COST MPO904 Action
„Single-and multiphase ferroics and multiferroics with restricted geometries”

Conference
of the Working Group 3

Recent advances in ferro/piezoelectric and multiferroic-based composites

22-23 Aprile 2013
National Research Council of Italy
Institute of Science and Technology for Ceramics
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INVITED talks
Ferroelectric and multiferroic micro- and nanostructures from core-shell particles

V. Buscaglia

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The coating of particles with a layer of a different compound has been extensively investigated to add new functionalities to many different materials or modify their properties. Core-shell particles and templates were prepared using colloidal chemistry techniques. The shell compound can be directly precipitated on the core particles suspended in a solution of an appropriate precursor. Hydrolysis of the solution and precipitation is induced by increasing temperature or changing the pH. Core-shell particles can be used as building blocks for the fabrication of dense dielectric, ferroelectric and multiferroic composites with 3-0 connectivity or ceramics with controlled composition and property gradients at the level of the single grains. Interdiffusion and interface reaction during densification can be minimized by using advanced sintering techniques such as spark plasma sintering. Some examples corresponding to the combination of a well known ferroelectric material such as BaTiO$_3$ with paraelectric (SrTiO$_3$, BaZrO$_3$), antiferroelectric (PLZT) and magnetic (Fe$_2$O$_3$) compounds will be illustrated. An other important application of core-shell particles is as templates for the synthesis of nanostructures with specific morphology by solid-state reaction. The core-shell assembly maximizes the contact surface and minimizes the diffusion distance between the two reactants. Therefore the reaction will occur at lower temperature leading to product particles with well defined morphology. If the core is a single crystal particle and the transformation occurs by a topochemical reaction, the core morphology will be preserved. However, the final geometry of the product particle will depend on the specific arrangement of the reactants in the starting core-shell template. Synthesis of nanowires, nanotubes and hollow particles using the above approach will be discussed.
Polymer based magnetoelectric materials: present status, application and challenges

P. Martins\textsuperscript{1,2} and S. Lanceros-Mendez\textsuperscript{1,2}

\textsuperscript{1}Centro/Departamento de Física Universidade do Minho, 4710-057, Braga, Portugal
\textsuperscript{2}INL-International Iberian Nanotechnology Laboratory, 4715-330 Braga, Portugal

Polymer based magnetoelectric (ME) materials represent a challenging research field ready to bridge the gap from fundamental research to applications. The current state of the art on the different materials and configurations for the development of sensors and actuators, as well as the ME couplings obtained for the different polymer based systems will be presented. Further, some of the specific applications in which polymer based ME materials will be addressed, together with the remaining challenges in this research field.
First-principles approach to multiferroics and magnetoelectrics

S. Picozzi

National Research Council of Italy - CNR-SPIN L'Aquila, Italy

The interplay between magnetism and ferroelectricity in transition metal oxides offers a rich and fascinating phenomenology, that can be successfully modelled via density functional theory combined with symmetry considerations and/or model-Hamiltonian approaches. We will present several examples where modelling can provide an explanation of the microscopic mechanisms at play in multiferroic and magnetoelectric materials, ranging from magnetically-induced ferroelectrics and charge-order induced ferroelectrics to novel multiferroics (both in their bulk phase as well as at the nanoscale). In all cases, the link between structural distortions (polar as well as non-polar) and electronic (spin, charge, orbital) degrees of freedom is found to play a key role in the observed phenomenology and often necessary for multiferroicity to develop.
Controlled extrinsic room temperature magnetoelectric effect in granular nanocomposites for engineering novel microwave devices

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CS 93837, 29238 Brest Cedex 3, France

The dynamical control of the dielectric response in magnetoelectric (ME) nanocomposites (NCs) renders an entire additional degree of freedom to the functionality of miniaturized magnetoelectronics and spintronics devices. In composite materials, the ME effect is realized by using the concept of product properties. Through the investigation of the microwave properties of a series of BaTiO$_3$/Ni NCs fabricated by compaction of nanopowders, we present experimental evidence that the compaction (uniaxial) pressure in the range 33-230 MPa affects significantly the ME features. The Ni loading was varied from zero (BaTiO$_3$ only) to 63 vol.%. We demonstrate large increases of the real and imaginary parts of the microwave effective complex permittivity of a series of (piezoelectric)BaTiO$_3$/(magnetostrictive) Ni nanocomposites under the action of a magnetic field, by about 10% at 2 kOe and 300% at 5 kOe respectively. We suggest that the magnetic field dependence of the effective permittivity is consistent with a magnetoelectric effect which can be qualitatively understood within a model in which the piezoelectric phase is mechanically coupled to the magnetostrictive phase. Our findings revealed that the ME coupling coefficient exhibits a large enhancement for specific values of the Ni volume fraction and compaction pressure. The coupling effects in the NCs were studied by looking at the relationships among the crystallite orientation and the magnetic properties. The magnetization curves for different directions of the applied magnetic field can not be superimposed. We suggest that the average magnetization measurements on these NCs under compressive stress are dominated by strain anisotropy rather than magnetocrystalline anisotropy. Overall, these observations are considered to be evidence of stress-induced microstructural changes under pressure which strongly affect the elastic interaction between the magnetostrictive and piezoelectric phases in these NCs. These results have a potential technological impact for designing precise tunable ME NCs for microwave devices such as tunable phase shifters, resonators, and delay lines.
Combined effect of depletion charges and interfaces on polarization stability and electrical domains in ferroelectric thin films

B. Mýsýrlýoðlu

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Interfaces in ferroelectric structures are important not only because these are the boundaries at which the regular structure of the crystal terminates but also because of the termination of the polar arrangement and nature of the contact with the electrodes if the system is electroded. Therefore, the treatment of ferroelectrics as polar semiconductors becomes inevitable both in computational studies as well as experimental work. In this talk, I will summarize the effect of electrical boundary conditions on ferroelectrics in thin film form and possible scenarios in case the ferroelectric has moderate to high densities of vacancies or impurities. The content of the talk will primarily involve our recent findings on coupling between electrical domains and depletion charges and how depletion charges alter the Curie point. The possibility that high densities of depletion charges might invert the thickness effect concerning the stability of polarization in ferroelectric films will also be discussed.
ORAL Presentations
Synthesis and functional properties of ferroelectric-carbon nanotube composites by Spark Plasma Sintering

C. E. Ciomaga¹, A. M. Neagu¹, C. Galassi² and L. Mitoseriu¹

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²CNR -ISTEC, Via Granarolo no. 64, I-48018 Faenza, Italy

In this work, the ferroelectric (Pb(Zr0.47Ti0.53)O3 -PZT) multi-walled carbon nanotubes (MWCNTs) composites were prepared by spark plasma sintering. By using Spark Plasma Sintering (SPS) we expect to obtain composites with new functional properties, which were previously not possible to fabricate using conventional processing routes, non-equilibrium composites. SPS can process the composites in very short intervals of time without structural or chemical degradation of the CNTs. Using this method can be developed ceramics with new electro-mechanical properties and applications, such as, heating elements, Electro Discharge Machinability (EDM), and high electrical and thermal anisotropy [1, 2].

The structural and microstructural investigation of (1-x)Pb(Zr0.47Ti0.53)O3-xCNT ceramic composites with different concentration of CNTs were perform by X-Ray diffraction and SEM analyses. The XRD diagram confirms the incorporation of CNTs in the perovskite lattice of PZT and the presence of two distinct phases (Fig.1). The Impedance Spectroscopy analyze was performed at room temperature in the range of frequency of 1Hz-1MHz. We have studied the influence of addition of CNTs on the dielectric properties of investigated ceramic composites. Thus, the dielectric investigations at room temperature have shown the formation of composites: the dielectric constant of the composites increases with the increasing of the volume fraction of CNTs due to the Maxwell–Wagner polarization originating from the CNTs (conductor) and PZT (insulator) interfaces. The dielectric losses are smaller than 0.35 in overall frequency range for all compositions (Fig. 2). In the microwave range (1MHz-1GHz), the ferroelectric-CNTs composites presents high values of dielectric permittivity around 1500 for x=0.2, at f=100MHz.

