Piezo 2013

Electroceramics for End-Users VII

Book of Abstracts

The Piezo 2013 conference is dedicated to Prof. Maricka KOSEC.

Marija Kosec, Piezo Institute Director, Scientific Councillor at the Jozef Stefan Institute (Ljubljana, Slovenia), Head of its Electronic Ceramics Department and Professor of Materials Science at the University of Ljubljana passed away on December 23rd 2012.

Our scientific community has lost one of its leading members and we have lost not only a researcher, with whom several of us have been collaborating for very many years, but also a friend. Maricka had an exceptional personality that was unanimously appreciated; working with her was always a great pleasure both because of her knowledge and vast experience and because of her kindness and wonderful sense of humour.

All our thoughts go to her co-workers at JSI and to her family.

Prof. Dr. Maricka Kosec

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Piezo INSTITUTE

The European Institute of Piezoelectric Materials and Devices

The Piezo Institute was launched in 2008 by the multidisciplinary EC-funded '*MIND'* consortium of academic researchers and leading European companies. It aims to promote piezoelectric-based technologies within Europe and to provide a focus for Europe's political and industrial agenda. It is an independent source of:

- Advice and expertise
- Education and training
- Standards, Research and Development
- News and events

The institute's expertise includes piezoelectricity, ferroelectricity, magnetoelectricity, electrostriction and pyroelectricity in materials including ceramics, single crystals, polymers and composites.

Members have skills in chemistry and process engineering, solid-state physics, materials characterisation and measurement science, micro and nano technology, MEMS, numerical and finite element modelling and the design and manufacture of materials and devices.

"The science of piezoelectricity has been known for more than a century," notes Wanda Wolny, a founding member and MD of piezo ceramics manufacturer MEGGITT in Denmark. "The institute is Europe's recognition that there is now far greater potential for piezo applications in healthcare, transport, energy harvesting and environmental protection. It will help us to keep up with the rapid pace of piezo development in Asia and North America."

The institute's executive board and founding members include researchers from Denmark, France, Italy, Latvia, Norway, Poland, Slovenia, Spain, Switzerland and the UK. The institute offers expertise in chemistry and process engineering, solid-state physics, materials characterisation, metrology, standards and the manufacture and testing of piezo materials and devices. The Piezo Institute also organises the biannual Piezo – 'Electroceramics for end-users' series of international conferences.

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INVITED SPEAKERS

- Prof. Susan Trolier-McKinstry Smart Materials Integration LaboratoryPennsylvania State University : Piezoelectric Films for Next Generation Logic Elements.
- Apl. Prof. Dr. Andreas Klein Surface Science Group TU Darmstadt Germany : A semiconductor perspective of ferroelectric materials.
- Prof. Philippe Benech.LAboratoire d'Hyperfréquences et de Caractérisation, Grenoble France : Piezoelectric materials and their applications in radio frequency domain and telecommunications.
- Prof. Dr. Ir. Nico de Jong Department of Biomedical Engineering Thoraxcenter, Erasmus MC Netherlands : New dual frequency phased array transducer for cardiac imaging.
- Prof. Dr. Thomas Becker Expert for Autonomous Sensor Systems EADS : Autonomous Wireless Health Monitoring for Aircrafts.

PIEZO 2013 Conference Programme

SUNDAY, MARCH 17, 2013	
7:00 pm - 7:00 pm	**Cocktail**
8:00 pm - 10:30 pm	**Dinner**
	MONDAY, MARCH 18, 2013
8:30 am - 8:45 am	**Opening of the conference**
8:45 am - 10:00 am	**ORAL SESSION**
08:45 - 09:15	**Invited paper**: New dual frequency phased array transducer for cardiac imaging - *Nico De Jong, Erasmus M,* Netherlands
09:15 - 09:30	Piezoelectric resonators for tunable phononic crystals - *Tommaso Delpero, ETH Zürich - Centre of Structure Technologies*, Switzerland
09:30 - 09:45	High Temperature Piezoelectric Transducers System for Long Range Ultrasound Structural Health Monitoring of Aging Power Plants - *Marko Budimir, INETEC – Institute for nuclear technology Ltd.*, Croatia
09:45 - 10:00	Rapid thermal processing for enhanced functional properties in PZT thick films - *Robert Dorey, Cranfield University,* UK
10:00 am-10:30 am	**Coffee break**
10:30 am - 11:00 am	**Industrial presentations**
11:00 am - 12:15 pm	**ORAL SESSION**
11:00 - 11:15	High Performance Screen Printed PZT Thick Film Actuators by In-Plane Mode of Excitation - *Ernst Dörthe, Fraunhofer Institute for Ceramic Technologies and Systems,* Germany
11:15 - 11:30	Flexible piezoelectric materials for emerging applications - *Konstantin Astafiev, Meggitt Sensing Systems A/S*, Denmark
11:30 - 11:45	Piezoceramic Fibers and Pearls Derived by the Polysulfone Spinning Process - *Kai Hohlfeld, TU Dresden, Institute of Materials Science,* Germany
11:45 - 12:00	Direct Piezo Ceramic Tester for Comparison of lead free piezoceramic vs PZT - *Elsa Gullaud, Yzatec*, France
12:15 pm - 4:30 pm	**Break**
4:30 pm - 5:45 pm	**ORAL SESSION**
04:30 - 05:00	**Invited paper**: Autonomous Wireless Health Monitoring for Aircrafts - *Thomas Becker, EADS IWSICO*, Germany
05:00 - 05:15	Piezoelectric miniature robot inspired by Ultrasonic motors - *Yves Bernard, Laboratoire de génie électrique de Paris*, France

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05:15 - 05:30	MEMS sensors for microscale piezoelectric metrology - *Jenny Wooldridge, National Physical Laboratory*, UK
05:30 - 05:45	Automotive cylinder pressure sensor based on lead free piezo-electric ceramic - *Alain Ramond, Yzatec*, France
5:45 pm - 6:15 pm	**Coffee break**
6:15 pm - 7:00 pm	**ORAL SESSION**
06:15 - 06:30	Piezoelectric evaluation of ultra-thin nano-confined polymeric nanowires - *Valentina Cauda, Center for Space Human Robotics, Istituto Italiano di Tecnologia*, Italy
06:30 - 06:45	Innovation in the growth of thick and high crystalline quality AlN layer on sapphire by HTCVD - *Nicolas Coudurier, Science et Ingénieurie des Matériaux et procédés*, France
06:45 - 07:00	Ultralong ZnO nanowire arrays using a template- assisted approach for piezoelectric - *Carminna Ottone, Center for Space Human Robotics and Instituto Italiano di Tecnologia, Dip. Scienza Applicata e Tecnologia, Politecnico di Torino*, Italy
8:00 pm - 10:30 pm	**Gala dinner**
	TUESDAY, MARCH 19, 2013
8:30 am - 10:00 am	**ORAL SESSION**
08:30 - 09:00	**Invited paper**: Piezoelectric Films for Next Generation Logic Elements - *Susan Trolier Mc Kinstry, Department of Material Science and Engineering, Penn State University, U.S.A.*
09:00 - 09:15	$BaTiO_3$ doped materials for ultrasonic transducer applications - *Gustavo Mata-Osoro, ENSCP-ParisTech, Laboratoire de Chimie de la Matière Condensée*, France
09:15 - 09:30	Properties of PZT Thick film integrated on Bare Silicon Wafer by Electrophoretic Deposition (EPD) - *Carmen Galassi, National Research Council of Italy, Institute of Science and Technology for Ceramics*, Italy
09:30 - 09:45	Lead Zirconate Titanate coating of Tungsten Carbide-Cobalt to enable smart coatings - *Paul Weaver, National Physical Laboratory*, UK
09:45 - 10:00	Synthesis, structure and ferroelectric properties of perovskite-like layered structured Pr3Ti2TaO11 compounds - *Chen Chen, School of Engineering and Materials Science, Queen Mary University of London*, UK

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10:00 am - 10:30 am	**Coffee break**
10:30 am - 12:15 pm	**ORAL SESSION**
10:30 - 10:45	Lead-free and high energy density ceramic for energy storage applications - *Tatiana Correia, National Physical Laboratory*, UK
10:45 - 11:00	Evolution of MEMS based piezoelectric thick film technology for energy harvesting applications - *Tomasz Zawada, Meggitt Sensing Systems A/S*, Denmark
11:00 - 11:15	Zinc Oxide Nanorod P-N Junction-Based Piezoelectric Energy Generators - *Markys Cain, National Physical Laboratory,* UK
11:15 - 11:30	A Novel Thermomechanical Energy Conversion Cycle: Demonstration - *Ian McKinley, University of California Los Angeles,* U.S.A.
11:30 - 11:45	Electro-optic effects in high temperature, bulk, piezoelectric ceramics – *Tim Stevenson, University of Leeds*, UK
11:45 - 12:00	Sodium potassium niobate-strontium titanate ceramics: environment friendly alternative to lead-based electrocaloric materials - *Barbara Malic, Jožef Stefan Institute*, Slovenia
12:00 pm - 4:30 pm	**Break**
4:30 pm - 5:45 pm	**ORAL SESSION**
04:30 - 05:00	**Invited paper**: A semiconductor perspective of ferroelectric materials - *Andreas Klein, Technische Universität Darmstadt*, Germany
05:00 - 05:15	Uniaxial pressure induced phase switching in the piezoelectric KBT-NBT - *Tim Comyn, University of Leeds*, UK
05:15 - 05:30	Synthesis and functional properties of piezoelectric lead free $K_{0.5}Na_{0.5}NbO_3$ ceramics and single crystals. - *Micka Bah, GREMAN, Université François Rabelais de Tours, France*
05:30 - 05:45	Ternary system of piezoelectric single crystals and its applications - *Sang-Goo Lee, iBULe Photonics*, Korea
5:45 pm - 6:15 pm	**Coffee break**
6:15 pm - 7:15 pm	**POSTER SESSION**
06:15 - 07:15	Ultrasound medical applications of electrophoretically deposited PZT thick films - *Franck Levassort, GREMAN, Université François Rabelais de Tours, France*
06:15 - 07:15	Different scale confinements of PDVF-TrFE as functional material for piezoelectric tactile sensors - *Giancarlo Canavese, Italian Institute of Technology,* Italy

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06:15 - 07:15	Analysis of Frequency and Voltage variation for effective modulation of piezoelectric fan speed - *Tushar Chitrakar, NITK Surathkal*, India
06:15 - 07:15	High aspect-ratio vertically aligned ZnO nanowires: electric and piezoelectric evaluation for energy nanogenerators - *Stefano Stassi, Center for Space Human Robotics, Istituto Italiano di Tecnologia, Dip. Scienza Applicata e Tecnologia, Politecnico di Torino*, Italy
06:15 - 07:15	Analysis of the contribution of elastic anisotropy to internal stresses in ferroelectric materials using a multiscale modelling approach - *Laurent Daniel, School of Materials, University of Manchester and Laboratoire de Génie Electrique de Paris*, UK
06:15 - 07:15	Autonomous aeronautical structural health monitoring system based on piezoelectric power harvesting devices for on- production line use. - *Christophe Delebarre, Institute of Electronics, Microelectronics and Nanotechnology* (IEMN), Université de Valenciennes, France
06:15 - 07:15	Characterisation of soft and hard piezoceramic materials using genetic algorithm based optimisation - *Julien Bustillo, GREMAN, Université François Rabelais de Tours*, France
06:15 - 07:15	Design and fabrication of a piezo-electric transducer array for intravascular ultrasound - *Gerrit J. van Dijk, Laboratory of Acoustical Wavefield Imaging – Delft University of Technology,* Netherlands
06:15 - 07:15	Electric field control of magnetic domains in patterned multiferroic thin film composites - *Rui Lopes, National Physical Laboratory*, UK
06:15 - 07:15	Electro-thermal coupling and new functional materials technology - *Paul Weaver, National Physical Laboratory* - UK
06:15 - 07:15	Fluid droplet monitoring using surface waves inductively generated by RF EMUS transducer - *Nicolas Wilkie-Chancellier, Systèmes et Applications des Technologies de l'Information et de l'Energie* (SATIE), France
06:15 - 07:15	Indirect Measurement of Electrocaloric Effect in Nonlinear Dielectrics - *Tatiana Correia, National Physical Laboratory*, UK
06:15 - 07:15	$K_{0.5}Na_{0.5}NbO_3$ thick films with potassium-sodium germanate sintering aid - *Tadej Rojac, Jožef Stefan Institute, Centre of Excellence NAMASTE,* Slovenia
06:15 - 07:15	Li diffusion and electrochemical activity in commercial battery materials - *Sergey Luchkin, Department of Materials and Ceramics Engineering & CICECO, University of Aveiro,* Portugal
06:15 - 07:15	Measurement of the effective d_{33} coefficient on PZT film integrated structures using laser interferometry - *Guy Feuillard, GREMAN, École Nationale d'Ingénieurs du Val de Loire, Université François Rabelais de Tours*, France

