Piezo 2017

Electroceramics for End Users IX

CERCEDILLA (MADRID) SPAIN

FEBRUARY 19 TO 22, 2017

Piezo INSTITUTE
The European Institute of Piezoelectric Materials and Devices

icmm
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

POLITÉCNICA

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PIEZO2017: ***Electroceramics for End-users IX"*** takes place in Cercedilla (Madrid, Spain) 19-22 February, 2017 and it is organised by Instituto de Ciencia de Materiales, Spanish Council of Research (ICMM-CSIC) and the Technical University of Madrid (UPM), together with the Piezoinstitute. This conference series has been running for a number of years and following the initial 'POLECER' FP5-GROWTH, Thematic Network of the EC, launch of Electroceramics for End-users I, in Interlaken Switzerland, 24th to 27th February 2002.

The meeting will continue its well established traditions of presenting the latest research and developments on piezoelectric and multifunctional materials, technologies and devices, and of bringing together academia and industry within the field for discussion and networking.

Simultaneously to PIEZO2017 conference and open to its attendees, we are organizing a JECS Trust funded Winter School on "Advanced Characterization of Piezoceramics". The proposed Winter School aims to discuss the role on piezoelectric ceramics processing and applications of the advanced characterization, microstructural, mechanical and electrical introducing both classical knowledge in these areas and novel techniques.

PIEZO2017 will gather together the first class touristic attraction of the city of Madrid and the possibilities of the Navacerrada sky resort. The site of the meeting, the The Forestry Residencia Lucas Olazábal of the is inside the Protected Natural Park of "Sierra de Guadarrama". The more than 33.000 hectare (60% of which belongs to the Madrid Autonomous Community) of this Park provides attractions to enjoy nature in different ways.

Sierra de Guadarrama National Park (in Spanish: ***Parque Nacional de la Sierra de Guadarrama***) is the fifth largest in Spain's national parks system. The National Park extends over the Sierra de Guadarrama mountain range, whose highest peak is the Peñalara summit (2428 m). Other outstanding features include the Puerto de Navafría pass (1773 m) and the La Morcuera (1796 m) and Siete Picos (2138 m) mountain ranges. Precipitation is plentiful. Snow falls in winter and part of the spring. The area's cold temperatures generally cause rain to freeze into snow from the end of November to the middle of May. In the highest zones, snow may last until July. With the excellent communications, this is a very popular area particularly at weekends and of course during the skiing season. In addition, walking and hiking are activities available and most substantial towns have a network of routes available usually from the local tourist office or town hall. Quite a number of walks are clearly marked.

Puerto de Navacerrada ski resort is the closest ski resort to Madrid and Segovia. It is divided into two areas: the upper area, with intermediate/difficult slopes, and the lower area with intermediate/beginners' slopes. They are well-sheltered slopes, running between pinewoods.

Puerto De Navacerrada is, with 19 slopes, a medium sized ski resort with 9 ski lifts (5 chair lifts, 4 surface lifts) that offers skiers a respectable 415 metres (1360 feet) of vertical descent. There are 5 km (3.1 miles) of cross-country ski trails. A small proportion of the slopes are covered by snowmaking.

PIEZO2017

"The forthcoming Electroceramics for End-users IX conference is the next scientific event in the series of conferences initiated in 2002 and dedicated to advances in electroactive, particularly piezoceramic, materials and devices. It will be combined with a professional exhibition.

Following the tradition of these conferences of combining science, networking between academia and industry and enjoying the beautiful mountains, ***PIEZO2017*** conference will take place in the charming town of Cercedilla (Sierra de Guadarrama, Madrid, Spain).

PIEZO2017 will continue its well established traditions of presenting the latest piezoelectric and multifunctional materials, technologies and devices research and development and of bringing together the international community within the field for discussion and networking.

There will be oral sessions, each with an invited keynote presentation. The oral sessions will be accompanied by poster sessions, offering additional opportunity for discussions with the authors and networking.

Tutorials, conducted by international experts are also planned. They will provide unique insights for researchers and those interested in broadening their skills.

Guy Feuillard. PiezoInstitute President."

"Since its establishment in 2002, the winter conference series "Electroceramics for the end users", centering on recent and novel applied piezoelectric technology has aimed to offer a bridge between materials and devices. It provides a platform for information and exchanges among users, developers and academics in the piezoelectric field.

Welcome to PIEZO2017!

Nava Setter, Honorary-President of the Advisory Board of PIEZO2017.