Fig. 1. Structural characterization of (1-x)PZT-xCNT ceramic composites after SPS.

Fig. 2. Frequency dependence of real part of permittivity of (1-x)PZT-xCNT ceramic composites (inset: Frequency vs. Imaginary part of permittivity).

Acknowledgements: This work was financial supported by CNCS-UEFISCDI grants TE 187/2010 and PN-II-ID-PCE-2011-3-0745. The collaboration in frame of the COST Action MP0904 is highly acknowledgements.

References
3D imaging by X-ray micro tomography of ferroelectric composite materials and numerical modelling of their properties

J. Lesseur\(^{1,2}\), C. Elissalde\(^{1,2}\), C. Estournès\(^3\), G. Chevallier\(^3\), D. Bernard\(^{1,2}\)

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Ferroelectric materials are commonly used to produce passive components for microelectronic and telecom applications. These applications require well-controlled modulation of their physical parameters (permittivity, temperature transition, dielectric losses…). Therefore, several approaches are explored to improve the properties of these materials. In this study, new design controlled composites are presented. Low loss non-ferroelectric particles (MgO) are introduced in a ferroelectric powder (Ba\(_{0.6}\)Sr\(_{0.4}\)TiO\(_3\)), to obtain, after sintering by Spark Plasma Sintering (SPS), non-ferroelectric inclusions within a ferroelectric matrix [1].

An innovative procedure is developed to propose a complete quantitative description of the ferroelectric composites based on: i) 3D imaging on the real micro geometry obtained by X-ray computed tomography (Fig.1), ii) measurement of the ferroelectric properties, iii) numerical modelling of the key processing steps and of the ferroelectric properties. Final anisotropic architecture of the composites is strongly defined by the initial powder mixing and by the inclusions deformation during high temperature compression. Image processing tools are used to characterize the microstructure and three-dimensional permittivity simulations are performed to investigate the link between microstructure and physical properties. Comparison with experimental results will be performed to validate the models.

![Figure 1: 3D rendering of a composite material sintered by SPS. On the 2D sections, the light grey zone corresponds to the BST matrix and the dark zones to the MgO inclusions. On the 3D rendering, the matrix is transparent and the inclusions are represented in yellow.](image)

References

Magnetoelectric Properties of BiScO$_3$-PbTiO$_3$/NiFe$_2$O$_4$ Ceramic Composites

H. Amorín$^1$, R. del Campo$^1$, P. Ramos$^2$, I. Martínez$^1$, E. Vila$^1$, M. Dollé$^3$, Y. Romaguera$^4$, J. Pérez de la Cruz$^4$, A. Castro$^1$, M. Algueró$^1$

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Piezoelectric oxides are being considered in combination with magnetic materials for the development of magnetoelectric two-phase composites, in which strain continuity across the interface is a key issue [1]. In this context, we are investigating novel methods for the preparation of ceramic composites that minimize phase interdiffusion and reactions during material preparation [2]. Novelty rests on using nanopowders of the ferroic oxides obtained by mechanosynthesis, and the spark plasma sintering (SPS) to obtain laminated composites.

We have chosen the morphotropic phase boundary BiScO$_3$-PbTiO$_3$ perovskite because it shows high piezoelectric coefficients comparable to those of Pb(Zr,Ti)O$_3$, with a higher Curie temperature, and better properties on grain size down-scaling [3]; and the NiFe$_2$O$_4$ spinel as the magnetostrictive phase. Fig. 1 shows a FEG-SEM image of the typical multilayer composite obtained by SPS with layers of 35-50 $\mu$m prepared by tape-casting.

Emphasis has been put on minimizing chemical reactions at and interdiffusion across the interface between the two phases to obtain dense composites with tailored interfaces. Interfaces were further investigated by using high spatial resolution techniques such as micro-RAMAN and piezoresponse force microscopy (PFM). The macroscopic electrical, magnetic and magnetoelectric properties are described, as shown in Fig. 1 for the latter case. A novel equipment, recently designed and implemented at ICMM, was used to characterize the magnetoelectric response. Results are correlated with the interface characteristics, and demonstrate the feasibility of preparing magnetoelectric composites by this approach.

**Figure 1** FEG-SEM image of a multilayer composite and their magnetoelectric response

**Acknowledgements.** This work has been supported by the Spanish MICINN projects MAT2011-23709 and AIB2010PT-00332. H. Amorín also thanks financial support by Ramón y Cajal Programme. The authors are grateful to Prof. Rodrigo Moreno and Ms. Tamara Molina (ICV-CSIC, Spain) for support in the processing of the materials. Serviciencia S.L. (http://www.serviciencia.es/home.htm) participation in the design and built-up of the magetolectric equipment is acknowledged.

**References**
Nanostructuring Fe$_3$O$_4$ - TiO$_2$ composites by Colloidal Approach Coupled with Spray-drying

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Composite nanoparticles with a magnetic core (Fe$_3$O$_4$, magnetite) and a photocatalytic shell (TiO$_2$, anatase) have been investigated for their promising properties as magnetically separable photocatalysts in water depuration systems [1]. Such structures can be improved by the deposition of carbon [2] or silica [3] based coatings onto magnetite surface, in order to prevent the photocatalytic activity reduction due to the unfavourable heterojunction between the titanium dioxide and the iron oxide. Several synthetic/colloidal approaches have been described to produce these hierarchical nanostructures where magnetite core is separated by a passive carbon or silica layer from TiO$_2$ shell. In this work we coupled a new and easily industrially scalable colloidal approach, with spray-drying technique at the aim of engineering TiO$_2$/magnetite based nanostructures suitable for water depuration systems.

![Figure 1- Design of TiO$_2$/ SiO$_2$/ Fe$_3$O$_4$ nanostructure and SEM micrograph of spray-dried TiO$_2$ powder](image)

Commercial sols of TiO$_2$, SiO$_2$ and Fe$_3$O$_4$ were characterized, optimized and a self-assembled layer by layer approach was followed in order to promote the heterocoagulation of silica onto magnetite surface and of titania onto silica coated magnetite, as schematized in Figure 1 (on the left). Once optimized, the colloidal mixture was spray-dried in order to obtain a granulated powder (Figure 1, on the right) with nano-scale reactivity, easy to handle and re-disperse in comparison to starting nanopowders, with the same surface properties of colloidal system.

References
Lead Zirconate Titanate – Acrylate Composites Fabricated by Inkjet Printing

D. Kuščer 1,2, M. Pajic 1, O. Noshchenko 1, U. Šebenik 3

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We studied the integration of lead zirconate titanate (PZT) piezoelectric ceramic that is widely used as sensors and actuators, with fabric to realise smart textile. The materials were deposited on fabric by piezoelectric ink-jet printing as a low-cost, reliable, highly-flexible, non-contact, digital and convenient patterning technique that enables in-situ deposition of liquid precursors onto various substrates in air atmosphere. In order to successfully integrate the ceramic material with a temperature-sensitive fabric, the ultra-violet (UV) systems were used for curing the as-deposited layer.

The critical parameters in ink-jet printing are the preparation and stabilization of nano-sized particles in a solvent and adjusting its physical properties to the values appropriate for a selected ink-jet printer. Colloidal suspensions containing 1–10 vol % of PZT were processed from micrometer-sized PZT powder prepared by solid state synthesis. The powder was stabilized in water at pH 10 and subsequently milled in a colloidal ball-mill. The polyacrylic acid was used as an additive. After 4 hours of milling the dispersion with volume particle size $d_v^{100}$ of 450 nm and a zeta potential of -50 mV was obtained. The surface tension of the aqueous suspension was regulated by adding a catalytic amount of an non-ionic amphiphile Triton X-100 that decreased the surface tension from 68 mN/m to a required value of 30 mN/m. The viscosity and drying behavior of the suspension were optimised by the addition of polyvinyl alcohol and hydroxylated ethylcellulose. The properties of PZT dispersion were appropriate for piezoelectric ink-jet printer (Dimatix DMP 2831).