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06:15 - 07:15	Modeling and study of hysteretic behaviour of piezoceramic materials under external electrical and mechanical stress - *Mathieu Domenjoud, GREMAN, Université François-Rabelais de Tours,* France
06:15 - 07:15	Piezoelectric energy harvester for bicycle - *Dejan Vasic, SATIE ENS Cachan*, France
06:15 - 07:15	Quantification of electromechanical coupling measured with Piezoresponse Force Microscopy - *Serban Lepadatu, National Physical Laboratory*, UK
06:15 - 07:15	Surface Functionalization of Zinc Oxide Transducers for Multiplexed Detection of Liver Diseases - *Azatuhi Ayrikyan, Boston University,* U.S.A.
06:15 - 07:15	The new approach to the determination of the material constants of solid materials - *Boris Zaitsev, Saratov Branch of Institute of Radio Engineering and Electronics of RAS,* Russia
06:15 - 07:15	Thermostability of glycine piezoelectrical phases - *Ensieh Seyedhosseini, CICECO & Department of Materials and Ceramics Engineering, University of Aveiro,* Portugal
8:00 pm - 10:30 pm	**Dinner**
WEDNESDAY, MARCH 20, 2013	
8:30 am - 12:30 pm	**ORAL SESSION**
08:30 - 09:00	**Invited paper**: Piezoelectric materials and their applications in radio frequency domain and telecommunications - *Philippe Benech, Institut de Microelectronique, Electromagnetisme et Photonique (IMPEP-LAHC), Grenoble,* France
09:00 - 09:15	Effect of the metallization and electrode size on the electrical admittance of piezoelectric ceramic parallelepipeds - *Oumar Diallo, GREMAN, Université François Rabelais de Tours*, France
09:15 - 09:30	Texturation of lead-free BaTiO3-based piezoelectric ceramics - *A Ngueteu Kamlo, Laboratoire de Science des Procédés Céramiques et de Traitements de Surface, Université de Limoges*, France
09:30 - 09:45	Langasite, lead-free piezoelectric thin layer synthesized through a "Chimie douce" route - *Mehdi Mevel, Institut Néel, Laboratoire SYstèmes et Matériaux pour la MEcatronique*, France
09:45 - 10:00	Defect-mediated phase stability in ferroelectric oxides - *Anna Kimmel, University College London, andNational Physical Laboratory*, UK

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10:00 am - 10:30 am	**Coffee break**
10:30 am - 12:15 pm	**ORAL SESSION**
10:30 - 10:45	Role of oxygen octahedra tilting and defects on the electrical and electro-mechanical response of rhombohedral Pb(Zr,Ti)O_3 ceramics - *Tadej Rojac, Jozef Stefan Institute,* Slovenia
10:45 - 11:00	Evaluation of the polarization state of light metal embedded piezoelectrics - *Agnes Eydam, Solid State Electronics Lab, TU Dresden*, Germany
11:00 - 11:15	Oxygen vacancies induced two-dimensional electron gas near SiO_2/$BaTiO_3$ interfaces - *Anna Kimmel, University College London andNational Physical Laboratory,* UK
11:15 - 11:30	Frequency and temperature stability of high electric field-induced strain in $K_{0.5}Bi_{0.5}TiO_3$ – $BiFeO_3$ ceramics - *Maxim Morozov, Norwegian University of Science and Technology*, Norway
11:30 - 11:45	Exceptionally large piezoelectric strains in high temperature $BiFeO_3$-$(K_{0.5}Bi_{0.5})TiO_3$–$PbTiO_3$ ceramics - *James Bennett, Institute for Materials Research*, *University of Leeds*, UK
11:45 - 12:00	BNT-based Lead-free materials - Alternative for PZT-based materials - *Antje Kynast, PI Ceramic GmbH* , Germany
12:15 pm - 12:30 pm	**CLOSING OF THE CONFERENCE**

New dual frequency phased array transducer for cardiac imaging.

De Jong Nico [1*], Neer Paul [1], Danilouchkine Mike [1], Verweij Martin [1]

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Although echocardiography is a commonly-used, safe, and noninvasive method for assessing cardiac function, it turned out to be problematic in patients with poor acoustic windows. The suboptimal image quality is partially caused by the artifacts, stemming from reverberations between the transducer and ribs. A considerable gain in image quality was achieved with tissueharmonic imaging (THI), which is based on the selective imaging of the 2nd harmonic component. A number of years ago, our group postulated and theoretically proved that the further reduction of those artifacts can be enhanced with superharmonic imaging (SHI) using 3rd to 5th harmonic.
The piezomaterial selection of the custom build array was done using the KLM model. Test arrays were built (element size 13 x 0.2 mm2, resonance frequency 4 MHz, no matching layer, backing 5.3 MRayl) and the receive transfer function and SNR were assessed on a per element basis.
To evaluate the new transducer, five healthy volunteers between 25-32y.o. without prior history of cardiovascular disease underwent a clinical examination on the commercial (iE33, Philips, NL) and our experimental scanner with the dedicated SHI dual frequency probe (Oldelft, NL).
In vitro measurements showed the most sensitive test array had an average peak receive sensitivity of 21 ?V/Pa and could detect a long sinusoidal burst with amplitude 1 Pa with 22 dB SNR.
In the clinical study all volunteers had comparable image quality in the parasternal view on both scanners. The SHI images of 2 volunteers in the apical 4-chamer view demonstrated significant reduction of the reverberation artifacts and resulted in clear improvement in cardiac septal wall definition.

Piezoelectric resonators for tunable phononic crystals

Delpero Tommaso [1*], De Simoni Luca [1], Di Lillo Luigi [1], Bergamini Andrea [,2], Ermanni Paolo [1]

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Phononic crystals and acoustic metamaterials have, in recent years, come under the spotlight for the development of devices which exhibit properties not expected from the individual entities that constitute them. Their features result from the tailoring of acoustic waves Bragg scattering events coupled, on demand, with internally resonating units.
In this work a phononic crystal whose acoustic band gap is altered by piezoelectric resonators is introduced. The basic idea is to use shunted piezoelectric discs as variable stiffness elements between the substrate, where the wave is propagating, and the periodic stubs responsible for the generation of the Bragg-type band gap. At the resonance frequency, the piezoelectric resonators isolate the mass of the stubs from the vertical movement of the substrate canceling, therefore, the band gap.
The isolation of the stubs is experimentally verified both on a single unit cell of the phononic crystal and on a one-dimensional periodic arrangement of the same unit cells. The results show, distinctly, the possibility to tune the amount of energy that propagates through the substrate or is reflected by the stubs.

High Temperature Piezoelectric Transducers System for Long Range Ultrasound Structural Health Monitoring of Aging Power Plants

Budimir Marko [1*], Mohimi Abbas [,2], Moustakidis Serafeim [,3], Hrissagis Kostas [,3], Selcuk Cem [,2], Pavlovi? Nikola [1], Mudge Peter [,2], Gan Tat-hean [,2]

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2 : Brunel Innovation Centre, Brunel University, Cambridge (BIC)
3 : Center for Research and Technology Thessaly, Volos (Cereteth)
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An important aftermath of the Fukushima accident is having governments all over the world reevaluating the safety of their nuclear power plants. Majority of the current nuclear reactors are either close to the end of their 40-years operating license granted, or already having the license extension and entering the extension period. Operators perform expensive «mid-life » refurbishments to address the security and economical soundness of keeping the plants running until they reach 80 or more years. Following the regulations updating, it will be essential to have effective and preventive in-situ continuous structural health monitoring techniques for aging plants. A powerful such tool is high temperature ultrasonic guided waves (UGW) for monitoring the plants pipework.
Two types of high temperature piezoelectric UGW transducers have been developed and tested in this work: PZT-based and LiNBO3-based transducers operating at 250°C and 580°C, respectively. Extensive work has been done on engineering of acoustically passive transducer materials. The electromechanical parameters of transducers, transmission and reception modes, and fatigue of the piezoelectric materials have been experimentally investigated as functions of temperature and time. The propagation of UGW through pipes at elevated temperatures has been studied theoretically for typical types of flaws, using finite element analysis.
A prototype ultrasonic pulser-receiver is developed, able to drive a high-temperature collar array housing the transducers. The electronics and the collar have been designed to withstand the environmental conditions present in power plants. The issue of decreased transducers signals at elevated temperatures has been tackled by advanced signal analysis that has been done through pre-processing techniques, such as feature extraction/selection and pattern recognition, along with signal focusing algorithms, that use time-reversal focusing and time-delay focusing techniques.
End user considerations have been made towards full validation of the system and the inspection procedure and quality have been tested in laboratory and field conditions.

Rapid thermal processing for enhanced functional properties in PZT thick films

Tillman Mark [1], Dorey Robert [1]

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High density piezoelectric ceramics are known to exhibit high piezo-properties. There exist a number of strategies to maximise the density in the case of bulk materials but this is more challenging in the case of thick films due to the constrained sintering conditions and the high surface to volume ratio. Short duration sintering of thick films has been shown to lead to metastable microstructures with enhanced piezoelectric properties.
Films sintered for 1 minute using a focussed infra-red irritation have been shown to exhibit atypical microstructures with films exhibiting a 2-3 fold increase in dielectric and piezoelectric properties. Heating for longer results in a degradation in properties to those expected for films sintered using conventional furnace treatments. Such improvements have been observed for spot and raster sintering were relative permittivity was increased from between 200-300 to 600-700 and piezoelectric properties (d33) were observed to increase from 20-30 pC/N to between 60 and 80 pC/N.
The enhancement in properties were attributed to increased densification and grain growth facilitated by high heating rates and short dwell times coupled with the ability of the local microstructure to undergo significant rearrangement
Such local processing offers exciting possibilities for the fabrication of thick films piezoelectric microdevices where it is not necessary to sinter the whole sample in a batch processing context.

High Performance Screen Printed PZT Thick Film Actuators by In-Plane Mode of Excitation

Ernst Dörthe [1*], Gebhardt Sylvia [1], Bramlage Bernhard [1], Schönecker Andreas [1]

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Screen printed PZT thick films offer distinct advantages in MEMS applications. The greatest benefits, compared to pick and place techniques, are the strong bonding of the net-shaped piezoceramic layer to the substrate, the feasibility of device miniaturization and the potential for high volume production. Using multilayer substrates 3D structuring and integration of electronic components are possible. During the last 15 years of experience in PZT thick films numerous applications were developed at Fraunhofer IKTS such as ultrasonic transducers, generators, sensors and actuators.
The most common device configurations published in literature are based on monomorphs consisting of 30-150 µm piezoceramic layers with flat top and bottom electrodes applied to a substrate. This layout enables for low driving voltage and results in the use of the d31-mode for bending. However, the majority of piezoceramic devices use the stronger d33-mode because of the higher performance(d33 ? -2 d31). To utilize this mode for screen printed piezoceramic films the application of interdigitated electrodes (IDE) are an appropriate means. Our most recent research focuses on such PZT thick film cantilevers for micro positioning applications. To this end force/stroke characteristics were measured for IDE-cantilevers with varied length of 11-23 mm. Free displacements of 31 to 152 µm and blocking forces of 152 to 260 mN have been measured on 100 µm thick PZT films on 250 µm thick Al_2O_3 substrates which is nearly twice as high as data received on thickness mode cantilevers.
Influence of electrode gap on actuator performance has been characterized in detail. Therefore electrode distance was varied stepwise from 400 µm, 600 µm, and 800 µm to 1000 µm. We found a significant increase of actuator performance with growing electrode gap. FEM simulations of the electrical field distribution were carried out to explain influence in detail. The experimental and calculated results will be presented.

Flexible piezoelectric materials for emerging applications

Astafiev Konstantin [1*], Zawada Tomasz [1], Elkjaer Karl [1], Ringgaard Erling [1]

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Recent progress in development of new functional materials that are flexible and can be processed at very low temperatures (below 100 °C) opens a new opportunity for new emerging applications, such as smart textiles, allowing incorporating active devices such as buzzing elements or motion sensors into the garments, non-destructive test systems (NDT), by applying active materials on large areas of different structures, including plastics, polymers etc., underwater acoustics, by using the piezoelectric materials with low acoustical impedance etc.
Nowadays, there are a number of piezoelectric polymer materials available (e.g. polyvinylidene fluoride (PVDF) family materials) that can be used for such applications, however, these polymer materials typically show relatively low piezoelectric activity, expensive, and therefore the practical application of such materials is limited.
The present work is devoted to the development of flexible piezoelectric materials on the basis of piezoceramic materials, including lead-free piezoelectrics, dispersed into polymer matrix. The newly developed materials (PiezoPaint? material) combine an increased piezoelectric activity (d_{33} coefficient up to 45 pC/N), extremely low processing temperatures (A number of prototypes, including the piezoelectric buzzers and motion sensors have been fabricated on the basis of flexible PiezoPaint? materials, printed onto different substrates. The results obtained clearly show that the functional piezoelectric materials with the increased piezoelectric activity that are compatible with a number of different substrates open new prospects in terms of developing intelligent clothing and smart garments, advanced NDT systems, and underwater acoustics.

