for specific applications. Lead zirconate titanate (PZT) based ceramics are nowadays the most used materials for piezoelectric devices. Dielectric and piezoelectric responses of soft PZT decrease when this material works under compressive static stress. However, the response of hard PZT rises with the increasing static compression. In any case, piezoelectric response exhibits a noticeable nonlinear behavior which is manifested as an increment of piezoelectric coefficient with increasing dynamical stress amplitude. An increase in dielectric and piezoelectric properties stability is displayed in submicrostructured soft PZT. Similar results are obtained in submicrostructured lead magnesium niobate lead titanate (PMN-PT). While the properties of these materials are not greatly affected by the reduction of grain size, the stability of their properties significantly improves when a compressive stress is applied. Results indicate that grain size reduction could be an approach to obtain piezoelectric materials able to withstand high mechanical stresses without significantly altering their functional properties.

Influence on the performances of a PZT thin film of two different adhesion layers deposited on Si₃N₄

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Lead-zirconate-titanate (PZT)-based MEMS technology is attractive for a wide range of sensor and actuator applications because of its appealing properties and easy integrability with standard processes. Devices based on PZT deposited on Si₃N₄ can offer higher performances compared with standard microstructures based on silicon and SiO₂. In fact Si₃N₄ shows higher Young modulus, higher tensile strength, superior electrical resistivity and dielectric strength with respect to SiO₂. Moreover the possibility to deposit Si₃N₄ by LPCVD as masking layer for bulk wet micromachining in KOH, and the low residual stress exhibited by the suspended structures, suggest that Si₃N₄ is the best candidate in high performing devices. Although these advantages, some experimental drawbacks have to be taken into account. In agreement with few previous studies on PZT deposited on Si₃N₄ coated by Ti-Pt electrodes, we have verified low adhesion strength of PZT layer, pronounced asymmetry in the polarization hysteresis loop, Ti oxidation during the annealing process and consequent corruption of the PZT stoichiometry. To overcome these problems we have tested on Si₃N₄ substrate the standard configuration based on Ti-TiO₂-Pt bottom electrode, already adopted for silicon and SiO₂ substrates. The experimental comparison between the two stack configurations clearly showed a marked improvement in term of PZT adhesion. Concerning the polarization and C-V curves, the asymmetry was also reduced. The experimental comparison has involved several investigation techniques as morphological and micro-structural analyses as well as dielectric and piezoelectric characterizations.
Characterizations of dip-coated PZT-based metal core piezoelectric fibers

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Piezoelectric ceramic fibers are easy to integrate onto any support because of their geometrical shape and can generate quite important movements thanks to their great piezoelectric constants. These fibers can, for example, be integrated into vibrations control systems. More precisely, metal core piezoelectric fibers can be used independently as sensor or actuator. Such fibers exhibit two advantages: the metal core is used as internal electrode and overcomes the ceramic fragility. In this study, a dip-coating process is investigated in order to obtain a homogeneous, dense, regular PZT-based coating on a Pt-wire. The Pt-wire is dipped in a PZT-based slurry and the coated wires are then conventionally sintered at 1150°C. For example, 50μm-thick sintered PZT coatings can be obtained by this way. The PZT-based metal core piezoelectric fibers are characterized in terms of microstructure and piezoelectric properties and compared to PZT bulk ceramics. Specific characterizations of piezoelectric metal core fibers are presented.

Influence of Ag-doping on ferroelectric properties of Bi5NaNb4O18 ceramics

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The bismuth layer-structured ceramics with the general formula of (Bi2O2)2+(Am-1BmO3m+1)2- are considered to be one of the appropriate candidates as the lead-free ferroelectric materials; therefore, the ferroelectric properties of the ceramics with various number of perovskite block have extensively investigated to date. The Bi5NaNb4O18 compound is known to belong to the m=2 member of the Aurivillius phases, and the crystal structure and ferroelectric properties of the compound have been reported. In the most of Bi-containing ferroelectric material, it is known that the evaporation of Bi during the sintering has a detrimental effect on the ferroelectric properties of materials. Therefore, many attempts have been carried out to clarify the influence of evaporation of Bi on the ferroelectric properties. In order to clarify the relationship between evaporation of Bi and ferroelectric properties of Bi5NaNb4O18, the Ag-doped Bi5NaNb4O18 ceramics were synthesized in this study. The XRPD profile of Ag-doped Bi5NaNb4O18 did not show the presence of Ag below 0.015 mol Ag doping. From the variations in the lattice parameter, it suggests that small amounts of Ag occupy the Bi-site in the Bi5NaNb4O18 ceramics. The Ag-doped Bi5NaNb4O18 showed lower current density than Bi5NaNb4O18 and a saturated P-E hysteresis loops was obtained by 0.004mol Ag doping (Pr=13μC/cm², Ec=110kV/cm). Thus, it is considered that small amounts of Ag doping are effective in enhancing the ferroelectric properties of Bi5NaNb4O18 ceramics.
A morphotropic phase boundary (MPB), where a phase transition is induced by compositional changes, is well known, the existence of the MPB enhancing the ferroelectric, piezoelectric, and electrical properties of the materials. The Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT) ceramic is one of the lead-free piezoelectric materials with rhombohedral perovskite structure; therefore, the BNT exhibits a large remnant polarization and a high Curie temperature. Moreover, the MPB between a rhombohedral phase and a tetragonal phase in Bi$_{0.5}$Na$_{0.5}$TiO$_3$ —BaTiO$_3$ system led also to the enhancement of the piezoelectric properties. Thus, in order to clarify the relationships between crystal structure and ferroelectric properties of Bi$_{0.5}$Na$_{0.5}$TiO$_3$ — Bi$_x$M$_{3/4}$W$_{1/4}$O$_3$ (M=transition metals) solid solutions, these solid solutions were synthesized and investigated in this study. The (1-x)Bi$_{0.5}$Na$_{0.5}$TiO$_3$ —xBiM$_{3/4}$W$_{1/4}$O$_3$ solid solutions were synthesized by the solid state reaction method. In the case of Zn-containing solid solutions, the X-ray powder diffraction (XRPD) profiles showed the single phase in the composition range of 0-0.05 and these diffraction peaks of the profiles shifted to the lower angle, though the secondary phase was detected at x=0.1. Such the diffraction peak shifts may closely relate with the Zn and W substitutions for Ti. The remnant polarization ($P_r$) values of the (1-x)Bi$_{0.5}$Na$_{0.5}$TiO$_3$ —xBiM$_{3/4}$W$_{1/4}$O$_3$ solid solutions varied from 35.2 to 39.4 C/cm$^2$ in the composition range of 0 —0.05, whereas the coercive field ($E_c$) was almost constant ($E_c$=75kV/cm).