Similarly, printable UV curable polymer system was developed. The acrylate-based monomers 2-ethylhexyl acrylate, 1,6-hexanediol ethoxylate diacrylate and dipentaerythritol penta-hexa acrylate were used. The procedure for optimisation the composition of acrylate mixture based on measuring surface tension and its viscosity will be reported. After the addition of photoinitiator 2-hydroxy-2-methyl-propiophenone the polymerization and curing of as-deposited acrylate layer as a function of photoinitiator amount and curing time was studied by infra-red spectroscopy.

The piezoelectric-polymer composites were prepared by two step printing method. Onto the ink-jet printed piezoelectric layer the optimised monomer mixture was printed. The monomers were UV polymerized and cured at optimal conditions. The functional response of the composite will be reported and related to the PZT particle size, microstructure and rate of the polymerisation.

Acknowledgements
The work reported in this paper was initiated by Prof. Marija Kosec, who died on December, 2012. Dr. Janez Holc is thanked for fruitful discussion. This research was supported by Slovenian Research Agency and 7 EU FP project MICROFLEX (CP-IP 211335_2).
Electrophoretic deposition of lead zirconate titanate on conductive and semiconductive substrates: deposition parameters for the control of film morphology

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Electrophoretic deposition (EPD) of piezoelectric (PE) materials is well documented in the literature, and a number of cutting-edge applications have been made possible by the flexibility of this technique, enabling engineers to produce complex-shaped devices and microdevices based on thick and thin coatings of piezoelectric ceramics on conductive substrates. EPD on semiconductor (SC) substrates, however, is much less developed, and the study of PE/SC interfaces with no interposed metallization, although interesting, is less documented, although a number of aspects relating to the equilibrium state of such interfaces has actually been discussed (see Ref. 1 and references therein). Co-sintered PE/SC interfaces are expected to pose even greater problems, due to the degradation of both PE and SC components in some region around the PE/SC interface, as mutual interdiffusion occurs at the high temperatures that are required to densify the PE material. We have in some cases been able to obtain both the EPD of niobium-doped PZT on p-type silicon and well-defined and adhered PZTN/Si interfaces by co-sintering the deposited wafers. We accordingly discuss some aspects of the process, and we report on our attempts to gain information on the physical state of the interface and its possible use.

References
New functional properties driven by interface reactions in core-shell structures

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The nanoscale coating of particles of a material with a dissimilar compound is an effective tool to engineer its surface, microstructural characteristics and functional properties. The method of using core-shell powders followed by an appropriate method of sintering is a very successful route to obtain desired microstructures with various degrees of connectivity in ceramic composites. Core-shell multiferroic formed by a magnetic core (Fe₂O₃ and (Ni,Zn)Fe₂O₄) and a ferroelectric shell (BaTiO₃) were prepared and then densified either by classical sintering at various temperatures (1050°C-1150°C) or by spark plasma sintering [1]. By employing various sintering strategies, dense and homogeneous ceramics were produced with: (i) di-phase compositions with fully isolated magnetic regions within a BaTiO₃ matrix (0-3 connectivity), (ii) multi-phase compositions, as result of the interface reactions between constituents. Besides the properties of the parent materials, variable amounts of secondary phases (Fe₃O₄, BaFe₁₂O₁₉ and Ba₁₂Fe₂₈Ti₁₅O₈₄) have driven to new functional properties in the ceramic composites. Dielectric, tunability and magnetic properties were determined and discussed in correlation with the sample microstructures, composition and degree of connectivity. The ceramics show interesting dielectric characteristics, with dielectric constant of 100-300 (Fig. 1 a) and low losses by comparison with other BaTiO₃-based magnetoelectric composites due to the isolation of the low-resistivity magnetic phase [2]. Peculiar magnetic properties, including “wasp-waisted” constricted M(H) loops were determined as result of the formation of magnetic phases with contrasting magnetic coercivities (hard and soft phases) (Fig.1 b, c). The present results demonstrate the usefulness of the core-shell approach in driving new functional properties in multifunctional composites by an appropriate control of the in situ solid-state nanoscale interface reactions.

![Figure 1](image)

**Fig.1** Functional properties of composite ceramics sintered from core-shell BaTiO₃@Fe₂O₃ composite nanopowders (a) permittivity vs. temperature for two composition, (b,c) FORC measured curves for same composite in which the weight of the soft/hard secondary phases is modified by thermal treatment.

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**References**
About ballistic transport in hybrid electronic devices

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We present our results in the investigation of ballistic electron transport in hybrid ferromagnet/semiconductor devices. Devices are produced by a series of two magnetic barriers of opposite polarity, placed on top of a Hall bar etched into a GaAs/AlGaAs heterostructure. The size of the Hall bar is comparable to the size of the magnetic structure and smaller than the mean free path of the electrons, which places the structure in the quasi-ballistic regime [1].

We investigate experimentally and by simulations the electronic response of such devices and we exploit the confinement capabilities of the magnetic barriers to control the electron flow.

The strength of the magnetic field profile is tuned by an external applied magnetic field, and the electron density is tuned by a metallic top gate. The magnetoresistance of the device is large (in the range of 100%) and shows non-ohmic behavior with characteristic transmission and reflection resonances. The measurements are in agreement with semi-classical simulations using the Landauer-Büttiker formalism with scattering [2, 3], and reveal the origin of the resonances residing in the quasi-ballistic transport of electrons confined by the edges of the Hall bar and the magnetic field profile.

References

Thermo-Raman spectroscopy study of phase transitions in barium and strontium titanate nanostructures

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The phase transition from ferroelectric to paraelectric phase in the case of perovskite materials is usually caused by structural phase transition. Typical example is BaTiO₃ (BTO) and SrTiO₃ (STO) where phase transition from tetragonal to cubic phase induces the transition from ferroelectric to paraelectric state. Expected phase transition temperature is between 380 and 420 K for BTO, and between 100 and 120 K for STO. These phase transitions depends on the different factors such as doping [1], grain and particle sizes [2] phase purity [3] etc. In this work the influence of the phase purity and morphology of the barium and strontium titanate nanostructures to the phase transition temperatures are investigated using Raman spectroscopy as the main method.

For the synthesis of potentially ferroelectric barium and strontium titanate nanostructures we apply two different approaches. In the first method we synthesize potentially ferroelectric titanate nanostructures by ion exchange barium and strontium ion with titanium ions in the crystal structure of titanate nanotubes and nanowires (H₂Ti₃O₇). For this synthesis we used different aqueous solution of barium and strontium salts and hydrothermally prepared titania nanostructures. In the second method we mixed strontium and barium hydroxide with titanium dioxide nanoparticles and hydrothermally prepared barium/strontium titanate nanostructures.

Obtained nanostructures were characterized by micro-Raman spectroscopy (RS), X-ray powder diffraction and high resolution transmission electron microscopy (HRTEM). Temperature dependent micro-RS measurements were done in situ at different temperature using Linkam heating stage.

Tetragonal phase of BFO, having 4mm simetry with c/a axis ratio close to one, is hard or impossible to distinguish from cubic phase by using diffraction techniques, so the phase purity and the crystal structure of the samples were studied by the combination of XRD and RS. The purity of the samples depends on the synthesis procedure. In situ low and high temperature RS was used for study of ferroelectric phase transitions from tetragonal to cubic structure in BTO and STO related nanostructures having different phase purity. The influence of the morphology and the phase purity to the temperature of phase transitions will be discussed.