Piezoceramic Fibers and Pearls Derived by the Polysulfone Spinning Process

Hohlfeld Kai [1*], Gebhardt Sylvia [,2*], Schönecker Andreas [,3], Michaelis Alexander [,4,5]

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http://tu-dresden.de/die_tu_dresden/fakultaeten/fakultaet_maschinenwesen/ifww
5 : Fraunhofer Institute for Ceramic Technologies and Systems (IKTS)
http://www.ikts.fraunhofer.de/
* : Corresponding author

Piezoceramic composites offer distinguished properties compared to bulk PZT ceramics where higher flexibility, lower density, and adapted performance is needed. Base of all piezocomposites are piezoceramic components such as powders, fibers, plates and more complex three-dimensional structures.
Recently, we introduced the polysulfone process as an appropriate technique to produce dense piezoceramic components with different geometries. Therefore, homogeneous slurry is prepared by dispersing a PZT powder in a polysulfone binder solution. Green body is formed by spinning the slurry into a precipitation bath, wherein the binder coagulates by an exchange reaction between solvent and water. Matching slurry viscosity and forming technology enables for a high variety of piezoceramic components from continuous fibers to three-dimensional structures.
Sintered PZT fibers cut to a length of 160 mm with diameters from 100-800 µm could be prepared by continuous spinning process and high solid concentration (PZT 5A) in the slurry. Piezoelectric properties were measured on 1-3 piezocomposites with fiber content of approximately 75 % in epoxy resin. After poling, specimen showed average values for relative permittivity ?33T/?0 of 900, dielectric loss factor tan ? of 0.016 and thickness mode coupling factor kt of 60%. Relative permittivity of 1250 for PZT fibers could be calculated using 2-phase-model. Strain and ferroelectric hysteresis measurements were carried out under electric field of 2 kV/mm. Relative strain of 1.2*10-3, remnant polarization of 22 µC/cm2 and coercive field strength of 1.3 kV/mm could be detected.
In addition, near spherical PZT samples were fabricated using a pulsed spinning process from low viscous slurries. The diameter of the so-called PZT pearls could be adjusted to 1-2 mm. Piezocomposites with embedded PZT pearls showed relative permittivity ?33T/?0 of 800, relative strain of 0.8*10-3 and remnant polarization of 10 µC/cm2.
Application of customized PZT components for smart structures and ultrasonic transducers will be shown.

Direct Piezo Ceramic Tester for Comparison of lead free piezoceramic vs PZT

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New European Standards urge for the suppression of lead in piezo ceramics. To select an alternative to PZT, characteristics and fatigue of potential materials for replacement need to be evaluated to examine the applicability of the developed materials to sensing devices.
A custom testing device for accurate piezo ceramic characterization was built. The system is designed to apply up to 1kN preload and up to 1kN dynamic load. The temperature testing range is from -40°C to 200°C. Custom Kovar holders were designed to test rings of various thickness and various diameters. The testing device shows a very good repeatability of less than 0.01%. The piezo sensitivity (d33), linearity and hysteresis are given by the bench as well as the sensitivity variation against preload and temperature. The variation of these characteristics are evaluated against time, 500 Million cycles on one piezo ceramic can be achieved 12 days. Insulation resistance and capacitance of piezo were also measured during cycling.
A lead free piezo ceramic (Bi-Ti03) and a PZT were tested on the bench for comparison. The lead-free piezo ceramic gives a sensitivity of 20 pC/N whereas the PZT has a d33 of about 130 pC/N. The lead free piezo shows no ageing compared to the lead material tested that shows a fatigue of 6% after 10 Million cycles. The temperature sensitivity variation is of the Bi-Ti03 is 200ppm/°C. The lead-free piezo ceramic shows better performance at ageing than the PZT. The drawback of the low d33 which can be problematic for some sensors can be overcome by treatment of the signal by a custom charge amplifier integrated in an ASIC.
These results demonstrate that some lead free material have the same characteristics as quartz in respect to linearity, hysteresis and ageing characteristics while exhibiting better sensitivity.

Autonomous Wireless Health Monitoring for Aircrafts

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Acousto ultrasonic testing offers a high potential for structural health monitoring in aircrafts. A network of piezoelectric transducers could be used for the monitoring of large aircraft structures. The density of such a network is mainly defined by the properties of the ultrasound waves, the piezoelectric materials and the related signal or data processing. The resulting network of e.g. hundreds of sensors may require a high cabling effort.

Autonomous operation by means of energy harvesting and wireless signal or data communication might be a good solution to reduce the installation work. Latest results have shown that this can be optimised by wireless data/signal communication. Therefore signal pre-processing and data reduction has an important impact on the design of such a system, especially on the suitable communication protocols. IEEE802.15.4 like standards might be interesting candidates since the power consumption is lower compared to the IEEE802.11 family of standards, but also the data rate is lower.

Energy harvesting may lead to fully autonomous operation and to save power cables for the monitoring system. Energy harvesting needs a careful selection of system components. Low power consumption communication protocols are needed as described above, but also an ultra-low power mode of operation of the transducers is necessary. Relatively high voltages in the order of several tens of volts are currently applied to the piezoelectric sensors in order to achieve reasonable signal to noise ratios. From energy harvesting perspective reducing the voltage levels for excitation is recommended to further reduce power consumption by avoiding high voltage conversion.

Finally piezoelectric Materials offer also interesting opportunities for energy harvesting. Currently thermoelectric harvesting is the most promising candidate for fixed wing aircrafts, however optimised materials might open the field for efficient piezoelectric harvesting devices.

Piezoelectric miniature robot inspired by Ultrasonic motors

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In this paper, we will present a new piezoelectric miniature robot design inspired from linear traveling wave ultrasonic motors. The idea is to generate a traveling wave in a beam structure to move this beam on a solid substrate using two piezoelectric patches bonded on the beam surface. Our design consists of a beam structure, with two non-collocated piezoelectric patches bonded on its surface. This idea is inspired from linear traveling wave ultrasonic motor and it is applied to robotic systems to move all the system instead of moving the slider as in the case of linear traveling wave ultrasonic motors. Several configurations were reported in literature to excite traveling waves in finite structures; among them is the two modes excitation, our case of interest in this paper.
At the beginning of this paper, we will introduce the two modes excitation operation principle of our traveling wave piezoelectric beam robot by illustrating first a short review on linear traveling wave ultrasonic motors. This will highlight differences between our proposed robot and these motors. After introducing the operation principal of our piezoelectric robot, modeling of the robot will be presented using a finite element matrix equation. Then the optimal design will be studied in details including dimensions of the robot, optimal operating frequency and traveling wave performance of the robot.
A prototype has been manufactured and the optimal operating frequency has been validated experimentally. Then, to characterize the robot, we measured the robot speed on a smooth glass flat surface for different applied voltages and for different embedded masses. We measured also robot speed versus mechanical load at a given applied voltage, to determine the nominal operating point of the robot.
At the end a comparison between our robot and some linear traveling wave ultrasonic motors is done.

MEMS sensors for microscale piezoelectric metrology

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A MEMS sensor has been developed for the determination of piezoelectric materials properties in small-scale systems. A vertical levitation comb drive actuator, manufactured at MEMSCAP with the MetalMUMPS process, applies a force to the test sample in the range of 1-33 ?N, and the resulting electric displacement from the piezoelectric material is measured using a charge sensitive pre-amplifier and lock-in technique, facilitating charge measurements down to 1×10-5 pC. The force output of the actuator was measured with capacitive micro-sensors from femtoTools, which were calibrated against a CSM Instruments Ultra Nanoindentation Tester using a Berkovitch tip. The system was tested against nine Pb(Zr1?xTix)O3 (PZT) ceramic cylinders and one Pb(Mg1/3Nb2/3)O3 ? xPbTiO3 (PMN-PT) single crystal, with piezoelectric coefficients in the range of 70-1375 pCN-1. The PZT cylinders were 15 mm in length (either 3 or 6 mm in diameter) and the PMN-PT crystal was 3.4×2.0×4.1 mm3 in size. Contact was made to the MEMS through a 2mm diameter sapphire bead attached to the piezoelectric. The size of these preliminary test samples was large in comparison to the MEMS device, so that the measured coefficients could be compared to those obtained with macroscopic measurement methods with a Berlincourt meter and through impedance resonance techniques. The coefficients obtained with the MEMS device showed a good correlation (r=0.9997) with the values obtained with macroscopic techniques. With this new MEMS device, we have successfully miniaturised the metrology for the measurement of the direct piezoelectric effect to evaluate the functional quality of piezoelectric films in the rapidly expanding market of piezoMEMS applications.

Automotive cylinder pressure sensor based on lead free piezo-electric ceramic

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The increasing requirements regarding emissions lead to a more various regulation of the engine. Improvement of closed loop control in Diesel engines plays a key role in the reduction of pollutant emissions. The injection and thus the efficiency of the combustion can be optimized with the information of in-cylinder pressure and helps to reduce NOx and CO emissions, in compliance with Euro requirements.
A new generation of piezo electric based cylinder pressure sensor was developed. The cylinder pressure sensing technology is integrated in the glow plug. The pressure information, amplified, calibrated and filtered by an ASIC, is transmitted to the engine control unit to enable closed loop control. The ASIC compensates for any drift due to pyroelectricty, and is immune to external electric perturbations. The sensor has an accuracy of ±2% in a range of 0 to 200 bars. The performances of the sensor have been tested on a various range of engine points and compared to a reference sensor from Kistler. The sensor exhibits a very high Signal to Noise ratio, with a signal free of resonances in a bandwidth of 0 to 5kHz. The quality of signal in this bandwidth allows to compute with a high precision the rate of heat release to determine precisely the time of injection on a cycle in each cylinder.
The mechatronic integration of the piezo electric element in the glow plug will be presented. The usage of a BiTa piezoelectric element in the severe environment of a diesel combustion engine will be demonstrated.
This unique ASIC developed device avoids the usage of high Ohmic isolation of piezo-electric sensors, while offering a long time constant. Thus, it opens the usage of polycrystalline piezo-electric elements in a numerous type of piezo-electrics sensor sofar made only with quartz.

Piezoelectric evaluation of ultra-thin nano-confined polymeric nanowires

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The construction of piezoelectric sensors and actuators with nanostructured materials gives access to miniaturized tools with high sensitivity and spatial resolution. One possible approach toward surface distributed piezoelectric devices is the tailoring of chemistry and structure at the molecular level, to design a material intrinsically converting mechanical pressure into an electric signal or vice versa. We report on the preparation and the piezoelectric properties of ultrathin polymeric nanowires in the oriented pores of mesoporous silica, which are embedded in the channels of a supporting anodic alumina membrane. Poly(vinylidenedifluoride) PVDF and its copolymer, poly (vinylidenedifluoride trifluoroethylene) PVTF, were both confined to two types of columnar silica mesopores of 5 and 10nm in diameter. The extreme spatial confinement induces a preferential orientation of the crystalline domains of the polymer into the ? ferroelectric phase, leading to ultrahigh-aspect-ratio nanowires distributed throughout the templating host, being 60? m long, comparable to the thickness of the hosting alumina. The resulting distributed array of piezoelectric nanowires are isolated from each other by a dielectric matrix, facilitating the handling and electrical contacting. We show that a remarkable piezo-response, in the absence of any poling or stretching, is obtained upon nanoconfinement on the PVDF polymer, which, in contrast, does not show any polarization when in bulk or film form without poling. The piezoelectric behavior was assessed by a piezo evaluation system (PES) and we visualized polar nanowire bundles via piezoresponse force microscopy (PFM). This «nano-structuration » represents a powerful approach, holding promise for applications as nanoactuators, nanowire-based large area bioinspired ciliated sensors, non volatile low voltage memories, nanotip-based protein biosensors, or stem cell differentiating guides through highly resolved mechanical or electric stimuli.

Innovation in the growth of thick and high crystalline quality AlN layer on sapphire by HTCVD

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The availability of industry-grade quality cheap AlN templates is currently a major concern for piezoelectric device like surface acoustic wave. Sputtering [1] is mainly used actually to obtain thin AlN layer (less than 200 nm) with slow growth rate and poor crystalline quality (more than 1.8° for the FWHM of the w-AlN 0002 peak). The main difficulty is that in addition to the fact that the lattice mismatch between sapphire and AlN is high (13.3 %), leading to strain and cracks in the grown layer, the first step of nucleation during the growth is hard to control with this kind of process.

Many studies have attempted to optimize the direct epitaxial growth on sapphire c-plane. High Temperature Chemical Vapor Deposition is one of the most promising ways to perform deposition of thick (from 0.2 to 20 µm) and high crystalline quality Aluminum nitride (less than 0.15° for the FWHM of the 0002 w-ALN peak) layer. The CVD reactor consists on a vertical cold-wall quartz reactor working at low pressure (10 torr). The sapphire substrate is placed on a graphite susceptor heated by induction at 1500°C. The reactants used are ammonia (NH3) and aluminum chlorides (AlClx) species in situ formed via Cl2 reaction with high purity aluminum pellets.

Regulation of the gas phase super saturation of the precursors (AlClx and NH3) allows us to control the quality of the nucleation layer. Higher growth rate can be used after this step to obtained thick AlN layer from 0.2 to 20µm.

Result of this study leads to the synthesis of 5 µm AlN templates grown at 5 µm/h with a crystalline quality of 0.12° for the FWHM 0002 reflectivity, exhibiting no cracks on two inches sapphire wafers.