BNT is a promising candidate to replace PZT in certain applications. It is miscible with various other ferroelectric perovskites and is highly modifiable in its behavior by doping with iso- and aliovalent metal ions. In this work we show the influence of Ti-nonstoichiometry on material parameters and the microstructure. Nonstoichiometric BNT can maintain stable vacancy concentrations on both A- and B-site by evaporating Bi and Na or with the formation of a titanium-rich secondary phase. Unlike other lead-free materials like KNN, whose melting point changes dramatically with the stoichiometric ratio of alkaline ions to Nb, BNT has a kind of self-healing ability which makes processing more easy. The formation of an electrical inactive secondary phase has, besides induced mechanical stress during deformation, no impact on the behavior of the material. The microstructure was investigated using XRD and SEM/EDX, electrical parameters include hysteresis loops, temperature dependent permittivity plots and small signal data at room temperature for permittivity, loss tangent and $d_{33}$. Density values were obtained using XRD for theoretical density and Archimedes’ method for disc samples.
Investigation of the structure and electrical properties of (K\textsubscript{x}Na\textsubscript{1-x})NbO\textsubscript{3} ceramics doped with Li, Ta and Sb

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(K\textsubscript{x}Na\textsubscript{1-x})NbO\textsubscript{3} (KNN) ceramics modified with Li, Ta and Sb were produced using the mixed-oxide ceramics synthesis route. Temperature-dependent synchrotron X-ray diffraction measurements were made from 12K to temperatures above their respective ferroelectric-paraelectric transition points. Rietveld refinement using the Fullprof software was used to refine the patterns. Depending on the composition and temperature, rhombohedral phases, orthorhombic phases, tetragonal phases, cubic phases and two-phase mixtures were obtained and space groups $R3c$, $Amm2$, $P4mm$, $Pm-3m$ and their combinations were used to refine them respectively. The presence of Li in the sample appears to suppress the formation of the rhombohedral phase. Temperature-dependent dielectric properties measurements were used to compare the phase transition temperatures with those from X-ray diffraction. Both Li, Ta co-doping and Li, Ta and Sb co-doping led to a wide temperature range of phase coexistence between the orthorhombic and the tetragonal phase and explains in part the higher piezoelectric activity in KNN-based ceramics with these compositions.

Calcination of (100-x)BNT-xBKT system investigated by high-temperature XRD

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The lead-free Bismuth sodium titanate $\rightarrow$ bismuth potassium titanate solid solutions offer good piezoelectric properties. For a successful production of high performing materials a better understanding of the formation reaction is necessary. Various compositions of (100-x)BNT-xBKT (x=0, 10, 25, 50, 75, 90, 100) were prepared by the mixed oxide route. All samples were analyzed by thermogravimetry coupled with mass spectroscopy and differential scanning calorimetry. An additional mass loss was detected below 650°C which can most likely be attributed to the volatilization of alkaline oxides. HT-XRD up to 770°C indicated emerging and vanishing of phases during the calcination. Special attention will be paid to the differences and similarities in behavior between the individual composition.

Influence of microstructural characteristic on the dielectric and nonlinear properties of BaSn\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3} ceramics

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The functional properties of BaTiO\textsubscript{3}-based solid solutions can be tuned by the nature and substitution level and by controlling the microstructural characteristics. In the present study, we analyzed the role of the grain size on the dielectric and ferroelectric properties of BaSn\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3} system (x=0.15, 0.20) produced by solid state method and sintered at
different temperatures (1300°C, 1350°C and 1400°C), generating different microstructural characteristics (different granulation and density). A ferroelectric-relaxor crossover is typically obtained by increasing the degree of substitution x, like observed for many BaM$_x$Ti$_{1-x}$O$_3$ solid solutions. By reducing grain size (lower sintering temperature), the diffuse character of the phase transition state is favored, i.e. the composition characteristic to the crossover is apparently shifted towards higher values of x. While other authors reported a full relaxor state for x>0.25, the present x=0.20 composition sintered at 1300°C/4h is already found in a predominantly relaxor state. The relaxor character is more evident for ceramic samples sintered at lower temperature.

This feature confirms the importance of the synthesis routes and of the sintering parameters (giving rise to specific microstructural characteristics) on the onset of the relaxor behavior in BaTiO$_3$-based solid solutions.

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Solid solution of sodium potassium niobate with the composition K$_{0.5}$Na$_{0.5}$NbO$_3$ (KNN) is one of the most studied lead-free piezoelectric materials. Since the KNN ceramic is difficult to consolidate, various approaches have been proposed to overcome this problem. One way to improve sinterability of KNN could be doping of KNN with strontium. (Malic et al. J Eur Ceram Soc 25, 2005)

The aim of our study was to systematically evaluate the influence of strontium addition on synthesis, densification, phase composition, crystal structure and functional properties of KNN. Ceramics with the nominal formula (K$_{0.5}$Na$_{0.5}$)$_{1-2y}$Sr$_y$NbO$_3$, for y = 0.005, 0.01 and 0.02, were prepared by solid state synthesis from Na$_2$CO$_3$, K$_2$CO$_3$, Nb$_2$O$_5$ and SrCO$_3$ with two calcinations at 800°C, 4h, with intermediate milling.

In order to understand the relationship between the phase composition, microstructure and functional properties, different methods, such as TG/DTA/EGA, heating stage microscope, XRD and Rietveld refinement were used. Both scanning and transmission analytical electron microscope were used for investigation of structure down to the atomic scale. The dielectric permittivity, losses (tan δ), mechanical coupling coefficients k$_p$ and k$_t$ and piezoelectric coefficient d$_{33}$ were measured.

The addition of strontium to KNN results in wider sintering interval. When sintered at 1120°C, the Sr-doped KNN exhibits smaller grains compared to pure KNN. With increasing amount of strontium, the volume of the monoclinic unit cell of KNN is decreasing, approaching the cubic syngony. The influence of strontium on dielectric and piezoelectric properties of KNN ceramics will be discussed.
Among advanced oxide materials with a rich magnetic phase-diagram, spinel-type structured manganites still require a better understanding of the relations between their crystallographic and magnetic structure.

Advanced oxide materials with NiMn$_2$O$_4$ nominal composition and spinel-type structure were obtained by a modified polymeric precursors method. The magnetic structure was studied by crystallographic and magnetic methods using powder X-ray diffraction and neutron diffraction associated to Rietveld refinement. Magnetization measurements indicate that the NiMn$_2$O$_4$ system is associated to the interplay between two-sublattices, one, ferromagnetic and the other antiferromagnetic, and takes place due to the cations occupation at the tetrahedral and octahedral sites. Both components are present in the ZFC (antiferromagnetic) and FC (ferromagnetic) magnetizations, independent of the applied field. The neutron diffraction data suggests a complex star structure due to the competition of the magnetic moment of Ni and Mn atoms in the B spinel site.