Acknowledgements

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References

Broadband dielectric spectroscopy of $0.6\text{BaTiO}_3-0.4\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ composite ceramics

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Multiferroic materials, exhibiting more than one ferroic property (ferromagnetism, ferroelectricity, ferroelasticity) in a single phase has drawn a wide scientific and technological attention in the present years for the fundamental research and due to the variety of possible practical applications. Here we present the dielectric studies of one of possible multiferroic composite – $0.6\text{BaTiO}_3-0.4\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (BT-NZF) ceramics. BT-NZF was successfully prepared by the co-precipitation method, and the presence of only the perovskite BT and spinel NZF phases was confirmed [1]. The results of the dielectric spectroscopy in the 100 to 500 K temperature and 20 Hz to 1 GHz frequency range will be presented.

![Graph](image-url)

Figure 1 Frequency dependence of real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of dielectric permittivity at selected temperatures

Dielectric spectra are dominated by conductivity at frequencies below 1 MHz at higher than room temperatures (Fig. 1). Such behavior must be primarily due to ferrite phase of the composite and it is likely to be related to the Maxwell-Wagner polarization mechanism [2, 3]. At higher frequencies, where the conductivity contribution is remarkably lowered, onset of a relaxation process can be observed, which extends to frequencies much higher than 1 GHz.

References
The role of the local electric field inhomogeneity on the electrical properties of ferroelectric composites

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Nowadays, the material scientists attention is focused in investigation of new dielectric materials with tailored properties: permittivity, tunability, P(E), etc. for specific applications. Unfortunately, the required electrical properties are not usually accomplished in single phase systems, and the researchers solution was the development of multiphase composite materials. By comparison with a single phase material, a composite is characterized by the presence of interfaces separating regions with different permittivities, which induce the formation of local inhomogeneous fields which should be taken into account when a theoretical model is proposed.

The aim of this work is the theoretical investigation of the role of the local electric field inhomogeneity on different electric properties of composites: effective permittivity, nonlinear tunability and P(E) response. The local field calculations were performed by Finite Element Method (FEM), by solving the Laplace's equation: \( \nabla \cdot (\varepsilon \nabla V) = 0 \), where \( \varepsilon \) is the local permittivity, \( V \) is the local potential and the local field is the potential derivative \( \vec{E} = -\nabla V \).

Different structures with various microstructure particularities were generated and investigated by FEM analysis in order to estimate different properties. A remarkable agreement between the experimental tunability features and the model calculations was obtained in nanostructured BaTiO\(_3\) ceramics (composite with di-similar grain bulk and grain boundary regions) with grain size between 5000 to 90 nm and for porous PZT materials (composite with ceramic bulk and air pores) with different porosity levels [1,2]. Others satisfactory results were derived for a combined FEM-Preisach model applied to estimate the field-dependence of the polarization (MHL and FORC) in ferroelectric composites (particular case: porous PZTN ceramics).

Acknowledgments:

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References:
Phase diagrams and interaction between polar and antiferrodistortive modes in the PZT and NBT-BT systems

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Thanks to the combination of dielectric and anelastic spectroscopies, it has been possible to probe the structural transitions involving the antiferrodistortive (AFD) tilt modes of the octahedra better than before in PZT [1] and NBT-BT [2]. In PZT close to the antiferroelectric phase, a new border \( T_I \) is identified with disordered tilting before the final long range ordered tilting of the \( R3c \) phase is established below \( T_I \). Such a line merges with \( T_C \), presumably giving rise to a combined ferroelectric-tilt transition. On the high-Ti side of our series of large grain ceramic samples, \( T_I \) does not cross the morphotropic phase boundary (MPB), but merges with it.

On the other hand, in NBT-BT it had already been established that the instability to the ferroelectric state \( T_d \) coincides with the tilt transition between tetragonal \( a^0ac^* \) and rhombohedral \( a'a'a' \) (in Glazer notation) over an extended range of Ba compositions.

These lines of combined polar-tilt transitions are vertically hatched in Fig. 1, and it is suggested that they are a consequence of cooperative interaction between the polar and the AFD modes, as proposed for the trigger-type transitions in the multiferroic BiFeO\(_3\) [3].

Figure 1 Phase diagrams of PZT and NBT-BT where the combined polar-AFD transitions are vertically shaded. The tilt patterns are given in Glazer notation S/LRO = short/long range order.

References
Comparison between hard/soft PZT composite materials with different degree of mixing

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In the present study, we analyzed the role of the length scale mixing degree on the dielectric and ferroelectric properties of doped lead zirconium titanate (PZT) system with soft/hard counterparts, which were mixed at different degree levels. Two types of ceramic soft/hard PZT composite materials were produced: (i) with macroscale mixing (“chess board table” – Fig. 1) and (ii) with microscale mixing. The composites are formed by the same compositions of soft PZT (conventional Nb doped PZT – PZTN: light color) and hard one (Nb, Mg, Mn and La doped PZT – PZTNMML: dark color). The investigated samples were prepared by solid state method and sintered at 1200°C for 2 hours. In Figure 1 it is shown a sample obtained by macroscale mixing of PZTNMML and PZTN phases with 50:40 volume ratio and in Figure 2 is presented a sample obtained by PZTN and PZTNMML phases micro mixing with 55.5:44.4 volume ratio.

![Figure 1](image1.png)  ![Figure 2](image2.png)

The phase purity and microstructures have been investigated by X-Ray Diffraction and by SEM. The impedance spectroscopy analysis for the presented systems showed differences resulted from the various mixing degree in the two types of samples. AFM and PFM analysis were performed in order to analyze the influence of length scale of mixing on ferroelectric domains formation. Interesting particularities of the switching characteristics at room temperature of the soft/hard PZT ceramic composites were obtained. The results were analysed by using the First Order Reversal Curves (FORC) diagrams, by recording minor hysteresis loops when cycling the sample between the saturation and a variable reversal field and by computing the corresponding diagrams with the numerical method [1].

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References:
Characterization of a novel M-type Ba-Sr hexaferrite for UHF patch antenna miniaturization

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In this contribution we discuss the theoretical and experimental aspects of a novel UHF patch antenna exploiting, for miniaturization purposes, a new M-type barium-strontium hexaferrite $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{Fe}_{12}\text{O}_{19}$ (BSFO) \cite{Pereira} as its substrate, in view of wearable application \cite{Aldrigo}. The BSFO is a Magneto-Dielectric (MD) material with a strong anisotropy, which allows to extend its frequency of operation in the UHF band. In this situation the upper frequency limit may be evaluated by a modified expression of the Snoek’s law exploiting the high anisotropy field $\mathbf{H}_k$ (elliptically-polarized), as follows:

$$\omega_r \min \cdot \mu_i = \gamma \cdot 4\pi M_s \cdot \frac{H_{K,\ell}}{H_{K,e}}$$

where $H_{K,\ell}$, $H_{K,e}$ are the cross-polar and co-polar components of $\mathbf{H}_k$ (respectively) with respect to the easy-plane of magnetization. By exploiting the value of relative permeability $\mu_r$ greater than unit, with lower values of relative permittivity $\varepsilon_r$, the same miniaturization factor in antenna design can be achieved. In Fig. 1a, the measured values of $\varepsilon_r=\varepsilon’-j\varepsilon''$ and $\mu_r=\mu’-j\mu''$ of the first prototype are plotted all over the band of interest, i.e. 750 MHz – 1 GHz. These behaviors are matched to the Drude model available in the electromagnetic simulator for antenna design. The BSFO has been produced at ISTEC (Faenza) by ceramic processing via the Mixed Oxide synthesis method by calcination (heating at 900 °C for 12 hours), followed by consolidation (die pressing at 400 kg/cm\textsuperscript{2}) and cold isostatic pressing at 3000 kg/cm\textsuperscript{2}. Heat treatment at 1250 °C for 5 hours has resulted into sintered bodies with the highest final relative density of about 96%. In Fig. 1b, the final prototype of a shorted $\lambda/4$-patch antenna is shown. The operating frequency is 868 MHz. The patch, the shorting-plate and the ground plane are made of a 4 μm-thick silver film. Good agreement between predicted and measured radiating performance has been obtained in realistic scenarios for wearable applications.