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Ultralong ZnO nanowire arrays using a template-assisted approach for piezoelectric

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Zinc oxide (ZnO) is a prominent example of a piezoelectric and semiconductor material. It can be grown in a reproducible way in a variety of nanostructures. This variety can be unique for many applications in nanotechnology, including piezoelectric field-effect transistors and diodes, self-powered nanogenerators and wireless nanosensors [1,2]. Both these wide-bandgap structures are useful in photoelectronic and optical applications [3]. In this study we report on the synthesis of long ZnO NWs by combining the template-assisted approach into nanosized hard and flexible matrices with the low temperature aqueous chemical growth method [4]. The wire diameter was controlled by varying the template that include either commercial and self-anodized alumina membranes (200 nm and 50 nm of pore diameter, respectively), mesoporous silica (5-12 nm in diameter) and flexible polycarbonate membrane (PC, 150 nm pore size). The FESEM images reveal the complete filling of the template channels and an enlargement of their diameter, producing NWs with larger diameter than the respective template one. Self-anodized alumina membranes as templates give the possibility to tune the channel size, thus the NWs diameter. The X-ray and TEM characterization reveal wurtzitic ZnO, also with the presence of alumina crystallites when used as templating matrix. Thus PC membrane as template has the advantage of having an inert behavior during the synthesis, yielding to a wurtzite mono-crystalline ZnO NWs. Piezoelectric characterization of the template-ZnO filled membranes show current switch peaks and polarization hysteresis loops, thus showing promising application in particular of the flexible PC matrices filled with ZnO as piezoelectric sensors or energy nanogenerators.

1 M. Choiet al. Adv. Mater. **2 R. Mohammed et al. Adv. Funct. Mater. 3 H. Dixit New Journal of Physics 13 (2011) 0630024 X. Hu et al. Thin Solid Films 518**

Piezoelectric Films for Next Generation Logic Elements

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A novel device architecture has been proposed for a replacement for Si-based CMOS electronics, which uses a piezoelectric actuator to trigger changes in the electrical resistivity of a piezoresistive element. In order for such a device to function, it is imperative to be able to maintain large piezoelectric constants at very small lateral length scales of the actuator (2:1 height:lateral feature sizes, reactive ion etching must be employed. This can change the distribution of defect dipoles, which in principle can significantly degrade the piezoelectric response, and may ultimately govern both the stability of d33,f and the device lifetime. Thus, new measurement techniques are being explored toquantitativelymeasure the piezoelectric d33 response of thin films with high spatial resolution.

BaTiO3 doped materials for ultrasonic transducer applications

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Since the discovery of lead-zirconate-titanate PbZr(1-x)TixO3 (PZT) in the 50's, several derived compositions have been developed to optimize the efficiency of this material. Nowadays, thanks to the use of dopants/additives and the improvement in the efficiency of the production processes, PZT-based compositions are the dominant piezoceramics as due to their electroacoustic properties. Despite this, PZT is associated to health and environmental problems because PZT contains lead. As a consequence, European Union and several countries around the world included PZTs in its legislation as hazardous substances to be substituted by safer materials.
Different lead-free compositions are being revised. Among them, barium titanate emerges as a very promising material. For ultrasonic transducers applications (typically with center frequencies of few MHz), the material requires several properties. The functional properties must be as high as possible to compete with PZT compositions (in particular the thickness coupling factor). Moreover, lapping or cutting is often required to reach the desired dimensions for piezocomposite fabrication. Consequently, high density and fine homogeneous microstructure are required.
In the present work, we investigate the effect of different dopants to satisfy all these conditions .Compositions with Co, Li and Nb were tested and differences between dielectric constant, mechanical losses and thickness coupling factor were highlighted.
In this sense, we found that an optimized doped-BaTiO3 has fine homogeneous microstructure (95%) and kt over 40% and therefore is a good candidate to be used for transducer applications.

Properties of PZT Thick film integrated on Bare Silicon Wafer by Electrophoretic Deposition (EPD)

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In recent times direct integration of ferroelectrics on silicon wafer has been attracting interest. Although a number of issues concerning the electrical behavior of the semiconductor/ferroelectric interface, and their effects on the electrical performance of a ferroelectric/semiconductor structure without metallization must be clarified1, the topic is currently the focus of some research work. EPD is an easily implemented deposition technique that requires only basic laboratory gear and a sufficiently stable colloidal suspension to produce ceramic and electroceramic films with thickness in the 100 nm ? 10 mm range2.
It was recently found in our laboratory3 that neat lead zirconate titanate (PZT)/silicon stacks can be produced by electrophoretic deposition (EPD) on bare silicon wafers followed by sintering at 850-950°C. The EPD of niobium-doped lead zirconate titanate (PZTN), performed in ethanol-based suspensions on bare silicon wafers on which Al/Si alloyed ohmic contacts were made, produced smooth green films that strongly pinned to the silicon substrate after sintering.
The results of the production of thick PZT films by EPD and sintering and some characterizations of the same are reported.
Thick and well-adhered sintered PZT films on silicon having thickness about 50 µm were thus obtained. Such structures could be the core of novel on-chip sensors/actuators.

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Lead Zirconate Titanate coating of Tungsten Carbide-Cobalt to enable smart coatings

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Smart coatings enable sensing and actuation functionality to be added to materials. Piezoelectric coatings, especially lead zirconate titanate (PZT), have been used on a wide range of metallic and semiconducting substrates. Tungsten Carbide-Cobalt (WC-Co), is extensively used in the metal processing industry due to its hardness and abrasion resistance. The ability to apply piezoelectric coatings close to a metal cutting edge would enable improved control of the cutting process resulting in improved quality and reduced power consumption in the manufacturing process. However, the WC is sensitive to oxidation at typical PZT processing temperatures presenting a challenge to the development of functional PZT films for this application.
This paper reports the use of a low temperature solution ? gelation (sol-gel) process to deposit high quality crystalline PZT ($Pb_{0.52}Zr_{0.48}TiO_3$) film onto a WC-Co substrate. Laser Doppler vibrometry showed significant piezoelectric activity with an effective d_{33} coefficient of 19pC/N. Both the dielectric constant and piezoelectric coefficient were lower than expected due to the formation of an insulating $PbWO_4$ oxide interlayer between the conducting WC-Co substrate and PZT. Accounting for this layer indicated a d_{33} piezoelectric coefficient for the PZT of 76pC/N .

Synthesis, structure and ferroelectric properties of perovskite-like layered structured Pr3Ti2TaO11 compounds

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The AnBnO3n+2 compounds have a perovskite-like layered structure (PLS) with perovskite layers withnoxygen octahedra separated by oxygen rich layers. Some of the 4-layer PLS compounds, Ln2Ti2O7 (n= 4, Ln = La, Pr, Nd), have been reported to have super-high Curie points and promising dielectric, ferroelectric and piezoelectric properties. To extend the study of the PLS family, we have synthesized the 3-layer PLS compound Pr3Ti2TaO11 (n= 3) and studied its structure, dielectric and ferroelectric properties. Both the traditional Solid State Reaction (SSR) and the chemical processing Co-precipitation methods were used to prepare the Pr3Ti2TaO11 powders. The powders prepared by SSR show a small amount of second phase, but the powders prepared by Co-precipitation are single phase within the sensitivity of the XRD technique. Spark Plasma Sintering (SPS) was used to obtain dense ceramics. Also a two-step hot-forging process was used to obtain textured ceramics. X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to study the crystal structure and microstructure. X-ray photoelectron spectroscopy (XPS) was used to study the chemical state of all the elements in Pr3Ti2TaO11. Analysis of the XRD, TEM and XPS results indicate that, the Pr3Ti2TaO11 compound has an alternating layer structure, which is made up of perovskite layers withn= 2 andn= 4. Second harmonic generation (SHG) results further prove that the Pr3Ti2TaO11 compound has a non-centrosymmetric structure with spontaneous polarization. All the texture and untextured Pr3Ti2TaO11ceramics prepared by SSR and Co-precipitation have stable dielectric permittivity and small dielectric loss in the frequency range from 103 to 107 Hz. Like the 4-layer PLS compounds, the 3-layer PLS Pr3Ti2TaO11 ceramic also shows a super-high Curie point (>1300 ?).

Lead-free and high energy density ceramic for energy storage applications

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Advances in portable electronic devices demand novel energy storage technologies. Capacitors are a promising solution for this purpose as these are characterized by high energy, fast discharging rate and are cost-effective. Among all the dielectrics, ferroelectric and antiferroelectric thin films are the most promising for energy storage applications due to its high field-induced polarization, electrical strength and nonlinear properties. Capacitors present a particular difficulty in this respect because conventional ceramic and electrolytic devices have poor temperature stability and/or low maximum operating temperatures and often need to be cooled. This paper presents a new development in ceramic dielectrics which achieves both a high energy density and temperature stability to temperatures above 200 °C. Results are presented on the energy storage capacity and temperature stability of the capacitance for this new class of high operating temperature dielectric material.

Evolution of MEMS based piezoelectric thick film technology for energy harvesting applications

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Energy harvesting covers a great body of technologies and devices that transform low grade energy such as solar energy, environmental vibrations and thermal energy into usable electrical energy. Energy harvesting is an enabling technology leading to development of wireless and battery-less solutions, which can benefit many applications, e.g. wireless monitoring systems, implantable devices, etc. It enables solutions where the sensors could be built-in into the object to be monitored, e.g. fuselage of an aircraft. Another advantage of using energy harvesting is the ease of deployment of the sensors and low maintenance costs.
This article describes the development of devices for vibration energy harvesting, where kinetic energy (displacement, strain, acceleration) is transformed into usable electrical energy. The technology of piezoelectric thick films integrated with MEMS (Micro- Electro- Mechanical System) structures is discussed in this paper with the focus on the evolution of the process as well as improvement of the properties. Two types of structures are discussed: MEMS based energy harvesters comprising unimorph cantilevers with integrated piezoelectric thick film and bimorph piezoelectric thick film cantilevers. In case of both types of harvesters PZT (Lead Zirconate Titanate) films of a thickness of 20 to 50 µm are deposited using screen printing technique. The MEMS devices are fabricated using conventional clean room techniques.
A summary of the properties including open circuit voltage, power output as a function of excitation frequency are presented for a variety of generations of devices. The progress in performance due to the improvement of the technology and design is shown. Moreover, the impact of the environmental parameters, such as temperature on the selected parameters is presented. The paper also summarises the properties of the wafer scale fabrication process, such as yield and distribution of properties on the wafer, which has great practical implications for the future industrial scale production.

Zinc Oxide Nanorod P-N Junction-Based Piezoelectric Energy Generators

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A p-n junction-based ZnO nanorod device is presented that generates a piezoelectrically-induced voltage and current. Low temperature solution-based techniques are used to produce inorganic-organic hybrid p-n diodes on flexible plastic substrates. Bending of devices leads to both voltage and current peaks, with maximums of 10 mV and 10 µA/cm2.

It has been demonstrated previously that using a rectifying structure allows the piezoelectric polarisation of ZnO nanorods to generate a measurable external voltage. The p-n junction device presented here provides an alternative to the Schottky diode used in previous designs. The diode comprises a dense array of ZnO nanorods, which are 1-3 µm long and 50-100 nm wide, covered by an organic p-type material.

Controlled vibration testing of the devices provides strong evidence that the effect results from a piezoelectric response in the material. The generated voltage increases linearly with the pressure applied to the sample, which is expected for a piezoelectric effect. When the devices are illuminated the voltage output drops significantly. This is attributed to the photo-induced conductivity of the ZnO, which is known to reduce the piezoelectric coefficient due to screening by conduction electrons. Load matching of the devices is performed showing a maximum power output at ~5 k?.

The input force to the hybrid device is measured using controlled bending. By simultaneously measuring the output power of the devices the energy conversion efficiency is calculated to be 0.0067 % with slow bending, increasing exponentially with bending rate up to ~8.5 % with much faster bending. This increase agrees with the proposed model of screening-limited energy output. These results not only demonstrate an alternative approach to the design of a ZnO nanorod energy harvesting approach, but also contribute to the understanding of the factors that limit the device performance, which could lead to improved future device designs.

A Novel Thermomechanical Energy Conversion Cycle: Demonstration

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This paper presents a new power cycle for direct conversion of thermoelectromechanical energy into electrical energy. It consists sequentially of an isoelectric cooling and an isothermal process performed in absence of mechanical stress, followed by an isoelectric heating and an isothermal process performed under uniaxial loading. The Olsen cycle is analogous to this new cycle but does not involve mechanical loading. The new cycle was demonstrated experimentally on [001]-poled 0.72PbMg1/3Nb2/3O3-0.28PbTiO3 (PMN-28PT) single crystals. The energy density was found to be nearly independent of frequency and, thus, the power density was almost proportional to frequency. The maximum power and energy densities obtained were 41 W/l and 41 J/l/cycle respectively for temperature span from 22 to 130oC, electric field between 0.2 and 0.95 MV/m, and with a 35.56 MPa uniaxial load at frequency 1 Hz. The new cycle produced positive energy for all temperatures considered. The performance and constraints on operating conditions of the new cycle were compared with those of the Olsen cycle. It demonstrated higher power densities than the Olsen cycle as it could be performed at higher cycle frequencies without reducing the energy density. It also was able to generate energy at temperatures below the operating range of the Olsen cycle. Overall, this new cycle can conveniently and directly convert mechanical and/or thermal energy into electricity and adapt to various thermal and mechanical energy sources.