Multiferroic materials have drawn much attention, because they display the coexistence of ferroelectric and magnetic properties. In this study, we have been able to synthesize large amounts of nearly uniform sized BaTiO$_3$ nanocrystals with size around 30 nm and with good solubility in organic solvents. In the following, BaTiO$_3$/CoFe$_2$O$_4$ nanocomposites with core/shell structures were obtained by incorporating CoFe$_2$O$_4$ components into the BaTiO$_3$ precursor matrix. The particles are systematically characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution TEM (HRTEM), thermogravimetric, differential thermal analyses (TGA/DTA), infrared spectroscopy (IR), and atomic force microscopy (AFM). The XRD results confirm the presence of both the spinel and the perovskite phases. The SEM-EDX and the AFM micrographs of BaTiO$_3$/CoFe$_2$O$_4$ nanocomposites show two-phase composite nanostructures of a cobalt ferrite core coated with a BaTiO$_3$ shell, the weight fraction of CoFe$_2$O$_4$ and the size of nanocomposites are the keys to the dielectric and magnetic properties of BaTiO$_3$/CoFe$_2$O$_4$ nanocomposites.
Substituted lanthanum manganites are of great interest due to colossal magnetoresistance effect, which gives novel functionalities for applications in various areas, in particular, in medicine. To date the large size and agglomeration of particles are the main drawbacks of these materials. We propose to synthesize particles from non-aqueous solutions and to modify the surface of nanoparticles by nonmagnetic phases, in particular SiO₂.

We synthesized Ln₀.775Sr₀.225MnO₃ nanoparticles by precipitation from non-aqueous solutions, by microemulsion method and by sol-gel method. Also the characteristics of SiO₂ coating prepared by layering and by direct synthesis on the surface of particles have been studied.

The phase composition were investigated using X-ray analysis. Particle sizes were measured using a transmission electron microscope. The magnetic properties of powders were measured using the quantum design magnetic properties measurement system. The use of sol-gel method allows decreasing the synthesis temperature of nanoparticles by more than 500°C in comparison with solid state reaction technique. At the same time, deposition from non-aqueous solutions and microemulsions method enable one to synthesize particles at low temperatures (~600°C), to decrease the particle size to 20-30 nm in comparison with the sol-gel method (50-70 nm), and to reduce agglomeration of particles during synthesis. The magnetic properties of the synthesized nanoparticles and particles coated with silicon oxide were investigated. It was shown that the synthesis method and SiO₂ layer at the surface affect the value of saturation magnetization and blocking temperature of samples.

The multiferroic behavior of ion modification using rare-earth cations on crystal structures, along with the insulating properties of BiFeO₃ (BFO) thin films was investigated by using piezoresponse force microscopy. Rare-earth-substituted BFO films with chemical compositions of (Bi₁₋ₓREₓFe₁₋₀ₓO₃ (x = 0.15), RE = La and Nd were fabricated on Pt (111)/Ti/SiO₂/Si substrates using a chemical solution deposition technique. A crystalline phase of tetragonal BFO was obtained by heat treatment in ambient atmosphere at 500°C for 2 hours. Ion modification using La³⁺ and Nd³⁺ cations lowered the leakage current density of the BFO film at room temperature from approximately 10⁻⁶ down to 10⁻⁸ A/cm². The observed improved magnetism of the Nd³⁺ substituted BFO thin films can be related to the plate-like morphology in a nanometer
Polarization reversal was investigated by applying dc voltage through a conductive tip during the area scanning. We observed that various types of domain behavior such as 71° and 180° domain switching, and pinned domain formation occurred.

BiFeO₃ shows multiferroic properties at room temperature. The high phase transition temperatures ($T_N=640K$, and $T_C=1100K$) make it very attractive not only for the fundamental physics but also from application point of view. BiFeO₃ epitaxial thin films have been reported to show excellent ferroelectric and magnetic properties. And a BiFeO₃ single crystal has also been reported to have a very high polarization, 60µC/cm². It has, however, been known that a BiFeO₃ ceramic with high resistivity and good ferroelectric properties could hardly be prepared by the conventional solid state reaction due to impurity phases and ionic defects. Recently, a single phase BiFeO₃ ceramic with excellent ferroelectric properties has been successfully prepared by a rapid liquid phase sintering at high temperature or sintering a mechano-chemically-activated BiFeO₃ powder at low temperature. In this work, BiFeO₃ ceramics were prepared by the conventional solid state reaction at various sintering conditions. Sintering a BiFeO₃ ceramic at a different temperature and/or with a heating rate produces a different phase evolution, ionic defect concentration and microstructure. And a sintering atmosphere influences the types and concentrations of ionic defects. The phase evolution and microstructure were investigated by using X-ray diffraction and scanning electron micrograph. The insulating resistance, dielectric properties, ferroelectric P-E hysteresis, and S-E characteristics were measured. The effect of sintering condition on the ferroelectric properties will be discussed.

The hexaferrites AFe₁₂O₁₉ (A= Ba, Sr, Pb) have been studied during the years due to their importance for technical applications. Their very good magnetic properties make them to be used as permanent magnets, components for microwaves or in recording media. During recent years, multiferroic materials, which exhibit simultaneous magnetic and ferroelectric ordering phenomena, have been intensively studied. Due to the fact that single phase materials, which exhibit multiferroic properties close to room temperature, are difficult to obtain, work has also been directed toward finding composite materials, wherein crystallites of chemically inert, magnetostrictive, and piezoelectric phases are intimately linked. In this study we have prepared magnetoelastic composites of (SrFe₁₂O₁₉)₀.₃(BaTiO₃)₀.₇ by spark plasma sintering (SPS) method using commercially available nanopowders as starting materials. SPS is considered a promising technique in order to mechanically link the grains of the starting materials by rapid sintering, allowing ample time for grain-linkage, but preventing extended chemical reaction of the two
constituents. The sintering was performed in the temperature range 800 - 1050 °C under an applied pressure of 75 MPa.

A negative magnetoresistivity effect was observed in the temperature range 100-300 K with an enhanced effect at lower temperatures. The temperature dependence of the resistance describes a variable-range hopping conduction mechanism. It was found that sintering temperature has a significant influence on magnetic properties and magnetoresistivity effect with an enhancement at higher sintering temperatures.

Multiferroic CoCr$_2$O$_4$ thin films grown by pulsed laser deposition

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Multiferroic materials display coexistence of ferroelectric and magnetic order. This can lead to a range of novel devices that use the control of the spontaneous magnetization (polarization) with an electric (magnetic) field.