ORGANIZING COMMITTEES

Chair Lorena Pardo, ICMM-CSIC (Spain)

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Honorary President: Nava Setter, EPFL (Switzerland)
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IN MEMORIAN, PROF. L. E. CROSS

Prof. Leslie Eric Cross, from Pennsylvania State University, PA (USA), passed away on the 29th of December, 2016.

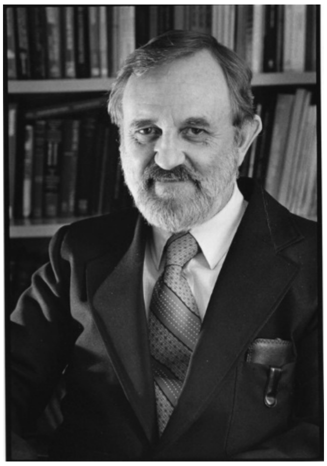
For all of us that had the fortune and privilege of have been in contact with him at a given point in our career this is very sad news.

For the international community he is a well-recognized key figure in the field of ferroelectricity that has had a great impact on many of the topics in which the Piezoinstitute is involved. The Piezoinstitute and the Organizing Committee of PIEZO2017 is dedicating to him a part of the Opening Ceremony in which Prof. Nava Setter will speak about him and his work."

Lorena Pardo.
Piezo2017 Chair

LESLIE ERIC CROSS

L. Eric Cross (1923-2016) passed away peacefully on the 29th of December. He was an Evan Pugh Professor Emeritus of Electrical Engineering, Penn State, a member of the US National Academy of Engineering, and a founding member of the Penn State Materials Research Laboratory. He was a world-leader in the field of ferroelectrics from a fundamental perspective, as an inventor of new characterization techniques, and in materials applications. He was beloved for his intelligence, vision, wit and humanity, as well as the charm with which he shared his fascination with ferroelectrics and his newest ideas. He was also an excellent mentor, and many of his students and postdoctoral researchers went on to scientific leadership position themselves.



Professor L. E.

Eric and his wife

He came to the field of ferroelectricity in its infancy, and this to the objection of his advisor E.C. Stoner, "Who referred to it as a trivial lattice phenomenon!" Stoner was famed for his contributions to magnetism. World War II interrupted Cross's undergraduate education at Leeds University (UK). During the war, he worked for the British Admiralty on a program using high frequency direction finding to track German U-boats, which ultimately allowed convoys to cross the Atlantic unharmed. Just two weeks after his transfer to that assignment, the boat that Cross previously served on was sunk in Atlantic, with no survivors. Ever after, Prof. Cross thought of himself as a lucky man. He was very proud of his long association with the Department of Defense and particularly the U.S. Navy, which supported much of his work in the field of sonar undersea transducers. He and his colleagues made many other societal contributions such as the piezoelectric transducer used in almost all modern medical ultrasound machines.

During his career, Professor Cross was honored by many professional organizations. He was a Fellow of the Materials Research Society, the American Physical Society, the Optical Society of America, the American Ceramics Society, and IEEE. In 1983, he was elected to the National Academy of Engineering for his contributions to the development of electroceramic, dielectric, and piezoelectric materials. He was also the 2010 recipient of the Von Hippel award of the Materials Research Society, its highest honor. Cross joined Penn State as a senior research associate in 1961, rose through the ranks, and in 1985, was named Evan Pugh Professor of Electrical Engineering; an Evan Pugh Professorship is the highest distinction that the University can bestow on a faculty member. He is the author or coauthor of more than 850 refereed papers; he held 20 patents, and published a comprehensive textbook, "Domains in Ferroic Crystals and Thin Films". At Penn State he mentored > 50 graduate students from across the world – including Prof. Yao Xi: the first Chinese Ph.D. (1982) educated in the US following the Cultural Revolution.

He will be sadly missed by all that knew him and worked with him. He shared his ideas freely with everyone that he met at scientific conferences, from graduate students to senior leaders in the field. He and his family, (wife Lucilla (Cilla) – a reluctant but gracious member of the ferroelectrics community by osmosis, and children Peter, Matthew, Daniel, Rachel, Elizabeth, and Rebecca) opened their home to generations of students and colleagues.

Very nice memories of the scholar, passion and personality of Professor Cross can be appreciated at [http://ethw.org/Oral-History:L._Eric_Cross.](http://ethw.org/Oral-History:L._Eric_Cross)

From: https://www.mri.psu.edu/mri/news/memory-l-eric-cross

VENUE

HOW TO REACH THE "RESIDENCIA"?