Electro-optic effects in high temperature, bulk, piezoelectric ceramics

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Electro-optic materials and devices are the basis of light controlled micro-electrical components and even offer potential for energy transfer methods to power micro electromechanical systems (MEMS) by combining with the photostriction and bulk photovoltaic effects.
Rhombohedral PZT doped with ~9% of La^{3+} (PLZT) is sufficient enough to de-stabilise the macro-polar ferroelectric order and synthesise transparent materials which can act as optical switches with the application of electric field, or modify the electrical properties when exposed to Ultra-violet wavelength light.
Three high Curie temperature piezoelectric ceramics, selected from the EMRP METCO project, have been studied as a function of applied electric field and elevated temperature, to investigate the effect on emissivity, refractive index and light transmission coefficients.
The 3 material systems selected (i) $BiFeO_3$ - $PbTiO_3$ (BFPT), (ii) $(K,Bi)TiO_3$ - $BiFeO_3$ - $PbTiO_3$ (KBT-BF-PT) and (iii) Mg doped $BiFeO_3$ - $BiScO_3$ - $PbTiO_3$ (BFM-BS-PT), like PLZT, display electro-optic effects due to various compositionally dependent mechanisms inherent to each system. For example, KBT-BF-PT displays a breakdown in macro-polar ferroelectric order to produce polar nano-regions with reducing PT content, and BFPT has been shown to couple magnetic order and electric stimuli, with the magnetism enabling the material to be manipulated by employing light. Initial results are discussed for which all show a significant change in electro-optic properties with increasing electric field and temperature, due to changes in the crystal structure, magnetic order and piezoelectric properties.

Sodium potassium niobate-strontium titanate ceramics: environment friendly alternative to lead-based electrocaloric materials

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The electrocaloric effect (ECE) in ferroelectric materials has been recognized for years, but due to small magnitude it has not attracted much attention until recently [1]. The effect is described as a reversible temperature change in a material under an applied electric field at adiabatic conditions and it could be used in solid-state cooling devices.
Lead-based relaxor ferroelectrics, such as PbMg1/3Nb2/3O3-PbTiO3, and (Pb1-3x/2Lax) Zr0.65Ti0.35O3 (x = 7 ? 9.5) exhibit the change of temperature vs applied electric field. High values of 2.5 K for bulk ceramics at the electric field amplitude up to 90 kV/cm at temperatures near the dielectric permittivity vs. temperature maximum were obtained [2].
Sodium potassium niobate-strontium titanate has been studied as an environment-friendly alternative to lead based relaxors [3]. In the contribution its ECE properties depending on the processing conditions have been investigated.
The ceramic with the 0.85K0.5Na0.5NbO3-0.15SrTiO3 composition was prepared by the solid state synthesis and sintered at 1240 oC. The material had the relative density exceeding 95 % and a uniform microstructure. The ECE temperature change was measured directly by a high resolution calorimeter as a function of temperature for different electric field amplitudes. As expected from the previous measurements of the ECE in various inorganic materials the maximum of this effect is achieved at the dielectric permittivity maximum temperature. At room temperature the electrocaloric effect was close to that observed in other lead based perovskite relaxor ferroelectrics.

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A semiconductor perspective of ferroelectric materials

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The energy gaps of ferroelectric oxides are often around 3 eV, which is at the boundary between insulating and semiconducting materials. Other oxides with similar energy gaps are well-known electronic conductors of either n-type (e.g. ZnO, SnO2, In2O3) or p-type (e.g. CuAlO2). Among the ferroelectric materials, BTO can also be made an n-type conductor at room temperature by La or Nb doping, leading to its application as positive temperature coefficient resistor (PTCR). Other ferroelectrics like PZT remain largely insulating for both donor and acceptor doping. The difference in electrical properties can be understood by considering oxide ferroelectrics as wide gap semiconductors, i.e. as materials with a well-defined Fermi level position. Whether a material is conducting or not is then determined by the Fermi level position with respect to the valence and conduction band edge, which can be determined directly using photoelectron spectroscopy (XPS). Experiments on a large number of thin films clearly indicate upper and lower limits of the Fermi level position, which correspond well with the known conductivity type. The limits of the Fermi level are determined by intrinsic defect properties of the materials and define a region of electrochemical stability. The limits of the Fermi level show a systematic behaviour when the valence and conduction band levels of different oxides are aligned on an absolute energy scale. The alignment, which has been determined using photoelectron spectroscopy for BTO, PZT, KNN, BNT, BFO and a number of non-ferroelectric oxides, also exhibits a systematic dependence on the orbital contributions to the electronic states. XPS measurements further reveal Schottky barrier heights at electrode interfaces and their dependence on redox treatments and ferroelectric polarization. The dependence of barrier height on polarization can drive the Fermi level outside the region of stability, providing a straightforward explanation for electrical fatigue.

Uniaxial pressure induced phase switching in the piezoelectric KBT-NBT

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There is increasing interest in lead free piezoelectric materials, in the light of potential changes in legislation. One potential system, xK1/2B1/2TiO3-(1-x)Na1/2Bi1/2TiO3, (KNBT) displays a piezoelectric coefficient of ca. 200 pm/V at x=0.2.
Here, we report on the effect of an applied uniaxial stress on the crystal structure, as observed using x-ray diffraction in transmission, utilising high energy synchrotron radiation. Data is presented whereby a uniaxial stress is applied, and data collected simultaneously. The applied stress develops considerable permanent texture, via 90° domain reorientation, and a transformation from rhombohedral to mixed phase tetragonal and rhombohedral. As within-situelectric field experiments, the resultant crystal architecture is extremely dependent on the rate of application, and magnitude, of the stress. Data is presented for materials in the range x=0.1 to x=0.3.
A symptom of the pressure induced phase switching is the generation of ambiguous results in this and other KNaNbO3 systems, when studying sintered materials using conventional laboratory x-ray diffraction. The simple action of mechanical polishing or crushing develops tetragonal phase in the surface, whereas the bulk is rhombohedral. The use of synchrotron radiation is imperative in determining the crystal structure in these systems.

Synthesis and functional properties of piezoelectric lead free K0.5Na0.5NbO3 ceramics and single crystals.

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Since 2003, the European community limited the use of some hazardous substances in electronic devices due to their toxicity for human health and environment. The lead zirconium titanate (PZT) which contains more than 60 weight % Pb, is widely used in electronic devices such as transducers for non-destructive testing (NDT), in medical imaging and in others piezoelectric applications.
Owing to their high dielectric, piezoelectric and mechanical characteristics, alkaline niobate (K, Na)NbO3 (KNN)-based solid solutions are a promising candidates for lead-free piezoelectric materials (Yasuyoshi Saito et al., Nature 432 (Nov. 2004) 84-87).
The purpose of this work is to study the dielectric, ferroelectric and piezoelectric properties of K0.5Na0.5NbO3 single crystals with controlled compositions and to compare them with their homologous ceramics.
The stoichiometric synthesis of K0.5Na0.5NbO3 from K2CO3, Na2CO3 and Nb2O5 precursors was studied. Milling conditions and thermal analysis (DTA-TGA, dilatometry) were used for the optimization of the powders preparation. The sintering conditions were carefully investigated to prepare high density pellets and rods. The crystals were grown by floating zone method in an image furnace and the growing conditions are searched closely. The obtained ceramics and crystals were characterized by X-ray diffraction (XRD), scanning electron microscopy and quantitative SEM-EDS analysis before the electric and piezoelectric measurements. The first results of this comparative study will be presented here.
Special attention is paid on the quality of KNN single crystals crystallographic structure as well as their micro-structural architecture. The identification of the electromechanical properties of the different single crystals will allow the selection of candidates with promising performances, available for ultrasonic applications.

Ternary system of piezoelectric single crystals and its applications

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iBULe Photonics has studied piezoelectric sensors with PMN-PT single crystals grown by iBULe's unique method, and has applied in medical and other many areas.
We manufactured the piezoelectric switch of disc type with its diameter of 20 mm and its thickness of 0.1mm together with EU company. We found that the existing PZT switch gained about 6 uJ of energy, whereas the PMN-PT obtained 27 uJ under the pressure of 2 bar. In addition, under the pressure of 4 bar, the PZT got just 16 uJ, whereas the PMN-PT did 70 uJ. Therefore, the energy obtained from the PMN-PT increased more than four times compared to the PZT.
However, the piezoelectric characteristics of PMN-PT with the composition applied to the switch decreased with environmental temperature changes. So We grew PMN-PT single crystal with PT consent of 28 % having dielectric constant of 5153, piezoelectric constant of 1308 and electromechanical coupling coefficient of 0.8. The phase transition temperature of this single crystal was 95 ?, about 9 ? higher than that of the existing composition.
With oriented PMN-PT single crystals with 28% PT composition, the various modes of specimens were produced and all the parameters needed in sensor design were derived by using resonance technique. Using these parameters, the hydrophone and tonpilz for SONAR were designed and fabricated, and we evaluated their performances. We found that the weight and volume of the PMN-PT sensors is reduced by more than half compared to the sensor consisting of PZT. Based on these results, we confirmed that oriented PMN-28PT is suitable for UUV SONAR systems with the purpose of low power consumption and miniaturization.

Analysis of Frequency and Voltage variation for effective modulation of piezoelectric fan speed

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There exist a plethora of cooling applications, like Variable air volume (VAV) techniques for heating, ventilating and High-voltage alternating current (HVAC) air-conditioning systems, where one needs a variable flow of air to monitor the cooling of devices. With the burgeoning advancements of technology and commensurate miniaturisation of electronic devices, it becomes imperative for us to devise appropriate cooling techniques employing variable fan-speed for these devices. Piezoelectric fan is one such technology that is being used for cooling heat sinks of miniature applications like the laptop and cell phones. But, the use of piezoelectric fans as a source for variable fan speed has not been examined scrupulously. This paper discusses the effective modulation of the piezoelectric fan speed through the variation of frequency and voltage. The tip-displacement of the fan was expressed as a function of both voltage and frequency, and the cooling rates of a heat-sink were observed at different points. It can be inferred from the study that for high tip-displacements, coarse modulation of the fan speed can be done through frequency control and the fine modulation through voltage control. In the intermediate region of displacements, frequency control is very coarse and not desired; Voltage control is to be used for both coarse and fine speed modulation. In the low tip-displacement region, either frequency or voltage control can be used for both coarse and fine tuning since they both change the tip-displacement by an equal measure in this region. By discretely demarcating various regions and by analysing the type of speed modulation to be used in these regions, this study provides an effective way to control fan-speed for applications requiring variable air-flow. Though this study has been considered for one type of fan, the observations can be extrapolated to any generic scenario.

Analysis of the contribution of elastic anisotropy to internal stresses in ferroelectric materials using a multiscale modelling approach

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Internal stresses and their evolution under electromechanical loading play a significant role in the durability of ferroelectric materials. Internal stresses can be induced by the manufacturing process or the packaging conditions. At a finer scale, due to the heterogeneity of ferroelectric materials (polycrystalline structure), part of the ferroelectric strain must normally be accommodated locally, resulting in internal stresses when an electromechanical loading is applied. In most modelling approaches the contribution of local elastic anisotropy to internal stresses is neglected compared to the domain switching contribution.
Using a multiscale modeling approach, we propose to compare these two latter contributions to the evolution of internal stresses under electromechanical loading. The model is based on an energy-based description of the electro-elastic equilibrium at the domain scale. A statistical description of the domain microstructure is used to define the single crystal behaviour introducing volume fraction of domain variants. Finally a self-consistent approach is used to describe the grain to grain interactions within the polycrystal. The internal stresses under several electromechanical loadings can be estimated, and the impact of neglecting the effects of elastic anisotropy are quantitatively evaluated.

Autonomous aeronautical structural health monitoring system based on piezoelectric power harvesting devices for on- production line use.

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It becomes necessary to develop in situ Non Destructive Testing techniques for the monitoring of last generation aircraft. This concept, called Structural Health Monitoring, has as main objective to detect and locate damages occurring within the aircraft structure during its flight. To ensure a good efficiency of this SHM system, a sensor network covering all the monitored areas has to be deployed which induces numerous difficulties due to wiring aspects. Consequently wireless communications as well as energy autonomy capabilities are required.

In this paper, the aim is to control aeronautical composite structures on production line since composite materials that are currently employed at an intensive rate for aircraft primary structures are extremely vulnerable to impact damages due to tool drops for example. To be able to detect and locate such an event on the full composite structure, a piezoelectric SHM wireless and autonomous sensor network has to be developed. Therefore, the feasibility of an innovative technique based on a piezoelectric harvesting device to obtain a self-powered SHM system is presented. More precisely, the SHM system aims to have a double functionality: it will carry out classical SHM tasks using piezoelectric transducers bonded onto the aircraft structure and will also be fully autonomous.

As natural vibrations are not available during the production process, the energetic autonomy of the system is provided thanks to a Lamb waves emitter strategically located in the middle of the sensor array. Using this new harvesting energy solution, a demonstrator is herein realized. After measurements, it is shown that this system is able to harvest 7.4 mill watts for a 100 mill watts mechanical power applied to the structure. This electrical power can be used both by the electronic detector and the WIFI transmitter for the detection of impacts of less than 1 Joule.