This rare magnetoelectric coupling is observed in bulk CoCr$_2$O$_4$ crystals [1]. CoCr$_2$O$_4$ becomes ferrimagnetic at 93 K, while below 26 K CoCr$_2$O$_4$ undergoes a magnetic transition to a conical spiral magnetic structure. The spin spiral rotates in the (001) plane, and has a spontaneous magnetization in the [001] direction. This magnetic spiral structure displaces the oxygen ions between the magnetic metal ions by the Dzyaloshinskii-Moriya interaction, pushing the oxygen ions off-center, realizing a polarization in the [-1 1 0] direction. Yamasaki at al. [1], showed that in the magnetic conical spiral state the polarization can be switched repeatedly by a magnetic field.

So far, there is no knowledge about the behavior of conical spiral structures in thin film materials. Here I present our preliminary results of thin films grown by RHEED controlled pulsed laser deposition (PLD). Quality and stoichiometry of the samples are checked by AFM, thin film XRD and XPS. Magnetic ordering is analyzed by MPMS SQUID magnetometry.

Preparation and characterization of nano ferrites

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In last few decades, several mechanical routes were used in order to produce a large variety of soft magnetic nanocrystalline/nanosized ferrites. Two basically mechanical ways are used for producing nanocrystalline/nanosized soft ferrites: the nano-ferrite is obtained directly by reactive milling of an oxides or other precursor's mixture and the ferrite is obtained by a classical method and then is subjected to a dry or wet milling in order to achieve a nanocrystalline/nanosized state. Novel approach to mechanochemical synthesis, based on reactions of solid acids, bases hydrated compounds, crystal hydrates, has been called soft mechanochemical synthesis. The dissolved substances in the solid state, substantially change their nature. It can influence on the composition and properties of the final product. Peculiarities of soft mechanochemical reactions consist in the high reactivity of surface functional groups, notably, OH groups.

The nanosized NiFe$_2$O$_4$ and ZnFe$_2$O$_4$ powders were prepared by mechanochemical synthesis in a Fritsch planetary ball mill during various milling times (3h - 25h). The natures of these powders were confirmed by various techniques, such as XRD, SEM, TEM, IR and Raman spectroscopy. Magnetic measurements and Mössbauer spectral studies indicated
that the as-prepared NiFe$_2$O$_4$ and ZnFe$_2$O$_4$ ferrites are typical for soft ferromagnetic materials. Dielectric properties such as dielectric constant and dielectric dielectric loss of both sintered ferrites at 900 °C have been investigated in the frequency range 100 kHz - 1 MHz. The variation of these parameters with frequency and temperature is explained qualitatively.

Defects-dependent properties of yttrium-iron garnet, Y$_3$Fe$_5$O$_{12}$, revealed through their isochronal recovery behavior are reported. Toroidal samples of YIG were prepared using the conventional ceramic processing technique involving high-energy ball milling and sintering at 900°C, 1100°C, 1200°C, 1350°C. One set of magnetic permeability, dielectric permittivity and electrical resistivity measurements were obtained for each sample three times: 1) after the sintering, 2) after a subsequent quenching in oil from 1000°C and 3) after annealing at 1000°C for two hours in air. Plots of each sample's permeability components, permittivity components and resistivity exhibit clear isochronal recovery behavior for the properties: original values changed by the quenching were recovered and bettered after the annealing. The results strongly suggest that the three important material electrical properties can have a strong dependence on atomic-scale defects and can be improved by quenching followed by isochronal annealing.

The angular dependence of exchange bias is of crucial importance in unraveling the nature of exchange coupling in the ferromagnetic/antiferromagnetic bilayers. Recently, the jump phenomenon in angular dependence of the exchange bias has been discovered. It is very useful to realize the maximum of the exchange bias field for the applications of the correlated magnetoresistance devices. However, only the uniaxial anisotropy was considered in these papers. In this work, the angular dependence of the exchange bias containing both uniaxial and cubic anisotropies has been investigated thoroughly. Based on the principle of minimal energy, the initial state of the system has been studied. the number and orientation of the intrinsic easy and hard axes can be obtained. These axes divides the whole magnetic orientations into some special regions. The magnetization reversal processes have been analyzed based on the coherent rotation model in every angular region. It is found that the exchange bias field and the coercivity will appear a jump when the field is applied along the orientations of the intrinsic easy and hard axes. Both the exchange bias field and coercivity have larger values at these magnetic orientations. Additionally, the dependence of the magnetization reversal processes on the orientation of the applied field has also been investigated, two types of the hysteresis loop, whole-plane rotated and half-plane rotated loops, has been discovered and explained in this work.
A series of polycrystalline $\text{Bi}_1-x\text{Ba}_x\text{Fe}_{0.95}\text{Ti}_{0.05}\text{O}_3$ with $x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25$ and $0.30$ ceramics were synthesized via solid state route. This study underlines the effect of $\text{Ba}^{2+}$ doping level on the phase formation, crystal structure, magnetic, dielectric and microstructure properties. Room temperature powder X-ray diffraction patterns indicated that secondary phase disappeared in the present of $\text{Ba}^{2+}$. The structure analysis carried out using a Rietveld refinement technique found that $\text{Ba}^{2+}$ was incorporated into the crystal structure with gradual evolution from rhombohedral to pseudocubic structure as $x$ increased. Further, the samples were characterized by infrared (IR) spectroscopy technique to investigate aspect of bonding. As the amount of $\text{Ba}^{2+}$ substitution was increased, the ferromagnetic hysteresis loops with increasing magnetization value were observed. This enhancement of magnetization is attributed to the presence of oxygen vacancies which leads to suppression of the spiral spin structure of the samples. The variations of the dielectric properties were also studied over a frequency range of 10Hz - 1MHz at the elevated temperature. Dielectric constant and dielectric loss were found to decrease as the frequency increased for all compositions. Microstructure and elemental analysis were carried out using Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) analysis, respectively. The microstructure shows remarkable changes in terms of grain size as $\text{Ba}^{2+}$ doping level increases, while EDX analysis confirms the stoichiometry formula of the samples.

Dielectric, X-ray, Mossbauer and piezoelectric studies of highly-resistive Li-doped $(1-x)\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ - $x\text{PbTiO}_3$ compositions with PbTiO$_3$ content up to 8 mol.%. $x,T$-phase diagram of the PFN-xPT solid solution system have been constructed using these data.

Lanthanide orthotantalates have been extensively studied because they exhibit a large range of environmental and energy-related applications. It is well known that these materials show polymorphic transformations as functions of lanthanide ionic radii and processing conditions. As a consequence, the literature frequently reports different structural assignments, and controversies have emerged. In this work, $\text{RETaO}_4$ ($\text{RE} = \text{La}$,
Nd, and Lu) compounds were synthesized by solid-state reaction in optimized conditions of temperature and time and their crystal structures and phonon modes were investigated by micro far-infrared reflectivity. It was observed that La-based compounds crystallized in the monoclinic structure, P2\(_1\)/c (#14, Z=4), while Nd-based materials exhibited the fergusonite M-type structure, I\(_2\)/a (#15, Z=4). Samples with Lu presented the fergusonite M'-type structure, P2\(_a\) (#13, Z=2). These two last groups of compounds exhibited phase transitions, which can be related to the processing temperature. The results allow us to understand the differences between these structures in terms of the vibrational-active modes assigned to each space group. Group-theory calculations were performed and the experimental results were in perfect agreement with theoretical calculations.