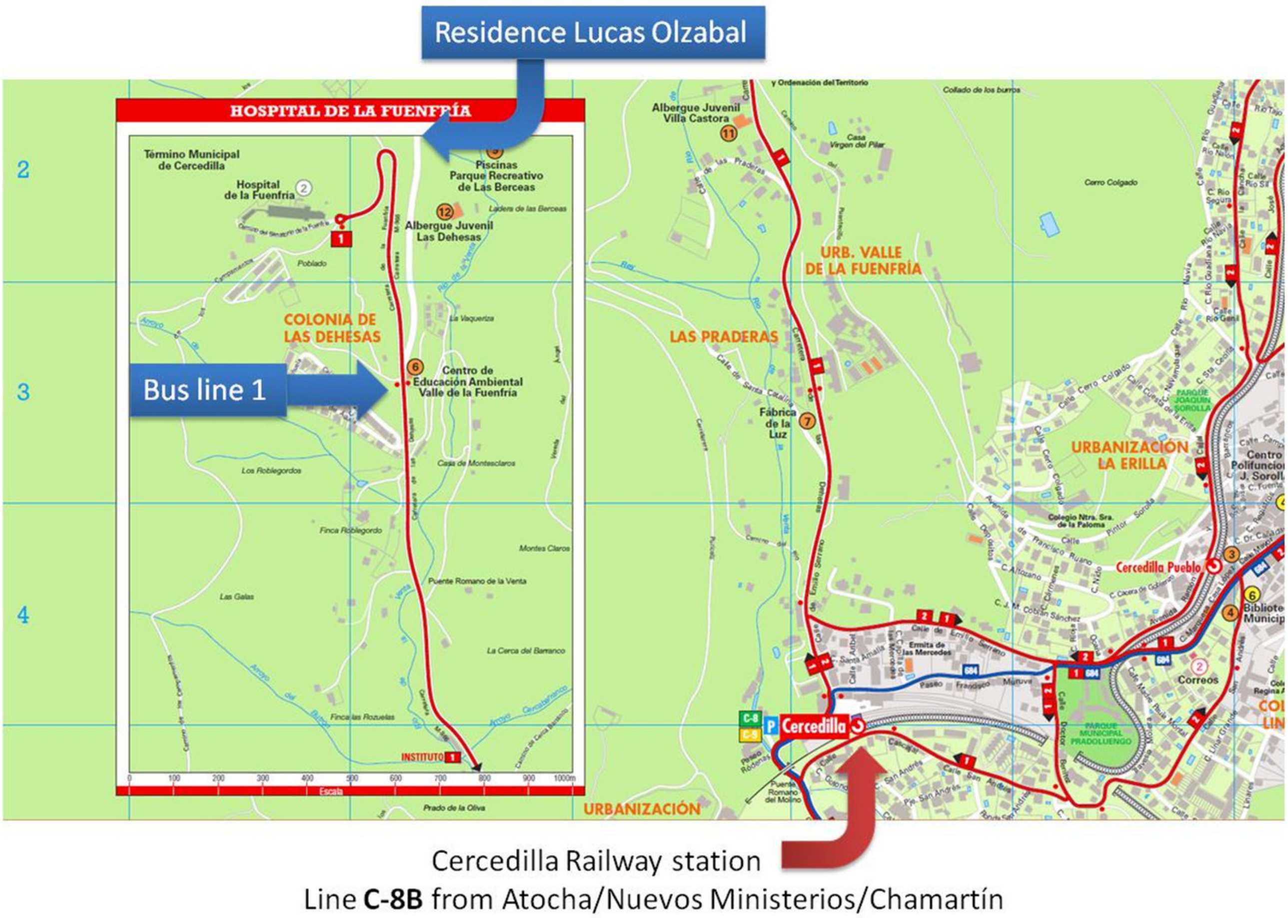
Directions
GPS coordinates: 40° 45′ 57.1″ N 4° 04' 14 .7″ W
Latitude = -4.070757
Longitude = 40.765856

By Train: From stations **Atocha, Recoletos, Nuevos Ministerios** and **Chamartín,** you can pick the **Linea C2** commuter, direction to **Cercedilla**. It takes, approximately, one-hour and twenty minutes.
From **Barajas Airport** (Aeropuerto-T4) you can pick **Linea C1** to **Chamartín**, and then transfer to **C8B**, direction to **Cercedilla**. It takes, approximately, one-hour and a half. (http://www.renfe.es)