Figure 1 a) measured and modeled values of $\varepsilon_r$ and $\mu_r$, b) detailed view of the wearable patch antenna.

References
Some thermodynamic aspects of preparation of dense and phase pure
Eu(Ba,Sr)TiO₃ ceramics

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Multiferroics exhibiting simultaneously ferroelectric and ferro- or antiferromagnetic order are known since the beginning of the 1960’s, but the interest in these materials underwent a revival in this century when the gigantic magnetocapacitive effect has been observed in EuTiO₃ [1]. Eu(Ba,Sr)TiO₃ ceramics are currently attracting significant interest due to their ferroelectric properties and their potential applications in information technology.

EuTiO₃ was up to now reported as a simple cubic perovskite. Some new investigation of structural and lattice dynamics studies of bulk EuTiO₃ ceramics showed lattice instability close to the room temperature. It can be possible that the structure in Eu(Ba,Sr)TiO₃ depends on sample preparation. The presence of pores and impurities deteriorates properties of sintered ceramics, as it was e.g. demonstrated for infrared reflectivity [2]. From this point of view the processing of pore-free and impurity-free Eu(Ba,Sr)TiO₃ ceramics is of primary interest of physicists and material scientists.

EuTiO₃, Eu₀.₅Ba₀.₅TiO₃ and Eu₀.₅Ba₀.₂₅Sr₀.₂₅TiO₃ ceramics were synthesized using mechanochemical activation of precursors and then calcined. The dried powders were pressed by uniaxial pressing as well as by cold isostatic pressing. The samples were then sintered in different kinds of reducing atmospheres, namely Ar + (7-10)%H₂, resp. 99.9%H₂ in case of pressure-less sintering; or in vacuum (enriched by CO vapors) in case of pressure-assisted Spark Plasma Sintering. The results showed the importance of highly reductive conditions during sintering. The samples prepared by SPS were dense (>90%TD), but not phase pure. In contrast to SPS, pressure-less sintered samples were phase pure, without pollutant phases. The proper choice of sintering temperature and time resulted also in dense samples (90-95%TD). Such samples were therefore suitable for evaluation of “true” physical properties (e.g. infrared reflectivity [3]), or for experimental confirmation of specific functionalities proposed from first-principles [4]. The thermodynamic conditions necessary for preparation of phase pure materials (namely the sintering atmosphere [5] and pad materials in the furnace) were calculated and discussed.

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References
Multiferroic properties of (Sm, Fe)-doped PbTiO₃ perovskite ceramics

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One of the main ways to obtain single-phase materials with ferroelectric and magnetic properties is to start from a ferroelectric perovskite oxide and substitute on the B site with magnetic ions while keeping the A site occupied by a cation with a stereochemically active ns² lone pair, like Pb or Bi. An alternative way, by keeping the d⁰ B cation ferroelectric and substituting on the A site with magnetic rare earth (R) ions with a partially filled f shell [1], gives compounds with very low temperatures for magnetic ordering. In this study we follow yet a different path, by adding also a transition element with large ionic radius, like Fe²⁺ (r = 0.92 Å) besides the R (Sm³⁺) ion, on the A site of PbTiO₃, while keeping B cation ferroelectric. Since the 3d orbitals of transition elements are less localized than 4f orbitals of R ions, the superexchange interaction through O 2p orbitals will be stronger. (Pb₀.₈₄₅Sm₀.₀₈Fe₀.₀₃₅)(Ti₀.₉₈Mn₀.₀₂)O₃ ceramic samples have been prepared by solid state reaction. The XRD analysis confirmed the obtaining of a pure crystalline phase of tetragonal P4mm symmetry with lattice constants \( a = 3.90197 \) Å, \( c = 4.09637 \) Å. Temperature dependence of dielectric permittivity shows a strong anomaly at 662 K (Fig.1(a)), at the paraelectric-ferroelectric transition, and a broader anomaly below 140 K where magnetization also increases, due to the magnetoelectric coupling between ferroelectric and magnetic states. A good spontaneous ferroelectric polarization (14 µC/cm²) and moderate ferromagnetism (remanent magnetization \( M_r \approx 2.3 \) emu/g) (Fig. 1(b)) have been found. Slim magnetic hysteresis loops are measured even at room temperature (\( M_r \approx 0.1 \) emu/g). The dielectric constant is 190, tan δ ~0.005 and the piezoelectric \( g_{33} \) constant is 25 mV×m/N.

![Figure 1](image_url)

(a) Figure 1 (a) Temperature dependence of the real part of dielectric permittivity, \( \varepsilon' \), at different frequencies for (Sm,Fe)-PbTiO₃, on heating and cooling; (b) Magnetization, \( M \), dependence on the applied magnetic field, \( H \), measured at \( T = 80 \) K for (Sm,Fe)-PbTiO₃ and for pure PbTiO₃.

References
O 17

2D Self-Organisations Of Co@CoO Core-Shell and CoO Hollow NCs. (S)TEM, HAADF And EELS Studies

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7 nm-Co nanocrystals (NCs) coated with dodecanoic acid are obtained via soft chemistry route involving micellar system. Once deposited on amorphous carbon covered TEM grid, these NCs self-organize in a hexagonal network [1]. Suitable annealing treatments (in dry-phase and solution-phase) induce the crystallographic transition from poorly crystallized to hexagonal close packed (hcp) single-crystalline structure that induces a drastic increase in the blocking temperature, from 100K to room temperature [2-4]. Whatever the thermal treatment is, the magnetic NCs keep their integrity without coalescence or oxidation. Their organization induces collective and intrinsic chemical properties (stability against oxidation) and physical one’s (magnetic and vibration one’s). Whatever the nanocrystallinity is, Co nanoparticles show enhanced stability against oxidation when they are closely packed in a 2D hexagonal network as opposed to the isolated one’s on the substrate [5, 6]. Depending on the oxidation treatment and the Co nanocrystallinity, Scanning Transmission Electron Microscopy (STEM), High-Angle Annular Dark Field (HAADF) and Electron Energy-Loss Spectroscopy (EELS) studies clearly evidence that Co NCs, 2D self-organized, undergo an oxidation process, giving rise to 2D hexagonal organizations of either Co@CoO core-shell NCs [5-7] or CoO hollow NCs [7]. Besides, the isolated NCs tend to fully oxidize to finally coalesce.

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Thin film multiferroic nanocomposites by a novel approach


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Two-phase ferromagnetic-ferroelectric thin film composites are key to the development of novel magnetoelectric integrated technologies, such as electrical-writing magnetic-reading random access memories [1]. However, film multiferroic nanocomposites investigated so-far, basically oxide columnar epitaxial nanostructures, neither show magnetization reversal under the electric field (magnetoelectric switching), nor electrical polarization induced by a magnetic field (direct magnetoelectric effect) comparable to that achieved with bulk ceramic and cermet technologies [2]. At ICMM, we have investigated the possibility of obtaining multiferroic nanoparticulate composites by a radically novel approach: ion implantation of magnetic species into ferroelectric single crystal targets.

Indeed, a first study was focused on the Co implantation of Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-PbTiO\textsubscript{3} single crystals, and showed the formation of an ensemble of ferromagnetic oxide nanoparticles embedded in an amorphized layer at the surface of the ferroelectric crystal [3]. In this communication, we present an analogous study using BaTiO\textsubscript{3} instead of PMN-PT. Furthermore, the recovery of the implantation damage by rapid thermal processing was also addressed. Results unambiguously demonstrate the preparation of a thin film multiferroic nanoparticulate composite of Co and BaTiO\textsubscript{3} by this procedure. They thus constitute a proof of concept for the feasibility of obtaining these key materials by the alternative novel approach.