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<th><strong>Ferroelectric-relaxor crossover in Ce-doped BaTiO(_3) ceramics</strong></th>
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<td>Zina Violeta Mocanu(^1), Lavinia Curecheriu(^1), Marco Deluca(^2,3), Vincenzo Buscaglia(^4), Marlies Van Bael(^5), An Hardy(^6), Liliana Mitoseriu(^1),</td>
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BaTiO\(_3\)-based ceramics are attractive as Pb-free relaxors with applications in microelectronics and wireless communications. Among the dopant ions, cerium is a special element with two oxidation states: Ce\(^{3+}\) and Ce\(^{4+}\), that can be incorporated at Ba-site (as Ce\(^{3+}\)), while Ce\(^{4+}\) will be preferentially incorporated on Ti-sites, having a solubility limit of Ce\(^{4+}\) substitutions on Ti-ion positions of ~30 at.%. 

In the present work, Ba(Ti\(_{1-y}\)Ce\(_y\))O\(_3\) ceramics with nominal compositions y=0.06; 0.1; 0.2; 0.3 were prepared by mixed oxide method and sintered at 1500°C for 4 hours. X-ray diffraction data showed the phase purity and SEM images demonstrated homogeneous microstructures (average grain size of ~1\(\mu\)m) and well-defined grain boundaries.

Impedance spectroscopy in the temperature range of (-50 to 200)°C shows a composition-induced ferroelectric-to-relaxor crossover with compositional-dependent shifts of the structural transition temperatures by comparison with ones of the pure BaTiO\(_3\). The dielectric characteristics indicate the possibility of either superposition of phases and/or the possible partial doping of Ce\(^{3+}\) on A positions. In order to clarify this aspect, a Raman spectroscopic analysis was performed on each composition. The presence of an extra mode at ~830 cm\(^{-1}\) on the y=0.06 and 0.3 compositions indicates A-site substitution of the Ce\(^{3+}\) cation, analogously to La-doped barium titanate. This result suggests that fluctuations in the oxidation state of Ce cations influence the functional properties. A temperature-dependent Raman analysis is currently planned to clarify the influence of doping on the shift of structural phase transition temperatures.

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### Dielectric properties of 5% Ce-doped BaTiO₃ ceramics: The role of Ti stoichiometry

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The microstructure, as well as the dielectric behaviour and non-linear characteristics versus temperature of Ba₀.₉₅Ce₀.₀₅TiO₃ and Ba₀.₉₅Ce₀.₀₅Ti₀.₉₈₇₅O₃ ceramics were investigated. Ce-doped BaTiO₃ ceramics were produced from powders synthesized by Pechini method. The nanopowders were densified at different temperatures. Dense ceramics with homogeneous microstructures, low losses and high dielectric constant were obtained for all the compositions. Impedance spectroscopy in the temperature range of -150 -150°C demonstrated the ferro-para phase transition around 25 -35°C for the non-stoichiometric Ba₀.₉₅Ce₀.₀₅Ti₀.₉₈₇₅O₃ samples, as well as for the stoichiometric Ba₀.₉₅Ce₀.₀₅TiO₃ ceramic sintered at 1200°C. Only the stoichiometric composition sintered at 1300°C presents a shift of its Curie temperature above 100°C, which might be related to small amounts of secondary phases and/or local compositional inhomogeneity which should be further investigated. Very high values of permittivity and sharp ferro-para phase transition are obtained for the composition with Ti-vacancies sintered at higher temperature. Values of tunability in the range of 1.60 to 1.90 at a field of 20 kV/cm are characteristic for all the samples. Landau-Ginzburg-Devonshire theory and its approximation (Johnson relation) approach in case of a single polarization mechanism in the polar state very well fit the experimental data. In the paraelectric phase, a model of random uncorrelated non-interacting dipolar units in a double well potential was considered to describe the dielectric non-linearity. The tunability behaviour was discussed in terms of the role of microstructure, composition and Ti vacancies.

### Thickness dependence of ferroelectric and piezoelectric properties in epitaxial PZT thin films

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Epitaxial (110)-oriented Pb(Zr₀.₅₂,Ti₀.₄₈)O₃ (PZT) thin films were fabricated on SrRuO₃-coated (001) YSZ/Si and SrRuO₂-coated (110) SrTiO₃ (STO) substrates with various thicknesses ranging from 0.1 μm to 1.0 μm by pulsed laser deposition. The effects of the film thickness on the structure, ferroelectric and piezoelectric properties were systematically investigated as a function of the film thickness. On the STO substrate the remnant polarization of the films increased from 36.6 to 45.5 μC/cm² with the increasing film thickness, while in the films on the silicon substrate the remnant polarization was in the range of 12.4 - 20.2μC/cm². The improvement of the remnant polarization with increasing film thickness was due to the reduction of the film/electrode interface effect which leads to improve the switching of domains. The films on the STO substrate were in a compressive stress, while in the films on the silicon substrate a higher tensile stress was found. Compressive stress causes the ferroelectric domains to orient along the longitudinal direction (c-domain orientation), which in turn can result in an increase of
the polarization. Moreover, the effective piezoelectric coefficient of the PZT thin films increased steadily with increasing thickness. This effect is likely related to a mechanism of elastic domains that can move more easily in thicker film, and that give rise to out-of-plane piezoelectric displacement.

**Influence of annealed atmosphere and poling on dielectric and transport properties of “hard” PZT ceramics**

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Lead zirconate titanate PbZrxTi1-xO3 (PZT) is nowadays the most used piezoelectric material due to its exceptionally high piezoelectric parameters, which are the highest among all piezoelectric ceramics.

In this work we investigate dielectric permittivity and conductivity of hard Pb0.95Sr0.05(Ti1-xZrx)O3 (x = 0.53) ceramics doped with 0.3% wt. of Fe2O3. The measurements were performed at frequencies from 10⁻² Hz to 10⁶ Hz and at temperatures between 300 and 800 K. Temperature dependence of permittivity in poled PZT ceramics does not exhibit any peak up to 750 K (heating rate 5 K/min), although the ferroelectric-paraelectric phase transition should occur around 600 K. The ferroelectric phase is overheated due to local strain and paraelectric phase appears at 750 K only within one hour dwelling time.