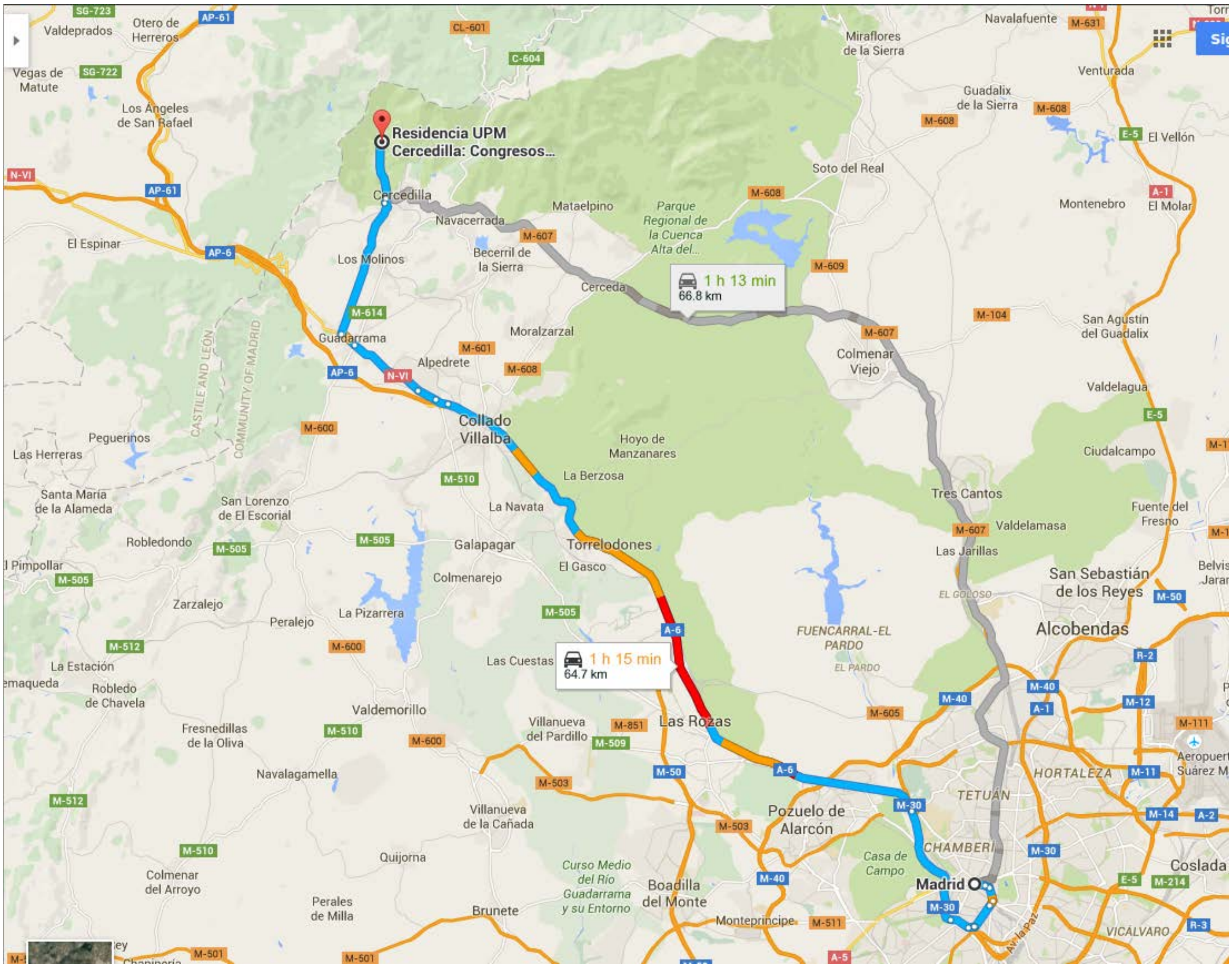
By Bus: Buses to **Cercedilla** (line 684) departure from **Moncloa** (C/ Princesa, 89).

Once you are at the train station of Cercedilla (by train or by bus) you have to catch the bus which leads to **Hospital Fuenfría**. The Residence is a short walk from there.

There is not public transportation all the way to the Forestry Residencia, but to the nearby Carretera de las Dehesas (1km away). Transportation from there will be provided by the organization upon request in case of bad weather.



By Car: From Madrid, drive along A-6 roadway. Take exit 42 toward N-VI/Guadarrama, and then follow N-VI and M-622 to Carretera de las Dehesas.