References
POSTER PRESENTATION
Influence of the lengthscale cation mixing degree on the dielectric and ferroelectric properties of BaZr$_x$Ti$_{1-x}$O$_3$ ceramics

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BaTiO$_3$-based ceramics are attractive as Pb-free relaxors with applications in microelectronics and wireless communications. The homovalent substitution with Zr$^{4+}$ ions shifts the Curie temperature below room temperature and bring high values of permittivity in desired temperature ranges, but also to significantly broaden the $\varepsilon(T)$ dependence. The Zr/Ti ratio is a very important parameter in the BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) solid solutions which tailors the ferro-paraelectric phase transition type, its characteristic temperature and functional properties. However, various dielectric properties were reported for similar BZT compositions and this raised the question about the possible role of the Zr and Ti cation distribution and mixing degree inside the ceramic body.

In the present work, BZT ceramics with nominal compositions x=0, 0.05; 0.1; 0.15; 0.2 and 0.4 and with different Zr/Ti mixing levels were prepared by solid state reaction from: (i) oxide precursors (BaCO$_3$, TiO$_2$ and ZrO$_2$), then calcined to promote the perovskite phase formation; (ii) by mixing in appropriate proportions perovskite BaTiO$_3$ and BaZrO$_3$ powders to produce a solid solutions in which the Zr/Ti mixing degree is expected to be lower than in previous case. After calcination all the powders were sintered at 1500°C for 4 hours. Dense ceramics (relative density above 95-98%) and homogeneous microstructures have been obtained for all the compositions. Impedance spectroscopy in the temperature range of (-150 to 150)°C shows a composition-dependent shifts of the structural transition temperatures by comparison with ones of the pure BaTiO$_3$ (Fig.1 a). The dielectric characteristics of the samples with same composition and different mixing level show a slight modification of the maximum permittivity, together with a small shift of the characteristic Curie temperature (Fig. 1 b, c).

![Fig. 1 Dielectric constant vs. temperature at f=1kHz BaTi$_{1-x}$Zr$_x$O$_3$ ceramics (a) solid solution with different composition; (b) x=0.10 (c) x=0.15 with different mixing level]

**Acknowledgements:** The financial support of the PN II-PCE-2011-3-0745, PNII-RU-TE-2012-3-0150 and COST Action SIMUFER grants are acknowledged.
Exploration of Single-phase Layered Perovskites as Candidate Magnetoelectrics

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Magnetoelectric multiferroic materials, exhibiting ferromagnetic and ferroelectric properties and a coupling between both, are very interesting in view of specific applications such as four state logic. An effective reversal of magnetization at room temperature is very important for its efficiency but still difficult to obtain. Benedek and Fennie \cite{1} proposed a mechanism by which this would be possible, i.e. hybrid improper ferroelectricity, based on first principles calculations. This mechanism entails the effect on the multiferroic properties of ABO\textsubscript{3} perovskite materials due to (a combination of) oxygen octahedral tilts and rotations. For their calculations, Benedek and Fennie used the Ruddlesden-Popper perovskite Ca\textsubscript{3}Mn\textsubscript{2}O\textsubscript{7}. Beneath a temperature of 280 K, a noncentrosymmetric phase is attained due to these distortions \cite{2}, and below 115 K the oxide showed antiferromagnetic properties \cite{1}. The effective coupling between these ferroelectric and antiferromagnetic properties is stated to be due to the strain that arises in epitaxial films.

Since this computationally predicted mechanism can be very interesting, not only for the investigation of Ca\textsubscript{3}Mn\textsubscript{2}O\textsubscript{7} but also in view of the extrapolation to other systems, it is worthwhile to experimentally confirm this. A first step in this, is the synthesis of this phase, to which end a chemical solution based synthesis is chosen. Here we present precursor synthesis and characterization. Due to the advantages of using water as a solvent, we worked on the development of an aqueous precursor for this oxide, using both citrates as well as acetates as complexing agents for the metal ions. Both precursors contain the metal ions in a Ca\textsuperscript{2+}:Mn\textsuperscript{x+} 3:2 ratio in view of synthesizing the correct oxide. The gel was thermally treated to obtain the desired oxide. An analysis of the samples has been done by FT-IR, ICP-AES, TGA-SDT, XRD and UV-Vis. For the citrate route, the ratio of citric acid to the total metal content is crucial for the stability against precipitation. The acetate route was based on an article by Daengsakul \cite{3} in which, amongst others, La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3} is being prepared.

Further investigation will focus on the phase formation and the deposition of epitaxial films and also on developing a method for hydrothermal epitaxy.

Acknowledgements
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References
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Temperature-dependent Raman analysis of the ferroelectric-antiferroelectric crossover in La-doped lead zirconate titanate ceramics

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Lanthanum (La)-modified lead zirconate titanate ceramics, Pb₁ₓLaₓ(Zr₁₋ₓTi₁₋ₓ)O₃ – PLZT (PLZT X/Y/1-Y, with X=100x, Y=100y), possess exceptional optical, dielectric and piezoelectric properties, which makes them especially suitable for electro-optic devices and actuators. La-doping induces in PZT a shift in phase transition boundaries at the Zr-rich side of the phase diagram, and induces relaxor behaviour in some cases [1, 2]. For Zr-rich compositions such as PZT 90/10 the room temperature structure was defined as rhombohedral ferroelectric (FE) with a doubled unit cell resulting from antiferrodistortive tilts of the oxygen octahedra (R3c space group) [3]. Small amounts of La added to the PZT 90/10 produce little changes in the structure, however La>4% already results in tetragonal symmetry. The morphotropic phase boundary (MPB) between the FE phase and the antiferroelectric (AFE) phase (normally present if Zr>94%) is also affected by La content, and for PZT 90/10 the presence of a transition to an AFE phase between La=2% and La=4% was reported [4]. La addition causes the AFE phase to extend within the material at the expenses of the FE phase.

The aim of this study is to investigate the crossover between FE and AFE phases in PZT 90/10 ceramics in dependence of La content in the range between 2% and 4% by Raman spectroscopy. It has already been demonstrated [5] that E(TO) and A₁(TO) modes present minima both in the FE phase below 2% La content and in the secondary FE phase within the AFE matrix above 4%. These minima not necessarily coincide with the Curie temperature (Tc) as detected from dielectric measurements. What happens for phases in between is not clear, namely it is necessary to locate the crossover at which the AFE phase becomes dominant. Several compositions of PZT 90/10 ceramics (produced by the solid state method) with different La content (La=2%, 2.5%, 3.1%, 3.2%, 3.3%, 3.5%, 3.8% and 4%) were subjected to Raman scattering studies in the temperature range between 4K and 873K, allowing determining the presence of FE and AFE phases, their coexistence and also the evolution of structural phases.

References
Multiferroic nanocomposite films from aqueous solutions

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Coupling between electrical and magnetic properties in multiferroic materials is important for the proper function of spintronics, information storage and logic devices. However, the number of single phase materials with co-existence of magnetism and ferroelectricity at room temperature is very limited. By combining ferroelectric and magnetic oxides in self-assembled composite films it is possible to enhance magnetoelectric properties due to elastic interactions between both phases and the substrate [1-3].

To grow multiferroic composite thin films, we started from aqueous solutions of Co, Fe, Ba, Ti and Bi-ion complexes with citric acid as the chelating agent. By mixing these solutions in different molar ratios we prepared $x\text{BaTiO}_3-(1-x)\text{CoFe}_2\text{O}_4$ and $x\text{BiFeO}_3-(1-x)\text{CoFe}_2\text{O}_4$ multiferroic precursors where $x = 0.5, 0.6$ or $0.7$. After spincoating the precursors on different substrates (LaAlO$_3$ (100), SrTiO$_3$ (100) and SrTiO$_3$ (111)) samples were thermally treated to obtain the desired crystalline phases.

This paper reports structural and morphological development of composite thin films via chemical solution deposition. According to X-ray diffraction, spontaneous phase segregation occurs during film growth and two-phase composites are formed epitaxially to the substrate. SEM analysis reveals different morphologies of obtained composite films depending on the type of substrate used.