Characterisation of soft and hard piezoceramic materials using genetic algorithm based optimisation

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Nowadays, piezoelectric materials are frequently used for with an external electrical DC field or a mechanical stress. The presence of such mechanical or electrical stresses in piezoceramic materials induces nonlinear hysteretic behaviours that significantly modify the piezoelectric characteristics through a shift of material properties from their stress-free values. Indeed, nonlinear ferroelectricity may be characterized by four typical hysteretic loops: electrical displacement versus electrical field, strain versus electrical field and two ferroelastic curves (stress versus strain and stress versus electrical displacement).
The main phenomenon underlying these effects is linked to microscopic domain switching. In a previous work, a model describing the domain walls switching has been developed. Effects of external electrical DC field or mechanical stress can be calculated using this model. In this work, inverse problem resolution is performed to retrieve material parameters such as permittivity, spontaneous polarization, spontaneous deformation, stiffness or piezoelectric coefficient.
The method was first applied to PLZT8/65/35, whose properties are well-known, for validation and then to one soft and one hard PZT ceramic. In order to solve the inverse problem, a genetic algorithm based optimisation is performed to fit theoretical data to experiments reported in literature. Depending on external load (electrical or mechanical), the curves used for these optimizations are electrical field based curves or mechanical stress based curves. The retrieved material properties are in agreement with literature, which validates the procedure.
This work shows that nonlinear behaviour of piezoceramic materials is well explained by domain wall motions. Moreover it is shown that genetic algorithm based optimisation is well adapted to solve complex inverse problems to characterise piezoceramic materials.

Design and fabrication of a piezo-electric transducer array for intravascular ultrasound

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Intravascular ultrasound (IVUS) is a medical imaging technique where a small ultrasound transducer mounted at the tip of a catheter is inserted in the artery to assess the condition of the arterial wall or to guide a stent placement. The transducers typically operate in the MHz range and are often fabricated using piezo-ceramic materials. During operation, cross-sectional images of the artery are obtained from pulse-echo measurements using a rotating single element or a circumferential array transducer. Volumetric images are obtained by combining successive cross-sectional measurements obtained by pulling the transducer through the artery. Due to respiratory and cardiac motion, the volumetric images are severely distorted. To improve the image quality, we propose to use instead of a single element a linear array of ultrasound transducers in the arterial direction. To assess whether this improves the image quality, we designed and fabricated a linear array which operates at 20 MHz. The array contains eight elements of dimensions 100 ?m x 350 ?m, separated by a kerf of 100 ?m. Hence, the array is small enough to fit in a 3 French catheter, and has a maximum length of 1.5 mm which allows for sufficient flexibility of the catheter. The array has been fabricated using a casting process, allowing each individual element to be mounted above a separate chamber. A coaxial cable is inserted in to each chamber to connect each element individually using conductive adhesive. Experiments performed with this linear array show that an improved image quality is obtained when compared with a single element transducer. During our presentation, we will both discuss the design and fabrication process and show some preliminary measurement results.

Different scale confinements of PDVF-TrFE as functional material for piezoelectric tactile sensors

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Poly(vinilydene fluoride tri-fluoroethylene) PVDF-TrFE shows remarkable piezoelectrical and pyroelectrical properties leading to a broad range of applications, non-volatile low-voltage memories, transducers, and tactile sensors. PVDF-TrFE readily crystallizes into the ? ferroelectric phase, showing a spatial arrangement of the fluorine atoms in anall-transconformation. A good piezoelectric response can be obtained by orienting the molecular dipoles of PVDF-TrFE in the same direction, by subjecting the material to mechanical stretching or to poling step. It was recently shown that the crystallization and consequently the polarization of PVDF-TrFE can be affected by confinement into porous micro and nano-templates. Here we prepared micro-sized pillars and nano-wires of PVDF-TrFE, thus studying the effect of micro and nanostructuration on the piezoelectric properties of polymers in comparison to thin films. The samples were prepared from a polymer solution to obtain: (i) thin films on metalized flexible polyimide substrate, (ii) micropillars of 10 um in diameter by microcasting into a PDMS mould; (iii) 1-D nanowires of 200 nm in diameter and several µm long upon wet-templating of porous anodic alumina. X-Ray diffraction and IR spectroscopy show that the crystallization of the polymer into the ferroelectric ?-phase is affected by the size of the confinement. The crystals consists of lamellae randomly oriented in the case of film, whereas oriented perpendicularly to the porous template channels in the 1-D nanowires. The favorable orientation of both micropillars and nanowires polarization axis results in crucial piezoelectric properties by applying an electric field along their axis, obtaining ferroelectric polarization hysteresis and displacement loop in absence of any poling. Thus the electromechanical characteristics of the three structured polymer show important improvements as far as the nanostrucutration is achieved. Application as tactile sensor devices with enhanced sensitivity based on these crystalline piezoelectric nano and micro structures is therefore under development.

Electric field control of magnetic domains in patterned multiferroic thin film composites

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The advanced properties of bulk multiferroic materials hinge on the intimate magneto-electric (ME) coupling, which occurs between the ordered ferroic phases inside the multiferroic materials. Multiferroics suitability for a wide range of applications has been already demonstrated. The next development stage in the physics of solid-state multiferroics is their transition from bulk to thin film structures. However is the fundamental ME coupling retained at micro/nano scale?
Some of these questions have already been addressed in a number of recent studies reporting the electric field induced magnetic domain formation observed via Kerr microscopy [1], local ME coupling measurements via scanning probe microscopy of continues surfaces [2-6] and scanning probe microscopy studies of nano-bar composite multiferroics [7].
In this work we report the study of patterned thin film multiferroic composites examined via magnetic force microscopy. Multiferroic composite, ferroelectric (FE) and ferromagnetic (FM) layers, structures were fabricated using lift off technique. The FE layer is 100 nm thin polycrystalline PbZrTiO3 (PZT) film on SrTiO3 substrate prepared by PHASIS Sarl. The FM layer is 50 nm NiFe thin film deposited on top of the PZT. The magneto-crystalline anisotropy combines with the shape anisotropy of the newly formed NiFe features to provide specific magnetic domain patterns. The magnetic domains have been imaged in ground relaxed state using a magnetic force microscope. After the characterization of the patterns in ground state the sample was submitted to an AC magnetic field large enough to reach magnetic saturation, the field was progressively reduced which demagnetize the sample. We show that voltage application after the demagnetization has a dramatic effect on the magnetic domain pattern via the strain mediated magneto-electric coupling between the FM and FE layers.
Under Nanomotion Project.

Electro-thermal coupling and new functional materials technology

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New technologies are being developed that will enable reductions in energy consumption and improvements in efficiency and reliability in automotive, energy, process, electronics and medical industries through the use of new functional materials which operate at elevated temperatures up to 1000 °C. These applications exploit the actuation, sensing and cooling functionality of ferroelectric materials which result from strong coupling between electrical, thermal and mechanical properties. Degradation of materials properties at high temperature means that these applications are currently limited to operating temperatures below 200 °C.
New solid-state cooling technologies are being developed based on the electrocaloric effect that will provide efficient cooling for computer chips and domestic and industrial refrigeration. New functional materials technologies are emerging to meet these needs, but are not currently supported by a metrological framework for traceable measurement of the coupling at high temperatures.
This p aperpresents a new project set up to develop the metrological infrastructure and facilities within Europe for the traceable metrology of thermal, elastic and dielectric properties of ferroelectric and electro-caloric materials at high temperatures and electric fields. This will support the development of new functional materials technologies and products.

Fluid droplet monitoring using surface waves inductively generated by RF EMUS transducer

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The optimization of new soft hybrid materials in the industrial domain needs an «on line » characterization of the first steps of their formation in liquid phase. Classical ultrasonic techniques that ensure a complete monitoring of the material formation require a wired excitation often unsuited for online monitoring inside. The aim of this study is to combine a radio frequency (RF) inductive excitation with ultrasonic techniques to characterize the rheological evolution of nanostructures. The interaction of surface waves with droplets is studied in order to characterize small volume samples.Within the view to unwire such sensors, a RF inductive electromagnetic ultrasonic (EMUS) transducer is proposed to monitor the interactions of surface waves with a fluid droplet. The sensor consists in a gold transmission line loop deposited on a piezoelectric substrate inductively coupled with a high quality radiant RF resonator. The shape of the sensor is optimized to generate ultrasonic shear waves. In this experimental work, a laser vibrometer is used to scan around and through the droplet deposited on the surface of the magneto-acoustic sensor. This magneto-acoustic system has been implemented for various droplets of tabulated viscosity (water ? glycerol mixtures). In order to extract the wave propagation information, the classical high resolution signal processing methods or 3D Fourier Transforms are not suitable to identify the transient and local aspect of wave propagation and mode conversion. The 3D Gabor transform is used in order to quantify these transient aspects in the Space-Time-Wave number-Frequency domains and recover the mode conversion sequence. These results are consistent with the literature. They suggest that this non-destructive technique can be used to extract the viscoelastic properties of materials.

High aspect-ratio vertically aligned ZnO nanowires: electric and piezoelectric evaluation for energy nanogenerators

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Nowadays, creating innovative devices of extremely small dimensions by using zinc oxide (ZnO) is increasing every day. In particular, ZnO possesses great potential because of its high electron mobility, wide band gap (~3.3 eV), semiconducting and piezoelectric properties. Additionally vertically-oriented ZnO nanowires were widely studied due to their large surface area, oxygen vacancies leading to high sensitivity to certain changes in the environment, and wetting properties, thus being suitable for gas sensing, piezoelectric nanogenerators, mechanical pressure piezoelectric sensors and dye-sensitized solar cells (DSSC) .
Here we show the use of vertically oriented ZnO nanowires on conductive substrates as energy nanogenerators. NWs were grown by hydrothermal method selectively on pre-deposited ZnO seed crystals. Careful tuning of the growth solution and reaction parameters allowed to obtain arrays of high aspect ratio, highly crystalline wurtzitic ZnO nanowires.The electrical evaluation showed a non-linear (Schottky) behavior of the current versus voltage characteristics. Interestingly, the conductivity of the ZnO nanowires is inversely dependent on their length. We found that longer nanowires would show a more pronounced piezoelectric effect, lower conductive behavior and higher the charge generated upon a mechanical stress. It was indeed reported that the lower the free carrier concentration due to the presence of crystallographic defects (e.g. oxygen vacancies), the lower is the conductivity of the material and the higher the resulting d33 piezoelectric coefficient. The piezoelectric properties of the synthesized ZnO nanowire arrays, thus the electric charge generated upon a mechanical stress, were evaluated. Upon a mechanical compressive deformation, the charge output of ZnO nanowires is converted by a charge amplifier into a proportional voltage, and used as an input variable for sensing application or stored in capacitors for energy harvesting purposes.

Indirect Measurement of Electrocaloric Effect in Nonlinear Dielectrics

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Electrocaloric cooling has been put forward as a promising technology able to provide an environmentally-friendly, cost-effective and efficient cooling solution. However, the future of electrocaloric coolers is determined by development of new electrocaloric materials, which in turn relies on the existing capabilities to deliver accurate measurements of electrocaloric properties in materials and cooling effectiveness in devices. In this talk, we review and evaluate the current status of metrology for measuring electrocaloric properties. Focus is given to the indirect method, from which electrocaloric effect is predicted from measured pyroelectric coefficient and assuming linear thermodynamic state equations and Maxwell relations. Sources of uncertainties and errors of this method and the validity of its application to nonlinear and non-equilibrium dielectrics are herein presented and discussed.

$K_{0.5}Na_{0.5}NbO_3$ thick films with potassium-sodium germanate sintering aid

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The family of alkali niobate based ferroelectrics offers an environmentally friendly alternative to the lead-containing ferroelectrics, e.g., lead zirconate titanate ($Pb(Zr,Ti)O_3$ or PZT). Among the alkali niobates the $K_{0.5}Na_{0.5}NbO_3$ (KNN) solid solution is still considered to be one of the most promising substitutes. An important step in the exploitation of the KNN is its integration into micro-electro-mechanical-systems (MEMS). This is usually done by integrating KNN components as thick films onto substrates using, e.g., screen-printing technology. So far, in contrast to KNN ceramics, literature offers little in-depth studies on how the processing parameters influence the microstructural, structural and functional properties of the KNN thick films.

We prepared fine and phase pure KNN powder via conventional solid state synthesis from alkali carbonates and niobium (V) oxide. To improve the sinterability, the KNN powder was mixed with 1 mass % of a liquid-phase sintering aid, i.e., potassium-sodium germanate (KNG). The powder mixture of KNN and KNG (KNN+1KNG) was mixed with an organic vehicle to form a suspension, which was screen-printed onto alumina substrates. The screen-printed thick films were sintered for 2 h at 1100°C both with and without the presence of the packing powder (PP), i.e., the KNN powder. The PP was used to avoid extensive sublimation of the volatile alkali oxides at the sintering temperature.

Microstructural properties of the films were determined using scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis, while the functional response of the films was characterized by measurements of piezoelectric d_{33} coefficients.

In this contribution, we present the effect of the PP on the microstructure and structure of the films. The sintered films exhibited orientation along preferred crystallographic directions, which we attribute to compressive stresses developed during cooling of the thick-film structure. The piezoelectric response of the KNN+1KNG thick films was measured and compared with that of bulk KNN ceramics.

Li diffusion and electrochemical activity in commercial battery materials

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Perpetual growth of demand for energy and power density, along with durability and safety, has driven a continual development of Li-cells of various designs. A thorough understanding and fundamental study of the degradation mechanisms associated with Li transport is necessary for future requirements of excellent reliability and long life specified, e.g., for automotive applications [1]. However, no systematic studies of the Li dynamics at the nanoscale in the commercial Li batteries have been reported.

In presented research, we applied Electrochemical Strain Microscopy (ESM) technique (in which the apparent piezosignal appears due to ionic motion) to the commercial intercalation materials. We studied Li diffusivity and electrochemical activity distribution with the nanoscale resolution in fresh and aged LiMn2O4 spinel cathodes. Samples were embedded in epoxy and polished. We found ESM responce on the LiMn2O4 active particles and strong PFM/ESM responce on the carbon black enriched regions of the PVDF matrix. Rest of the matrix was not electrochemically of piezo active.