Sunday February 19th		
14:30		Registration
Winter School on Advanced Characterization of Piezoceramics **Session 1.** Chair: Luis E. Fuentes-Cobas		
15:00	Lecture 1	*X-ray absorption study of functional materials* María Elena Montero Cabrera Centro de Investigación en Materiales Avanzados, S.C., Miguel de Cervantes 120, Complejo Ind. Chihuahua, C. P. 31136, Chihuahua, Chih. Mexico.
16:00	Lecture 2	*Numerical Characterization of Piezoelectric Discs Using Resonance Curves* Nicolás Pérez. Universidad de la República, Facultad de Ingeniería, Montevideo, Uruguay
17:00		Coffee break
Winter School on Advanced Characterization of Piezoceramics **Session 2.** Chair: María Elena Villafuerte Castrejón		
17:30	Lecture 3	*Implementation of advanced microscopies in an atomic force microscope* *J. J. Gervacio-Arciniega* *Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, AP 14, Ensenada 22860, B. C., México.* *CONACyT-Facultad de Físico Matemáticas, Benemérita Universidad Autónoma de Puebla, Ciudad Universitaria, San Manuel, C. P. 72570, Puebla, Puebla., México.*
18:30		
19:15		Welcome reception

Monday February 20th

08:00		Registration
08:30		**Opening session**
09:00		In Memoria: Prof. Leslie Eric Cross
		Piezo2017 Session M1: Piezoelectrics, ferroelectrics , relaxors, tunable materials… Chair: Markys Cain
09:15	Invited talk	*Insight into Structure, Properties, and Mobility of Ferroelectric Domain Walls* Nava Setter Ceramics Laboratory, Materials Department. EPFL Swiss Federal Institute of Technology 1015 Lausanne, Switzerland
10:00		*Parametric study of a thin piezoelectric cantilever for energy harvesting applications* T. Hoang (1,2), G. Ferin (1), B. Rosinski (1), C.Bantignies (1), H. Le Khanh (1), An Nguyen-Dinh (1), G. Poulin-Vittrant (2), F. Levassort (2), M. Bavencoffe (2) 1. Advanced Research dept., VERMON S.A., Tours, France 2. Université François Rabelais de Tours, INSA Centre Val de Loire, GREMAN UMR CNRS 7347, 3 rue de la Chocolaterie, CS 23410, 41034 BLOIS Cedex, France.
10:15		*Temperature Dependance of Piezoelectric Properties in Lead-free Ceramics* Amir Khesro (1)*, Dawei Wang (1), Antonio Feteira (2), Derek C. Sinclair (1), and Ian M. Reaney (1). 1. Functional Materials and Devices Lab, Department of Materials Science and Engineering, Sir Robert Hadfield Building, University of Sheffield, Sheffield, S1 3JD, UK. 2. Materials and Engineering Research Institute, Sheffield Hallam University, Howard Street, Sheffield, S1 1WB, UK.
10:30	Keynote	*Non-Rayleigh dynamic nonlinearity in barium titanate* M.Tyunina (1,2) and M. Savinov (2) 1. Microelectronics Research Unit, Faculty of Information Technology and Electrical Engineering, University of Oulu, P.O. Box 4500, FI-90014, Finland 2. Institute of Physics, CAS, Na Slovance 2, 182 21 Prague, Czech Republic
11:00		Coffee break
		Piezo2017 Session M2: Applications I Chair: Henrik Ræder
11:30		*Aligned Porosity Pyroelectrics for Energy Harvesting* Yan Zhang, Mengying Xie, James Roscow, Chris R. Bowen Department of Mechanical Engineering, University of Bath, BA2 7AY, United Kingdom
11:45		*3D printing of ferroelectric devices using standard fused deposition modelling method* Andreas Geiger (1,2), Miriam Bach (1,3), Tony Lusiola (1), Mark Melnykowycz (1), Frank Clemens (1) (1) Empa Material Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Schweiz (2) Fachhochschule Münster, Bismarckstraße 11, 48565 Steinfurt, Deutschland (3) Institute of Ceramic, Glass and Construction Materials, TU Bergakademie Freiberg, Agricolastrasse 17, 09599 Freiberg, Germany
12:00	Keynote	*PLZT x/90/10 ceramics for energy storage* I. V. Ciuchi (1,2), L. Mitoseriu (2), and C. Galassi (1) 1. CNR-ISTEC, Istituto di Scienza e Tecnologia dei Materiali Ceramici, Via Granarolo 64, I-48018, Faenza, Italy 2. Dielectrics, Ferroelectrics & Multiferroics group, Faculty of Physics, “A.I. Cuza” Univ, .Bv.Carol I, n. 11, 700506 Iasi, Romania
12:30	Keynote	*Piezoelectric based ice protection system - preliminary modelling and experimental results* Erling Ringgaard, Konstantin Astafiev, Ruichao Xu, Michele Guizzetti, and Tomasz Zawada Meggitt A/S, Kvistgaard, Denmark
13:00 14:00		Lunch & PI General Assembly