Influence of annealing in air, O₂ and N₂ performed at 875 K was as well investigated. We found that the annealing in O₂ and air enhances conductivity and dielectric loss, while the annealing in N₂ reduces conductivity and losses. The influence of annealing is enhanced, if we measure at 475 K and the annealing time is longer. This discovery explains why the PZT ceramics can be more easily poled at 475 K, if the ceramics were first annealed in N₂ atmosphere.

**Intense photoluminescence emission at room temperature at calcium copper titanate powders**

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In this work a study was undertaken about the structural and photoluminescent properties at room temperature of CaCu₃Ti₄O₁₂ (CCTO) powders synthesized by a soft chemical method and heat treated between 300 and 800 °C. The decomposition of precursor powder was followed by thermogravimetric analysis (TG-DTA), X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Fourier transform Raman (FT-Raman) and photoluminescence (PL) measurements. XRD revealed that the powders annealed at 800 °C are free of secondary phases and crystallizes in the cubic structure. The most intense PL emission was obtained for the sample calcined at 600 °C, which is neither highly disordered (400-500 °C), nor completely ordered (800 °C). The lower wavelength peak is placed around 480 nm, and the higher wavelength peak at about 590 nm. The UV/vis absorption spectroscopy measurements suggested the presence of intermediary energy levels in the band gap of structurally disordered powders.
A large amount of energy is wasted as unused heat whenever fossil fuels are burnt, such as in coal power plants and internal combustion engines in automobiles. Due to diminishing fossil fuel reserves, thermoelectric materials are becoming increasingly important as alternative power sources. Thermoelectric devices consisting of both p-type and n-type semiconductor components can be used to scavenge energy from waste heat and convert it into useful electricity. Currently the highest performing thermoelectric materials are based on metallic semiconducting alloys, such as n-type Bismuth Telluride. However these are unstable at temperatures experienced in environments such as found in automobile exhausts, therefore research has intensified in the metal oxide thermoelectric materials based on the sodium (Na$_x$Co$_2$O$_4$) and calcium (Ca$_3$Co$_4$O$_9$) cobaltites.

Na$_{0.5}$Co$_2$O$_4$-based materials with Copper substitutions have been prepared using the standard mixed oxide route, including the use of high energy milling, high pressure sintering and Spark Plasma Sintering (SPS). For laboratory processing, the powders were calcined at 830°C for 24 hours, and then sintered at 830°C for 12 hours under a pressure of 180kPa. The use of SPS yields significantly higher density and products with superior thermoelectric properties. The families of materials have been characterised by XRD, SEM, and in terms of thermal conductivity, electrical resistivity and Seebeck coefficients.

Both high pressure and SPS methods produced high density samples with oriented grain structure. The effect of processing method on the microstructure and thermoelectric properties will be discussed.

Direct conversion of waste heat into electrical energy by thermoelectric modules offers tremendous potential for reducing the overall energy consumption. The efficiency of these devices can be improved by designing “phonon-glass/electron-crystal” materials, which have a high thermopower and electrical conductivity combined with a low thermal conductivity.

Single crystals of Na$_x$CoO$_2$ show very promising thermoelectric properties, however overall performance is limited by a high lattice thermal conductivity. It is expected that this can be improved in Na$_x$CoO$_2$ thin films, due to enhanced phonon scattering. The growth of these thin films is reported, however thermoelectric characterization is very challenging because of chemical instability in air.

We present a method to obtain single-phase Na$_x$CoO$_2$ thin films by pulsed laser deposition, which are chemically stable in air. Chemical stability of these films is now achieved by the in-situ deposition of an amorphous AlO$_x$ capping layer, which prevents reaction of the thin film with moisture and CO$_2$ from air. No degradation of the structural and electrical transport properties of these capped thin films is observed for several months.
Subsequently we report a detailed growth study, which results in control over the structural properties of these stable Na$_x$CoO$_2$ thin films. We show that layer thickness, deposition parameters and substrate material can be used to tune the crystalline properties of the thin films. In relation to these structural changes we studied the electrical transport properties and thermopower, demonstrating significantly enhanced thermoelectric potential of these stable Na$_x$CoO$_2$ thin films.

Transparent ZnO films on a glass substrate prepared by low-temperature hydrothermal growth
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The applications of transparent-conductive thin films (TCFs) in the technologies of flat-screen displays, touch screens and solar cells are critically dominated by indium tin oxide (ITO). The boom in these applications, the limited resources of indium and consequently its high price emphasize the strong need for the development of cheaper alternatives. ZnO-films are good candidate to replace ITO films. They can be deposited onto substrates by different solid-vapour-based techniques. However, in recent years solution-based synthesis methods are being increasingly developed because of the advantages in cost, easier transformation to large-scale production and the reduced pollution effects.

Transparent and conductive ZnO films on glass substrate were prepared using low-temperature hydrothermal synthesis at 90°C from aqueous solutions of Zn-nitrate and Na-citrate. In the first and second step ZnO seed layer on glass with the proper thickness, size, connectivity and orientation of seed grains has to be prepared to enable the nucleation and growth of smooth and dense (0001) oriented ZnO films from the solution in the third step. Films with a thickness of about 8 µm had optical transparency in the visible range of the spectrum of about 80% and a relatively low sheet resistance for undoped ZnO of the order of 80 Ωcm. The preparation of the ZnO seed layer on glass and its influence on the growth of the highly (0001) textured polycrystalline ZnO film under spatially confined oriented growth (SCOG) mechanism will be discussed.

Investigation of Co-doped PZT films deposited by rf-magnetron sputtering
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In the last years, there is a great interest in preparation and investigation of different types of ferroelectric thin films for device fabrication due to the technological applications, such as: piezoelectric devices, non-volatile random access memory devices, surface acoustic wave filters (SAW), micro-electromechanical systems (MEMs) and nano-electromechanical systems (NEMS) applications.

The focus of the present paper is to describe the preparation procedure and to investigate the microstructural characteristics and the electrical properties of Co-doped PZT films deposited by rf-sputtering by using a “mixture” target system onto Au-electroded Al$_2$O$_3$ ceramic substrates. The X-ray diffraction patterns of the Co-doped PZT thin films as a function of the annealing temperature confirmed the formation of pure perovskite phase started with temperatures of 600°C, but a perfect crystallization was
achieved at a temperature of ~700°C. The microstructures strongly depend on the thermal treatment temperature and indicated a discontinuous surface without large pores and with a bimodal grain size distribution. The XPS analysis demonstrated that the dopant element is present mainly in its Co²⁺ state. The macroscopic P(E) hysteresis loops were recorded in different locations of the films surface and demonstrated ferroelectric behaviour with a resistive leakage contribution.

Acknowledgements: The present work was supported by CNCSIS-UEFISCSU, project number PN II-RU TE code 187/2010. The financial support of the CNCS-UEFISCDI project PN-II-ID-PCE-2011-3-0745 is also highly acknowledged.