This research can clarify the microscopic origin of degradation of commercial Li batteries materials by determining local Li-diffusion coefficients and observing corresponding microstructure changes.

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[1]. «Basic Research Needs for Electrical Energy Storage», DOE BES Workshop

Measurement of the effective d33 coefficient on PZT film integrated structures using laser interferometry.

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It is well known that the clamping reduces the measured properties of piezoelectric materials compared to those in stress free conditions. In this work, we examine the effect of clamping in thin film piezoelectric materials laid down on a substrate. Using a finite element model, an integrated structure consisting of a PZT thin film electroded on both faces laid down on a silicon substrate is modeled as a function of the properties of the materials. The displacement at the surface of the integrated structure is calculated as a function of the input voltage. A theoretical effective d33 coefficient is calculated and compared to the unconstrained d33 parameter.xml: namespace prefix = o ns = "urn:schemas-microsoft-com:office:office" />
To confirm these theoretical results, PZT thin film integrated structures corresponding to the configuration modeled by the finite element method were fabricated. The PZT films were deposited by sol gel enduction on a Pt bottom electrode. The deposited film thicknesses ranged from 260 nm to 400 nm. Measurements of the displacement created by a quasistatic electrical field were carried out on the top surface of the sample by Laser interferometry. An effective d33 coefficient was then determined. The experimental set-up allows d33 to be cartographied on a 1.7x1.7 mm^2 sample. Cartographies at a quasistatic frequency of 1 kHz for 1 V and 5 V input voltages are reported and an average effective d33 is determined. First measurements on a bulk PZT ceramic cube lead to a d33 coefficient of 0.39 nm/V in accordance with that of the ceramic manufacturer. For the integrated structure, according to material properties, an estimate of the unconstrained d33 coefficient is deduced and compared both to the theoretical results and to that of the bulk material.

Modeling and study of hysteretic behaviour of piezoceramic materials under external electrical and mechanical stress

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Nowadays, piezoelectric materials are frequently used for various applications. They can operate under various environmental conditions, such as high temperature, high pressure, external electrical DC fields or mechanical stress that can either be residual or applied. The presence of high mechanical or electrical stress in piezoceramic materials induces nonlinear hysteretic behaviours that significantly modify the piezoelectric characteristics through a shift of material properties from their stress-free values. Indeed, nonlinear ferroelectricity may be characterized by four typical hysteretic loops: the dielectric (electric displacement versus electric field), the butterfly (strain versus electric field) and two ferroelastic curves (stress versus strain and stress versus electric displacement). The main phenomenon underlying these effects is based on microscopic domain switching process. Thus, the purpose of this study is to model the nonlinear hysteretic behaviour of piezoceramic materials under an external (mechanical or electrical) stress. The principle consists in starting with the characteristics of microscopic domain distribution to deduce the macroscopic nonlinear behaviour.
Choosing the remanent strain and remanent polarization as internal variables, a 2-dimensions domain orientation distribution is used to describe the evolution of these parameters and to develop a phenomenological model of ferroelasticity for electromechanical loading histories. The longitudinal and transversal strains, electric displacement and associated parameters (dielectric, elastic and piezoelectric) are evaluated as a function of uniaxial electrical and mechanical loading. The behaviours of four piezoceramic materials (soft and hard) are simulated and the results are discussed and compared to experimental data found in literature.
This work is a contribution to a better understanding of the effects of domain wall motions in piezoceramic materials under mechanical or electrical stress, and it leads to an improvement of models to predict device performance under such operating conditions.

Piezoelectric energy harvester for bicycle

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For several years, various electric accessories can be installed on bicycles like lamps or communication devices. Powering theme from ambient energies will avoid the use of batteries and improves the availability of these devices when the bicycle is not used for a long time. In this paper, we propose an alternative solution to improve the battery lifetime of embedded devices on a bicycle by using a piezoelectric energy harvester. The bicycle frame vibrations induced by rolling were investigated as an alternative power source. In the bicycle, the vibration amplitude at the fork during rolling on a cycle track reaches up to 2.5 m/s2 at frequencies around 18 Hz. However, the amplitude of vibrations at the paved runway is much higher. Spectral amplitudes up to 10 m/s2 were observed at frequency around 18 Hz. The amplitudes in the frequency domain reveal that low frequencies and frequencies around hundred Hz are present in the bicycle. The largest amplitudes are found in the range of 2-30 Hz. Hence, the harvester doesn't need a broad frequency response. The mechanical to electrical energy conversion is performed by the piezoceramic elements. An electric interface called SSHI is introduced to increase the electromechanical conversion. The self-powering of the SSHI interface is achieved by integrating two additional piezoelectric patches. One patch is used to sense the velocity zero crossing to drive switches of the SSHI circuit. The other one is used to provide the DC voltage source to supply the electronic circuits. The power generator was tested on a shaker at the resonance frequency and energy is successfully harvested, stored in the capacitor and supplied to the electrical load. The results show that for a bicycle speed of 21 km/h on a paved track, the power in the electric load is 3.4 mW @ R = 200 k?.

Quantification of electromechanical coupling measured with Piezoresponse Force Microscopy

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Piezoresponse force microscopy (PFM) is an invaluable tool for measuring the piezoresponse of functional materials at the nanoscale, allowing for high resolution measurements of the electromechanical coupling of thin films. In this work we address the challenges facing quantification of PFM by developing standards both through in-house work and inter-laboratory comparisons.
PZT 20-80 epitaxial thin films have been grown to 100 nm thickness on 10×10 mm2 1 at% Nb-doped SrTiO3 substrates by PHASIS Sàrl in Geneva, Switzerland, and poled along the c-axis which lies perpendicular to the substrate plane. Optical lithography was used to define a series of top electrodes with varying dimensions, capacitance values, proximity and thickness, at INEX, Newcastle University. By varying the top electrode structure various effects are quantified and calibrated, including substrate bending, electrode clamping, electric field non-uniformity, tip-surface contact resistance and PFM tip displacement. PFM and laser Doppler vibrometry (LDV) measurements were carried out at NPL.
LDV measurements of circular capacitor structures have shown uniform displacement amplitude, linearly dependent on driving voltage amplitude. For 10 µm diameter top electrode typically d33 = 41 ± 1 pm/V. Good agreement of LDV and PFM measurements was obtained where the tip displacement is measured for driving voltage applied directly to the electrodes, resulting in d33 = 39 ± 3 pm/V. Calibrating for the tip-surface contact resistance and modelling of the tip-surface interaction allows for measurements of d33 values when driving the voltage through the PFM tip both on the capacitor structures and on the PZT thin film in scanning mode.
In conclusion, in this work we propose a measurement procedure for calibrating against various artifacts affecting PFM measurements using a standard procedure and sample. Further inter-laboratory comparisons should reveal any systematic differences in PFM measurements, working towards a PFM standard.

Surface Functionalizatio of Zinc Oxide Transducers for Multiplexed Detection of Liver Diseases

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Background, motivation and objectives: Piezoelectric biosensors are a rapidly growing tool for disease detection and diagnosis. However, many challenges remain to their effective clinical implementation. In particular, the need for a tool that can detect multiple diseases at a time presents an engineering challenge in the ability to adhere several different antibodies to a piezoelectric surface. Our aim is to investigate the means to optimize this process. Thiol monolayers serve as a bridge between the transducer and the biochemical detectors such as antibodies that are exposed to the target analytes. We examine and characterize optimal thiol adhesion to piezoelectric transducers, and demonstrate functionalization of this surface using antibodies for hepatitis B and hepatic carcinoma. Statement of contribution/methods: We have grown zinc oxide transducers using both sol-gel synthesis and RF sputtering. On these zinc oxide thin films we have grown copper and aluminum thin films that will act as electrodes in the final transducer and then examined the adhesion of thiol monolayers by FTIR analysis on these electrode thin films.. Our next step is to examine the adhesion of antibodies to these thiol monolayers. Results: Our preliminary results show that thiol adheres preferentially to copper surfaces bound on zinc oxide. Discussion and conclusions: As a result, we anticipate that antibody surface functionalization will be optimized with the use of copper as an electrode and binding surface for the biochemical sensing component of a piezoelectric biosensor. These results will be available for the conference.

The new approach to the determination of the material constants of solid materials

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In previous papers concerning with the analysis of the mechanical oscillations of solid samples by the variation method the calculations were carried out without considering the mechanical loss. However it is known that for dissipative systems one can use the traditional variation method with the dissipative function in the expression of Lagrangian. If the source of the loss is viscosity the introduction of dissipative function leads to the complex elastic constants. Previously such approach allowed us to estimate the viscosity coefficients of some piezoceramic materials. But the consideration of the mechanical loss opens the possibility of the determination of the material constants by using the fitting the theoretical frequency dependencies of the real and imaginary parts of the electrical impedance of the samples to the experimental one. Such method extends the possibilities of the method because allows to find not only elastic, piezoelectric and dielectric constants but also viscosity coefficients. So the objectives of the work are the development of the method of the determination of all material constants by using one-three resonant peaks and its examination on some piezo-materials.
For carrying out the work the samples of the cubic form of piezoceramics PZ21 and PZ26 differing by values of Q-factor were chosen. The frequency dependencies of the real and imaginary parts of the electrical impedance of the pointed samples were measured with the help of the LCR meter. The calculation program was developed based on the fitting the theoretical frequency dependencies of the electrical impedance to the experimental ones which allowed to find all material constants including components of the viscosity tensor. The obtained data is in a good agreement with the reference data.

Thermostability of glycine piezoelectrical phases

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Recently, organic and bio-organic materials have been focused by researchers as new piezoelectric materials. This prompted a new wave of interest in these low-molecular-weight, polar amino acids. However, up to now, only several amino acids which show piezoelectricity are known: glycine, DL-alanine comparable to quartz. L-ananine, L - valine, L- glutamic and DL-tyrosine have much weaker piezoelectric activity. Glycine is the simplest of the 20 nonessential amino acids. Strong piezoactivity and polar properties in glycine opened up a new perspective for their use as biocompatible nanoactuators, nanomotors, and molecular machines. In this work, we investigated domain structures, the phase transition behaviour and its effect on thermal stability of the piezoelectric properties of the glycine crystals.
Glycine has three polymeric crystalline forms: ?, ? and ?. The ? form crystallize in centrosymmetric structure while the ?- and ?-glycine crystallizes in non-centrosymmetric structure. These polymorphs have completely different physical properties. Comparative x-ray, dielectric and local piezoresponse force microscopy (PFM) measurements have been made on micro- and macrocrystals on glycine different phases. The dielectric constant of ?-glycine obeys apparent Curie-Weiss (CW) law with the CW constant ~2000, Weiss temperature, TCb = 300°C and transition temperature at Tc =142°C. The piezoelectric properties of microcrystals are expected to be dependent on the crystal size with respect to the possible instability of the polar phase. The results indicate the ability to obtain high piezoelectric effect up to 110°C. The temperature dependence of the piezoelectric response is associated with the structural phase transition to the low-symmetry piezoelectric phase with a large number of piezoelectric coefficients. The specific features of the phase transitions with the symmetry change have been discussed.

Ultrasound medical applications of electrophoretically deposited PZT thick films

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Ultrasound devices operating in the frequency range 20-50 MHz for medical applications enable imaging of superficial tissues such as skin or eye. Such devices require piezoelectric materials with a thickness of a few tens of micrometers deposited on a conductive substrate. The acoustical beam needs to be focused to increase the lateral resolution. In this presentation, the piezoelectric film was directly patterned on a curved substrate to obtain a geometrical focusing. This avoids the addition of a lens and consequently the decrease of sensitivity due to acoustic attenuation, which is particularly high at such frequencies.
Electrophoretic deposition (EPD) process is well adapted to obtain geometrical focusing, as PZT piezoelectric structures can be patterned on curved substrates. Indeed, EPD enables the deposition of various materials on conductive substrates by applying a DC electric field. A stable PZT (Pb (Zr0.53Ti0.47) O3) ethanol-based suspension with Ethyl cellulose additive to avoid crack formation was prepared. PZT was deposited at a defined constant current density onto an electroded alumina substrate or a golded porous PZT substrate. We obtained crack-free deposits with uniform and controlled thickness. Deposited films were sintered in a PbO-rich atmosphere. Films obtained from this procedure were functionally and electromechanically characterized. Thickness coupling factors over 40 % were measured for PZT films.
A PZT layer was deposited on a curved golded porous PZT substrate. The piezoelectric structures obtained were used to fabricate high-frequency ultrasonic transducers with a center frequency over 30 MHz and a high bandwidth. This transducer was integrated in an echographic probe to obtainin-vivoskin images.

Piezoelectric materials and their applications in radio frequency domain and telecommunications

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The market of telecommunications has grown rapidly this last decade. The main parameter regarding users is the data flow which must be increased with each new standard. In these conditions, it is mandatory to improve the use of allocated bandwidths. These was done in different standards, but the counterpart was to use efficient digital modulations and consequently multi carriers and multi channel standards. To reach this goal, the constraints on electronics circuits and devices for RF front-end, were increased drastically particularly to obtain high quality filters but not only and, other devices like duplexer, antenna switch... are concerned. In this context, piezoelectric materials and devices offer the only way to reach the required objectives. From this point of view, RF filters represent the more important devices as it is impossible to reach low insertion losses and high rejection at the same time, with conventional filters. A lot of works were performed, by several research teams in the world, devoted to materials, to technological steps and to devices.