Therefore, solution based processing is shown to be a cost-effective and easily accessible way for obtaining self-assembled multiferroic thin film composites.

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References
Microstructural and dielectric properties of epoxy resin-PZT thin film composites

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In this work, we report a preparation method for epoxy resin-ferroelectric Pb(Zr,Ti)O\textsubscript{3} composite (EPR-PZT) films with compositional gradient along its thickness. The aim of this work is to increase the dielectric permittivity and polarization of polymer-ferroelectric composites with the addition of ferroelectric phase. The dielectric characteristics are discussed in correlation with phase and microstructural features (Fig.1a).

Composite PZT-EPR with different compositions ranging from 2.5\% to 15 vol\% were prepared by gravitational casting method at room temperature [1]. The intrinsic dielectric properties of the composites can be observed only at high frequencies due to the fact that at low frequencies the extrinsic contributions are significant. Therefore at \(\sim10^4\) Hz the dielectric permittivity of the composite is between 6-10 (Fig. 1 b).

![Fig.1](image)

**Fig.1 (a) SEM image of the 5 vol. \% of PZT-EPR film; (b) Frequency dependence of dielectric constant for frequencies in the range of \((1-10^6)\) Hz**

The composites exhibit a permittivity gradient and act as a natural impedance match system in the frequency range of 2-6 GHz, resulting in very low reflections. The compositionally graded PZT-epoxy resin composite thick films are suitable as adapting impedance materials for microwave applications.

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**References:**


PLD Deposition and Characterization of Heteroepitaxial SrTiO\textsubscript{3} Thin films

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The aim of this work was to investigate processing conditions and deposit heteroepitaxial STO (SrTiO\textsubscript{3}) thin films with smooth and well defined interfaces for further research. Influence of deposition temperature, laser fluence and repetition rate, ambient pressure on growth mode and film quality was studied.

Heteroepitaxial STO thin films were deposited on LSAT ((LaAlO\textsubscript{3})\textsubscript{0.3}-(Sr\textsubscript{2}AlTaO\textsubscript{6})\textsubscript{0.7}) single crystal substrates with LSMO (La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3}) electrode layer by pulsed laser deposition with KrF excimer laser (\textlambda=248 nm). STO and LSMO ceramics were used as the targets. Substrates were cleaned with acetone and isopropanol and annealed in oxygen flow at 1250°C at the same time controlling La vapour pressure at LSAT substrate surface [1] to get atomically flat surface (Fig. 1a).

Best quality STO films were obtained at 780°C deposition temperature, with 2 Hz laser repetition rate and 38 mJ energy. The oxygen pressure was 0.1 mBar during deposition and was raised to 1 mBar during cool down. Both LSMO electrode and STO thin films showed good epitaxy (Fig. 1b) and crystallinity, XRD STO 002 reflex rocking curve FWHM was 0.037° (STO film thickness 82 nm, LSMO electrode thickness 15 nm).

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

Figure 1 AFM images of a) LSAT (001) single crystal substrate after treatment, b) SrTiO\textsubscript{3} heteroepitaxial thin film STO/LSMO//LSAT (STO thickness - 82 nm, LSMO – 15 nm).

Acknowledgements
This work has been financed by the Sciex-NMS\textsuperscript{ch} programme, project code 11.016 “Thin Ferroelectric Films” and Lithuanian-Swiss cooperation programme "Research and development" joint research project "SLIFE", project code LSP-12 007.

References
Measurement of Dielectric Permittivity and Magnetic Permeability of Barium-Strontium Hexaferrite in Microwave Frequency Range

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The aim of this work is to measure dielectric permittivity and magnetic permeability of disk-shaped barium-strontium hexaferrite samples in radio frequency range using non destructive measurement methods.

Microstrip method was chosen in order to measure $\varepsilon^*$ and $\mu^*$. Numerical methods were used for calculation of these properties because of parasitic capacitance and inductance on connection ports. To verify dielectric permittivity measurement results obtained using microstrip technique, a method of capacitor in shortened coaxial line was used. Measurement results of $\text{Ba}_{0.15}\text{Sr}_{0.85}\text{Fe}_{12}\text{O}_{19}$ ceramics are presented in fig 1. As we see, $\mu'$ is close to one and $\mu''$ is close to zero. Thus, we can conclude that this particular composition has no noticeable magnetic properties.

![Fig. 1. Frequency dependences of complex dielectric permittivity and magnetic permeability using microstrip (black dots) and capacitor in shortened coaxial line (white dots) methods.](image-url)
The role of porosity on the ferroelectric properties of PZTN ceramics: experiment and modeling

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There is a huge interest in developing porous ceramics given by the fact that the introduction of tailored porosity can lead to new properties (which cannot be achieved by conventional dense ceramic) which is in accordance with the performance required in new fields of applications. A porous ceramic material can be considered as a di-phase composite, e.g. combining a PZT ceramic with air pore phase.

In the present paper, porous Pb\textsubscript{0.988}(Zr\textsubscript{0.52}Ti\textsubscript{0.48})\textsubscript{0.976}Nb\textsubscript{0.024}O\textsubscript{3} (PZTN) ceramics composites prepared by direct sintering have been investigated and discussed. For fundamental aspects, the materials with porous structures are model systems to investigate the porosity-dependence functional properties. The dielectric and ferroelectric properties are discussed in correlation with ceramics microstructures. The results are discussed in terms of porosity influences on the functional properties of PZTN porous ceramics. The novelty of the present paper consists in using a theoretical model in order to understand and describe the role of porosity on the ferroelectric properties of PZTN ceramics. Our approach is to simulate the ferroelectric response for different porosity content with a combined Classical Preisach Model (CPM) and a Finite Element Method (FEM) (Fig.1).

![Fig. 1. P-E hysteresis loops for PZTN ceramics: (a) experimentally and (b) modeling](image)

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Structural, microstructural and electrical analyses of PZTNb/CoFe$_2$O$_4$ multilayer composites prepared by electrophoretic deposition

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Multilayer composite of Nb doped lead zirconium titanate (PZTNb) and CoFe$_2$O$_4$ (CFO) were prepared by electrophoretic deposition (EPD). The EPD technique enables the production of unique microstructures and nanostructures as well as novel and complex material combinations in a variety of macroscopic shapes, dimensions and arrangements starting from micron-sized or nanosized particles. This technique has recently gained increasing interest both in academia and industrial sector not only because of the high versatility of its use with different materials and their combinations but also because of its cost-effectiveness requiring simple apparatus.

The Pb$_{0.988}$(Zr$_{0.52}$Ti$_{0.48}$)$_{0.976}$Nb$_{0.024}$O$_3$ (PZTNb) powder had been prepared by the mixed oxide method and then mixed with absolute ethanol (Fluka, >99.8% assay). The magnetic nanoparticles of CoFe$_2$O$_4$ (CFO) were obtained from solution of CFO nanoparticles suspensions in DEG were provided by Ce.Ri.Col. (Colorobbia Research Center, Empoli (Italy)). Suspensions of CFO were either used as received or after dilution with water and after many dilution steps we added the absolute ethanol (FLUKA). After dried and obtaining the CFO nanopowder was mixed with absolute ethanol (Fluka, >99.8% assay), and a milling charge made of zirconia (ZrO$_2$) spheres. For both powders, PZTNb and CFO, a dispersant PE65 and a binder, PVB, were added in order to improve dispersion and to obtain well-adhered green films [1]. From the suspension solutions of PZTN and CFO by EPD were obtained multilayer PZTNb/CFO/PZTNb green films which were sintered at 900°C/1h.

Phase compositions and microstructures of the thick films were investigated by X-ray diffraction and scanning electron microscope. X-ray diffraction indicated that the films consisted the both perovskite PZTNb and spinel CoFe$_2$O$_4$ phase. Microstructures of the deposited film were examined using SEM technique. Gold top electrodes were sputtered through a shadow mask in order to measure dielectric properties. Electrical and dielectric properties of the thick films were investigated.