Bismuth ferrite [BiFeO₃; BF] and bismuth sodium titanate-barium titanate [(Bi₀.₅Na₀.₅)₁₋ₓBaₓTiO₃, BNBT] thin films have been prepared by chemical solution deposition. Bismuth nitrate pentahydrate and iron (III) acetylacetonate, with acetic acid and 1,3-propanediol as solvents, were used to obtain the BF solution. Several layers of this solution were deposited onto Pt-coated silicon substrates by spin-coating, dried and crystallized by Rapid Thermal Processing [RTP] at 500°C. The BNBT films were treated at 650°C by RTP. Both types of films show the formation of the perovskite phase, as detected by X-ray Diffraction [XRD] analysis.

The BF films present large leakage currents that make difficult to obtain a well-defined ferroelectric response at room temperature. In contrast, the BNBT films are excellent dielectrics, but with slim ferroelectric hysteresis loops and low remanence for the morphotropic phase boundary (MPB) composition at a x~0.10 (BNBT-10).

A combination of MPB BNBT and BF phases in a multilayer composite film may lead to an improvement of their respective properties, like it has been observed recently in lead-containing MPB relaxor-ferroelectric thin films combined with conventional ferroelectrics in a multilayer structure. Therefore, lead-free multilayer composite thin films of multiferroic BF and piezoelectric MPB BNTBT have successfully been prepared here and properties have been studied to discuss the mechanisms that lead to the variations of the behavior observed with respect of the single phase films.

The state-of-the-art material in piezoelectric sensors and actuators, PbZrₓTi₁₋ₓO₃ (PZT), is the preferred piezoelectric material in most applications due to its superior performance. But as lead is toxic, the European Union in 2003 included PZT in its legislature to be substituted as a hazardous substance by safe materials as soon as a practical substitution becomes available. KₓNaₓNbO₃ (KNN) has the potential to meet the properties of PZT ceramics and contains elements that are much less toxic than lead.

KNN thin films were deposited on platinized Si substrates by spin coating of a homogeneous solution. The effect of solution chemistry, spinning procedure and heat treatment on the microstructure and phase composition was studied by field emission gun scanning electron microscopy and grazing incidence X-ray diffraction.
Studies to the structure-property relationship of various materials play a central role in thin film research. With physical vapor deposition techniques, we are able to control crystal growth on an atomic level. Such precise control of a material’s structure led to the discovery of materials with unique properties, like the high mobility electron gas at a perfect \( \{100\} \) \( \text{LaAlO}_3-\text{SrTiO}_3 \) heterointerface.

Most of these advanced materials can only be produced on single crystal substrates with closely matching lattice parameters. A drawback of using such substrates is that they are usually small and costly, hampering the translation of the technology into various applications. Recently, inorganic nanosheets were proposed as excellent candidates to replace the expensive single crystalline substrates.

Nanosheets of \( \text{Ti}_{0.87}\text{O}_{2} \) and \( \text{Ca}_2\text{Nb}_3\text{O}_{10} \) were synthesized and placed on a silicon substrate by Langmuir-Blodgett deposition. Using pulsed laser deposition, \( \text{SrRuO}_3 \) films were formed on the substrates containing the nanosheets seed layer. The presence of nanosheets had a clear impact on both the morphology of the films (as observed by AFM) and the orientations of the crystals (as observed by XRD). When \( \text{Ti}_{0.87}\text{O}_{2} \) nanosheets were used the \( \text{SrRuO}_3 \) films were preferentially \((110)_p\) out-of-plane aligned, while \((001)_p\) orientation was observed on \( \text{Ca}_2\text{Nb}_3\text{O}_{10} \) nanosheets. The \( p \) in this context refers to the pseudocubic lattice of \( \text{SrRuO}_3 \). The ferromagnetic properties of the films were studied by VSM and compared to films deposited on \( \text{SrTiO}_3 \) single crystal substrates.

Ferroelectric thin films are intensively studied for applications, such as in ultrasound generators or non-volatile memories. The synthesis of self-organized ferroelectric nanostructures is especially challenging in order to achieve very large storage density. Nanometric periodic domains patterns can be obtained by using epitaxial strain in ferroelectric thin films grown on an adequate substrate. The film-substrate material combination is particularly important to promote domain formation as the only relaxation mechanism, so the mismatch at the growth temperature has to be kept as small as possible.

So far, very small periodic ferroelectric-ferroelastic \( 90^\circ \) domain patterns have been demonstrated in thin \( \text{PbTiO}_3 \) films grown on \( \text{DyScO}_3 \) substrates [1]. This materials combination presents indeed nearly zero mismatch at the growth temperature and a slightly tensile strain at room temperature, which gives rise to well defined periodic domains with in-plane \((\alpha \text{ domains})\) and out of plane \((\gamma \text{ domains})\) ferroelectric polarization. But since lead-containing materials are to be avoided, other materials combinations have to be investigated.

A good candidate is \( \text{BaTiO}_3 \) on \( \text{NdScO}_3 \). In this system, the formation of periodic \( \alpha/c \) domains is also expected. I will present our work on the epitaxial growth of \( \text{BaTiO}_3 \) thin
films on NdScO$_3$(110) substrates using pulsed laser deposition, X ray photoemission spectroscopy (to study the chemical composition), atomic force microscopy and X ray diffraction measurements (to access the films structure).


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<th>P.128</th>
<th>Transport mechanism in CaCu$_3$Ti$<em>4$O$</em>{12}$ films prepared by RF magnetron sputtering</th>
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<td>Cesar R. Foschini$^1$, Ronald Tararam$^1$, Milan Zunic$^{1,2}$, Alexandre Z. Simões $^3$, Mario Cilense $^1$, Elson Longo $^1$, Jose A. Varela $^1$</td>
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<td>$^1$Physical-Chemistry Department, Instituto de Química, UNESP, Araraquara, SP, Brazil, 14800-900; $^2$Department of Materials Science, Institute for Multidisciplinary Research, Belgrade, Serbia, 11000; $^3$Faculty of Mechanical Engineering, UNESP, Guaratinguetá, SP, Brazil</td>
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There is a constant need in the modern electronic industry for capacitors with high capacity per volume in order to use in many applications such as memories devices, energy storage, microwave filters, among others. The synthesis, characterization and study of materials with a very high or giant dielectric constant are in particular important and have been studied by many investigators. The CCTO electrical behavior has been intensively discussed in the literature and has been attributed to intrinsic and extrinsic defects. The objective of this work was to deposit nanostructured thin films on different types of substrates by RF sputtering technique using CCTO targets prepared by mixed oxide method. Films morphology was characterized by Field Emission Scanning Microscopy (FE-SEM) and show homogeneous microstructure. The dependence of annealing atmosphere on the AC and DC transport measurements were analyzed and a mechanism that controls materials properties is proposed.