Among piezoelectric materials, some of them are candidates for telecommunications applications. After a review of the main piezoelectric materials, the desired characteristics will be analysed and finally few materials are retained. The main characteristics of these materials are high frequency of operation up to several giga Hertz, high power capability up 2 W, compatibility with collective manufacturing processes like microelectronics processes. The use of piezoelectric material has also some drawbacks. The main problems will be also presented in particular the control of the thickness for resonant structures.

Some applications and devices will be presented coming from research teams but also from manufacturers that provide such devices mainly to the industry of mobile communications objects.

Effect of the metallization and electrode size on the electrical admittance of piezoelectric ceramic parallelepipeds

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The resonance ultrasound spectroscopy method allows the complete set of elastic, piezoelectric and dielectric properties of materials to be identified using a single small sample with a cubic shape. To be an efficient technique, all types of modes (transverse, longitudinal and torsional) have to be generated and detected. Thus, very often, generation is performed by a wide band transducer located on a corner of the cube while detection can be performed by Laser interferometry. In the case of a piezoelectric ceramic, generation can be carried out by two electrodes. In this case, the size and the location of these electrodes will affect the frequency response of the cube. The purpose of this work is to examine these effects on the mechanical and electrical admittance spectra.
The eigen frequencies and the eigen modes of a piezoelectric cube with a full electrode on one side and a partial electrode on the opposite side are calculated and the electrical admittance is deduced from the charge density calculation on both electrodes. Depending on the size and the location of the partial electrode, several modes can be generated or annihilated. The shear components can be preferentially generated when the electrode is located on a corner of the cube while the thickness modes are preferentially generated with a centered electrode. Experiments were conductedon piezoelectric ceramic cubes (a PMN-34.5PT and a PZ26 ceramic manufactured by Megitt-Ferroperm) with various electrode sizes and locations. They confirm the theoretical results. Based on this analysis, a tensorial characterization method of a piezoelectric ceramic using electrical admittance measurements only is proposed and the full elastic, piezoelectric and dielectric tensors including mechanical and dielectric losses of the studied ceramics are reported.

Texturation of lead-free BaTiO3-based piezoelectric ceramics

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Nowadays, piezoelectric ceramics are integrated in a wide range of devices, in particular in ultrasonic applications (underwater sonar systems, medical imaging, non-destructive testing...). Most of them use Pb(Zr,Ti)O3 (PZT). However, due to health care and environmental problems, lead content must be reduced in such applications [1]. Recent reviews demonstrated that few lead-free materials families can be considered: the alkaline-niobates (K0.5Na0.5NbO3), the alkaline-bismuth-titanates (Na0.5Bi0.5TiO3 Ka0.5Bi0.5TiO3), the bismuth layered compounds (Bi4Ti3O12) and barium titanate based materials (BaTiO3) [2, 3].
One of the limitations of ceramic is their isotropic nature. This is the reason why texturation process has been developed in order to improve their properties in particular electromechanical parameters. The aim of the present study is thus to obtain textured BaTiO3 based materials by using the templated grain growth process and to measure their piezoelectric properties.
Nanosized BaTiO3 powders were prepared by solid state route at relatively low temperature while BaTiO3 templates of different morphologies were elaborated by a molten salts process. Dispersing agent, binder and plasticizer, the mixture of the templates and matrix particles was then dispersed in the appropriated solvent. The slurry was then tape-casted on plastic film. After drying, the green sheet was cut, stacked and pressed and then sintered at the appropriated temperature. This process allowed obtaining highly-oriented materials with interesting piezoelectric properties.

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Langasite, lead-free piezoelectric thin layer synthesized through a ?Chimie douce? route

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According to European directives, lead is forbidden in industry except for piezoelectricity applications. Nevertheless, the research for new lead free piezoelectric materials and devices is becoming very important because this exception is not definitive. In this context, our goal is to develop a textured lead-free piezoelectric thin layer on a flexible substrate for future piezoelectric devices. We have based our work on langasite (La3Ga5SiO14: LGS) as the lead-free piezoelectric compound. The final substrate will be a Ni/W flexible metal substrate coated with a buffer layer of textured La2Zr2O7, already achieved for superconductivity applications in our laboratory [1]. The piezoelectric LGS is made by «chimie douce». The use of different precursors in different solvents was studied and various atmospheres were tested for the thermal treatments. Finally, a pure LGS powder could be obtained after thermal treatment at low temperature (850°C) from a melt of nitrate metals and alkoxide silicon [2].
Then, LGS thin layers depositions have been performed on MgO (100) crystalline substrates by spin coating and dip coating. After annealing at 1000°C, the thickness of a monolayer, deposited by spin coating, is about 200 nm. When several layers are deposited on the substrate, X-ray diffraction patterns show a (101) preferred orientation. The first tests of deposition on metallic substrates are just starting.
In our presentation we will expose the different solutions leading to pure crystalline LGS after thermal treatment. The results on the langasite films (orientation, thickness and roughness) and also about the bottlenecks for the deposition on a metal substrate which requires an inert atmosphere will be discuss.

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Defect-mediated phase stability in ferroelectric oxides

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The effect of oxygen vacancies on the structural properties of the rhombohedral, orthorombic, tetragonal and cubic phases of $BaTiO_3$ was investigated using density functional theory calculations. It is shown that neutral oxygen vacancies induce a local perturbation of the rhombohedral perovskite structure leading to the formation of local tetragonal regions. Depending on the vacancy concentration, this can result in the coexistence of the vacancies oriented along different crystalline axes and, consequently, nucleation of «striped pattern» of alternating 90 degree tetragonal domains.

Role of oxygen octahedra tilting and defects on the electrical and electro-mechanical response of rhombohedral Pb(Zr,Ti)O3 ceramics

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Understanding the electrical and electromechanical properties of ferroelectric ceramics form the basis for the design of such materials in various piezoelectric applications. The complexity of the structure(microstructure)?properties relationship lies in the numerous interdependent material's features, such as charged defects, tilted oxygen octahedra in perovskites, ferroelectric domain structure and grain size, that may affect the functional response.
Perovskite materials are structurally characterized by oxygen octahedra. Depending on the size of the A- and B-site cations in the ABO3, the octahedra may be rotated (tilted) along certain crystallographic directions. Early studies revealed that the domain switching and piezoelectricity in the long-range octahedrally tilted R3c Pb(Zr,Ti)O3 (PZT) ceramics are significantly affected by these tilted patterns [1,2]. However, there are still disagreements as to the exact microscopic mechanism of the interaction between the tilted octahedra and domain walls. In addition, defects, such as oxygen vacancies, may affect domain-wall motion in a similar manner, giving rise to the same type of double-like polarization-field loops and a reduction of the extrinsic part of the piezoelectric response, as observed in the tilted R3c PZT.
The aim of the present contribution is to elucidate the role of tilted octahedra and defects on the switching behaviour, dielectric and piezoelectric properties of the rhombohedral PZT ceramics. Two compositions are compared, i.e., the R3c PZT75/25, which is characterized by the tilting at room temperature, and the untilted R3m PZT60/40. Nonlinearity and frequency dispersion of the dielectric permittivity, direct and converse piezoelectric d33 coefficient of the two PZT compositions are compared. The study made possible to separate the influence of the defects and tilts on both switching and weak-field properties of PZT.
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Evaluation of the polarization state of light metal embedded piezoelectrics

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Integrated piezoelectric sensors and actuators find application for health-monitoring, for reducing noise emission, for vibration control and damping, etc. Thermal wave methods are a promising approach for the non-destructive evaluation of such smart structures. The polarization state of the piezoelectric material is determined from the pyroelectric response of the devices being irradiated by a modulated laser beam. The time or frequency dependence of the pyroelectric current provides insight into the polarization distribution.
In this work, we apply the thermal wave method to piezoelectric transducers embedded into high pressure die-casted aluminium and glued between two bended metal sheets, respectively. The transducer consists of a Pb(Zr,Ti)O3 (PZT) plate or PZT macrofibers embedded into polyimide and epoxy resin, respectively. A modulated laser beam is absorbed by the upper metal layer and thermal waves propagate into the sample. Due to the exponential decay of the amplitude and the large heat capacity of the aluminium, the pyroelectric current is very small. The pyroelectric current spectrum is affected by off-axis positioning of the piezoelectric patch and cracks created during die casting. During bending of the actuator, mechanical loads are capable to degrade the polarization.
A transient thermal analysis of the actuators was performed using the finite element modeling package ANSYS®11.0. The penetration depth of the thermal wave was determined for characteristic modulation frequencies. The thermal loss to the environment was described by thermal relaxation times. Transfer functions describing amplitude attenuation and phase lag at each modulation frequency were assessed and fitted to appropriate models, for instance, a harmonically heated piezoelectric plate exhibiting thermal losses to the environment characterized by a single relaxation time. Since the average charge induced by the pyroelectric effect is determined by the mean sample temperature, sample heating was evaluated by charge monitoring and the measurement results were compared to the ANSYS simulation.

Oxygen vacancies induced two-dimensional electron gas near SiO2/BaTiO3 interfaces

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An atomistic model of SiO2/BaTiO3 interface was constructed usingab initiomolecular dynamics. Analysis of its atomistic structure and electronic properties reveals that (i) the band gap at the stoichiometric SiO2/BaTiO3 interface is significantly smaller than that of the bulk BaTiO3 and SiO2 and (ii) the interface contains ~5.5 nm?2 oxygen vacancies (V2+) in the outermost TiO2 plane of the BaTiO3 and ~11 nm?2 Si-O-Ti bonds resulting from breaking Si-O-Si and Ti-O-Ti bonds and subsequent rearrangement of the atoms. This structure gives rise to the interface polar region with positive and negative charges localized in the BaTiO3 and SiO2 parts of the interface, respectively. We propose that high dielectric response, observed experimentally in the SiO2-coated nanoparticles of BaTiO3, is due to the electron gas formed in oxygen-deficient BaTiO3 and localized in the vicinity of the polar interface.

Frequency and temperature stability of high electric field-induced strain in K0.5Bi0.5TiO3 ? BiFeO3 ceramics

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Stability of electromechanical performance with respect to temperature, as well as frequency and amplitude of the driving electric field is one of the key issues in development of lead-free piezoelectric ceramics for actuator applications. We have prepared and examined ferroelectric ceramics in a wide range of composition in the system (1-x)(K0.5Bi0.5)TiO3 ?xBiFeO3 (0.1 ? x? 0.9). Ceramics with high density and phase purity have been prepared by conventional solid state reaction, previously reported to be challenging. The dielectric and electromechanical properties have been shown to reach a maximum value atx? 0.25 demonstrating a high strain performance (250 - 370 pm/V in the temperature range 25 - 175 °C). The strain response in this ceramic is shown to be mainly electrostrictive and frequency stable above 100 °C, though the piezoelectric contribution affects this stability below 100 °C. Thus, the material demonstrates good electromechanical performance at elevated temperatures and can be considered as a cost-efficient lead-free alternative for actuator applications.

Exceptionally large piezoelectric strains in high temperature BiFeO3-(K0.5Bi0.5)TiO3?PbTiO3 ceramics

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There is currently a need for high strain piezoelectric actuators that are capable of operating under extreme temperatures and pressures in applications such as aerospace, deep sea oil drilling and in chemical processing. PZT is currently the dominant piezoelectric ceramic material in actuators, sensors and transducers, however, PZT has a restricted operating temperature.
Polycrystalline ceramics of type (1-x-y)BiFeO3-x(K0.5Bi0.5)TiO3-yPbTiO3, wherex=0.15 andy=0.275 (BF-KBT-PT) have been produced via a conventional mixed oxide method. Ceramics were characterized using X-ray diffraction which confirmed an electric-field-induced phase change from predominantly rhombohedral to mixed phase tetragonal and rhombohedral structure upon poling. The selected composition exhibited a remnant polarization of 34 µC/cm2 and a peak-to-peak strain of 0.805% at 6.5 kV/mm, the highest electric-field induced strain reported in a polycrystalline material. A room temperature d33 of 205 pm/V was measured. Rayleigh analysis was used to quantify the extrinsic contributions, a Rayleigh coefficient, ad, of 59 x10-18 m2/V2 was measured. Electromechanical coupling, kp, was found to be 0.29 and a TC of 575 ° C was determined via permittivity measurements.
We demonstrate a number of important results that may have wider implications. Ternary and psuedoquaternary systems have recently been subject to large amounts of research as many of the possible binary systems have been explored. This has led to a raft of materials with reported high-strains, these are often electrostrictive or have limited operating temperatures. The strain-field measurements reported are the largest reported for a polycrystalline material with a strain of 0.805%. This system shows that with only small amounts of a third end member such as lead titanate in BF-KBT, the properties of a binary system can be drastically altered.

BNT-based Lead-free materials - Alternativ for PZT-based materials

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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.
One of the most popular candidates for lead-free piezoelectric ceramics is the BNT-based system. Although this system shows 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.
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.
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). Furthermore, the materials show a strong anisotropic behavior, which makes the material suitable for ultrasonic transducers in the MHz range. The typical behavior under small and large signal driving conditions will be presented and discussed.

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