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References
Processing of lead zirconate titanate ceramics derived from poly(methyl methacrylate) template

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We have studied the processing of lead zirconate titanate ceramics for ultrasound transducer applications. Pb(Zr₀.₅₃Ti₀.₄₇)O₃ (PZT) ceramics with tailored porosity was processed with heterocoagulation of the oppositely charged ceramic powder and an organic template. With this process one can carefully control the amount of porosity, the pore size and the pore size distribution. The PZT powder was synthesized by calcination of the oxide powder mixture at 1100 °C. The median particle size was 0.6 μm. Commercially available poly(methyl methacrylate) (PMMA) particles with the median particle size of 1.5 μm were used as the template. Water-based suspensions of PZT stabilized by polyethylenimine (PEI) and PMMA particles with PZT-PEI/PMMA volume ratios of 80/20 and 70/30 were prepared within the pH range 5-9. The suspension was dried at 105 °C, the powder was pressed into pellets and sintered at different temperatures. After the drying the PZT-PEI/PMMA powder mixture consists of homogeneously distributed PZT and PMMA particles as evidenced by scanning electron microscopy (SEM). From the TG/DTA analysis it is evident that the PEI and PMMA from the PZT-PEI/PMMA mixture decompose up to 400 °C. The organic-free PZT powder was sintered at 1000, 1050, 1100 and 1150 °C. The PZT ceramic exhibited homogeneous microstructure with a micrometer sized pores. We observed that the porosity of the ceramic, determined by mercury porosimetry, is higher for the PZT containing higher amount of PMMA. The sintering temperature has a significant effect on the pore diameter and the density of the ceramic. The effect of the sintering temperature and PZT/PMMA ratio on the pore size and porosity of the ceramic will be reported.
Shape control of photoreduced silver nanostructures on ferroelectric templates


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Spatially defined arrays of metallic nanostructures can be placed on patterned ferroelectric templates via photoreduction. The patterning of these templates via electric field poling or a proton exchange process, which reverse or modulate the ferroelectric polarization, respectively, can be used to control the location of these arrays of structures. By varying the concentration of aqueous AgNO₃, it was found that the height of the structures can be controlled [1]. The width can be controlled by changing the proton exchange depth, which is controlled by the exposure time to the proton source, benzoic acid [2]. The resulting nanostructures have been functionalized with Raman and fluorescent probe molecules. A possible application of these nanostructures could be in nanocircuitry or in biosensing of different biomolecules to study cellular behaviour.

Figure 1. (a) Atomic force microscopy (AFM) topography image of a proton exchanged lithium niobate crystal and (b) corresponding cross section line profile. (c) AFM topography image of the same sample after photodeposition for 30 minutes in a 10⁻² M AgNO₃ solution and (d) corresponding line profile.

Acknowledgements
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References
Synthesis and Properties of $\text{NiFe}_2\text{O}_4$ and $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$
Prepared by Auto-combustion Method

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$\text{NiFe}_2\text{O}_4$ (NF) and $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (NZF) powders as a part of multiferroic composites were prepared by auto-combustion method starting from nickel, zinc and iron nitrates. After the process of self-ignition, fine precursor powders were thermally treated at 1000 °C for 1h forming the nickel ferrite and nickel-zinc ferrite powders [1]. XRD analysis proved the formation of well crystallized cubic spinel structure in both ferrites. Particle size distribution measurements showed the existence of agglomerates. SEM micrographs showed the existence of polygonal grains ~ 100-500 nm. The results of powders characterization are presented in the table 1.

<table>
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<th>SAMPLE</th>
<th>$D_{\text{V50}}$ (μm)</th>
<th>SSA (m$^2$/g)</th>
<th>$D_{\text{BET}}$ (nm)</th>
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<td>14.3</td>
<td>1.903</td>
<td>588</td>
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</tr>
</tbody>
</table>

Table I: Results obtained from powders characterization

Ceramics materials were obtained by sintering at 1250 °C for 4 h in the tube furnace. XRD analysis showed the formation of well crystalline spinel structure in both materials. Magnetic measurements of ferrites were carried out and presented in Figure 1. Saturation magnetization moment of NF was lower than for NZF and the fields at which saturation occur was almost the same for both ceramics. The coercivity $H_c$ (Oe) was higher for the NZF indicating that it is “softer” than NF [2]. Permeability vs. frequency measurements showed that NZF possesses much higher permeability that NF. On the other hand, the NF permeability value keeps constant values in a broader frequency range than NZF ceramics.

Figure 1 Magnetic measurements of NF and NZF ferrite sintered samples

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References
Synthesis and characterisation of barium and strontium titanate nanostructures

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Last years, increasing attention has been dedicated to the synthesis of various BaTiO₃ and SrTiO₃ nanostructures, such as nanoparticles, nanorods, nanowires and nanotubes, because dependence of their ferroelectric and piezoelectric properties on their dimension and size [1,2].

For the synthesis of potentially ferroelectric barium and strontium titanate nanostructures we apply two different approaches. In the first method we synthesize potentially ferroelectric titanate nanostructures by ion exchange barium and strontium ion with titanium ions in the crystal structure of titanate nanotubes and nanowires (H₂Ti₃O₇). For this synthesis we used different aqueous solution of barium and strontium salts and hydrothermally prepared titania nanostructures. In the second method we mixed strontium and barium hydroxide with titanium dioxide nanoparticles and hydrothermally prepared barium/strontium titanate nanostructures.

Obtained nanostructures were characterized X-ray powder diffraction, Raman spectroscopy and high resolution transmission electron microscopy (HRTEM). The size distribution of nanostructures was measured with DLS (dynamic light scattering). The results of these measurements were compared with size obtained from TEM images.

Acknowledgements

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References

Composite ferrite/titanate thin films obtained by chemical solution deposition technique

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Aim of the presented research was to perform synthesis and characterization of multiferroic thin film structures composed of barium-titanate perovskite layers and nickel-ferrite spinel layers deposited in alternating order. The films with different thickness (six to eleven layers) were obtained heat treated at different temperatures up to 1100 °C for 60 min. Optimal precursor solution composition was investigated, and also influence of different chemical solution deposition techniques on thin film structures. Change of viscosity and particle size in solutions with time was monitored. It was shown that most appropriate deposition techniques was spin coating of acetic titanate solution and 2-methoxyethanol ferrite solution. X-ray diffraction patterns confirmed presence of desired spinel and perovskite phases. Structural characterization by scanning electron microscopy, transmission electron microscopy and atomic force microscopy shown that obtained multilayer films were are crack-free, with the thickness of ~500 nm, uniform surface texture and rounded grains having grain size in the nanometer range.
Barium ferrite doped-SrFe$_{12}$O$_{19}$: sol-gel synthesis and electro-magnetic characterization

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Ba$_x$Sr$_{1-x}$Fe$_{12}$O$_{19}$ ($x=0.05-0.35$) (abbreviated as BSFx) ferrites were prepared by sol-gel method and their structural characteristics, electric and magnetic properties were investigated. The powders show a decrease of their grains size with the increasing of $x$. Thus, the sample BSFO$_{0.05}$ has size grains between 1 and 3 µm compared with BSFO$_{0.35}$ which has grain size between 0.1 and 0.8 µm. BSFx ceramics derived from powders prepared by sol-gel change their granular structure with increasing of barium ferrite amount, to a structure of platelets. The BSFx ceramics derived from gel show a nonlinear variation of dielectric constant with increasing of the concentration of BaFe$_{12}$O$_{19}$. The remnant magnetization ($M_R$) decreases with temperature and Ba concentration. Similar to the remanent magnetization, the saturation magnetization $M_S$ decreases with temperature and concentration $x$. The ferrites BSFOx derived from gel precursor shown good dielectric and magnetic characteristics.
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