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<th>P.129</th>
<th>Direct patterning of oxide interface with high mobility 2DEG without physical etching</th>
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Discovery of highly mobile two dimensional electron gas (2DEG) at the atomically engendered interface between two wide band-gap perovskite insulators, SrTiO$_3$ (STO) and LaAlO$_3$ (LAO) has opened up enormous possibilities of applications of oxide materials in cutting-age electronic devices like high mobility electron transistors (HMET). In spite of excellent interfacial transport properties manifested, challenges remained in structuring these heterointerfaces without damaging the STO single crystal underneath in order to integrate them in circuit components. Top-down physical etching process was an unsuitable choice to serve the purpose since it induces substrate conductivity through creation of oxygen vacancy. In our presentation we will demonstrate development of a novel procedure for fabricating patterned functional interfaces based on epitaxial-lift-off technique. With its help devices incorporating patterned interfaces of LAO-STO was fabricated devoid of any physical etching process performed and temperature dependent magneto transport properties were investigated. The results demonstrated conservation of the high-quality interface properties in the patterned structures enabling future studies of low-dimensional confinement on high mobility interface conductivity as well as interface magnetism.
This work presents the study of the isotropic films based on ferroelectric polyvinylidene fluoride PVDF, performed by atomic force microscopy. The isotropic films were prepared on a glass by crystallization from solution in acetone. Two copolymer films P(VDF/HFP) of 93/7 and 86/14 was investigated. Crystallization of both films is carried out in a mixture of α- and γ- phases. This conclusion was obtained by IR spectroscopy, which detects the presence isomers in conformational TGTG- (α- phase) and T3GT3G- (γ- phase). It was found that the increase in the chain of the copolymer fraction of HFP groups with high steric hindrances accompanied by an increased proportion of isomers with the conformation TGTG . The kinetics of local polarization after applying a rectangular DC pulse at film has characteristic decay time τ, which depends from the sign of polarizing field and has a value order of tens seconds. So the relaxation kinetics is controlled not only the external field, but also the space-charge field. The latter can be configured as its own (impurity) carriers, and the charges injected from the electrodes. In the case of the copolymer 93/7 values are considerably higher than for the copolymers of 86/14. This we attribute to the fact that small crystals of the polar γ-phase will be a source of deep traps and thus increase the Maxwell relaxation time for the “free” carriers, forming a space charge field.

The highly non-linear current-voltage characteristics of zinc-oxide varistor materials are microscopically described by a network of so-called Double-Schottky Barriers (DSB) at the grain boundaries. Variations of electrical properties of single grain boundaries can have a crucial influence on the macroscopic device properties of MLVs with low breakdown-voltage.

In this study special ZnO multilayer varistors (MLV) samples with 1 to 2 active grain boundaries between the electrodes were investigated. The integral current-voltage characteristics of these samples show a difference in the current up to one order of magnitude with respect to different voltage polarities.

On a microscopic scale Joule heating along current paths between the electrodes has been detected by a P- lock-in thermographic measurement setup. For example two different main current paths in the same specimen have been found for opposite voltage polarity by this technique. This result can be explained by considering asymmetric barriers at grain boundaries with respect to the voltage polarity. Additionally, the microstructure and the local electrical properties at the dominant current paths have been analysed with advanced atomic force microscopic techniques. To interpret the experimental results, a 3D network simulation model has been developed to analyse the influence of individual DSBs on the integral electrical properties.
Optimization of La$_2$NiO$_4$ cathode for SOFC

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The commercialisation of Solid Oxide Fuel Cells requires stable and cheap components. Although La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ is an excellent cathode material, it suffers from Cr-poisoning by the metallic CroFer interconnect, which has led to a search for Cr-resistant cathode materials. One of the possible candidates is La$_2$NiO$_4$ (LNO), a layered compound with high (2-D) ionic conductivity and high surface oxygen exchange rate. The influence of microstructure on the electrode properties are investigated with impedance spectroscopy. Addition of a dense LNO-layer by Pulsed Laser Deposition between electrolyte and the porous, screen printed LNO electrode significantly lowers the electrode polarisation. Interpretation of the impedance analysis indicates that the electronic resistance of the LNO-electrode is a performance limiting factor. It is also evident from the observation of a predominant Gerischer contribution to the impedance of the porous cathodes that surface diffusion of (possibly charged) oxygen species is the main oxygen transport mechanism. The cathode with the 800 nm LNO-PLD layer can be modelled with a previously developed model for a dense layer electrode where the oxygen exchange rate is modified by the porous LNO structure on top of the layer.

Electrical Properties Of Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ Ceramics Measured at High Frequency

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High planetary mill has been used successfully to produce lead zirconate titanate Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ using commercial mixtures of PbO, ZrO$_2$ and TiO$_2$ powders. The milled powders were studied by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) for phase formation and microstructure characterization. The X-ray diffraction (XRD) patterns indicate that the perovskite phase of PZT was formed after milled for 40 hours. After samples were sintered at 950 °C for 1 hour, the analysis proved the formation of Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ single phase. According to SEM results, the grain sizes of the powders have been estimated to be ~200 nm while after sintered a dense and clearly uniform grain size were observed to be about ~2µm. Dielectric properties were measured at frequency range of 1 MHz to 1 GHz. It was found that the dielectric constant of PZT ceramics to be ~7000, meanwhile, the dielectric loss is ~0.04 measured at 1 MHz. Moreover, results also indicate that high planetary mill is an effective technique to improve the sinterability of PZT ceramics where the relative density of sintered samples was measured to be about 99.93% from the theoretical density.

Influence of growth conditions on PbZr$_{0.20}$Ti$_{0.80}$O$_3$ thin films

Werner Wessels, Anuj Chopra, Gertjan Koster and Guus Rijnders

MESA+ Institute for nanotechnology, University of Twente, Enschede, The Netherlands

We report on growth and ferroelectric properties of epitaxial PbZr$_{0.20}$Ti$_{0.80}$O$_3$ (001) films. Single phase epitaxial films were grown on vicinal SrTiO$_3$ (001) and DyScO$_3$ (110) substrates with a layer of SrRuO$_3$ as bottom electrode by pulsed laser deposition. In order to investigate the influence of oxygen background pressure on microstructure and
ferroelectric properties of PZT films, the background pressure for PZT growth was varied from 0.08 mbar O$_2$ to 0.274 mbar O$_2$. The crystal orientation and topography of the films were analysed by X-ray diffraction and atomic force microscopy respectively. The influence of oxygen pressure on microstructure was studied through RHEED during the growth and afterwards investigated by RSM. Further, ferroelectric and piezoelectric properties of these films were investigated macroscopically and microscopically.
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