Monday February 20th

Piezo2017 Session M3: New processing techniques Chair: Barbara Malič		
14:00	Invited talk	*New trends on the syntesis of piezoelectric lead-free materials* María Elena Villafuerte Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México (UNAM), México
14:45		*Processing of strontium doped sodium potassium niobate thick films obtained by electrophoretic deposition* Hugo Mercier (1,2,3), Barbara Malic (1,2), Hana Ursic (1), Jitka Hreščak (1), Franck Levassort (3), Danjela Kuscer (1) 1: Jozef Stefan institute, Electronic Ceramics Department, 1000 Ljubljana, Slovenia 2: Jozef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia 3: Université François-Rabelais de Tours, GREMAN UMR7347 CNRS, Tours, France
15:00		*Exploring the Potential of Bismuth Sodium Titanium Thick films for Microelectronic Applications* Amit Mahajan, Ewa.M.Jakubczyk, Rebecca.L.Townsend, Haixue Yan, and Mike J Reece and Robert A Dorey Queen Mary University of London, UK
15:15	Keynote	*High piezoelectric response and evolution of ferroelectric properties of single crystals grown in BaTiO3-CaTiO3-BaZrO3 pseudo-ternary solid-solution* G. Buse (1,2), P. Veber (1,2), M. Pham-Thi (3), C. Xin (1,2,4) and M. Maglione (1,2) 1. CNRS, ICMCB, UPR 9048, 87 av. A. Schweitzer, Pessac F-33600, France 2. Université de Bordeaux, ICMCB, UPR 9048, 87 av. A. Schweitzer, Pessac F-33600, France 3. THALES Research and Technology, 1, av. Fresnel, Campus de l'Ecole Polytechnique – F-91767 PALAISEAU Cedex, France 4. Luxembourg Institute of Science and Technology, Department of Materials Research & Technology, 41 rue du Brill, L-4422 Belvaux, Luxembourg
15:45	Keynote	*Texturation of lead-free BaTiO3 based piezoelectric ceramics* A. Prato, F. Levassort, C. Bantignies, M. Pham Thi, P. Marchet Univ. Limoges SPCTS UMR 7315, France
16:15		*Self-poling of BiFeO3 thick films induced by the annealing through the ferroelectric-to-paraelectric phase transition* Evgeniya Khomyakova (1,2), Matej Sadl (1), Hana Ursic (1,2) John Daniels (3) Barbara Malic (1,2) Andreja Bencan (1,2) Dragan Damjanovic (4) and Tadej Rojac (1,2), 1. Electronic Ceramics Department, Jozef Stefan Institute, Jamova cesta 39, Ljubljana, Slovenia 2. Jozef Stefan International Postgraduate School, Jamova cesta 39, Ljubljana, Slovenia 3. School of Materials Science and Engineering, University of New South Wales, NSW 2052, Australia 4. Ceramics Laboratory, Swiss Federal Institute of Technology in Lausanne-EPFL, 1015 Lausanne, Switzerland
16:30		*Highly-Sensitive Pressure Detection by AlN Piezoelectric Thin Film on a Flexible Substrate* H. Bishara, S. Berger Faculty of materials science and engineering, Technion, Haifa, ISRAEL 32000
16:45		Coffee break
Piezo2017 Session M4: Lead-free ceramics and other sustainable materials Chair: Carmen Galassi		
17:15	Keynote	*Solution-derived sodium potassium niobate thin films: influence of donor doping on microstructure...* B.Malič (1,2), K. Vojisavljević (1), T. Pečnik (1), H. Uršič (1), A. Matavž (1,2), V. Bobnar (1,2) 1. Jozef Stefan Institute, Jamova cesta 39, Ljubljana, Slovenia 2. Jozef Stefan International Postgraduate School, Jamova cesta 39, Ljubljana, Slovenia
17:45		*Tuning ferroelectric properties of BiFeO3-BaTiO3 ceramics via isovalent and donor substitution using La^{3+}* Ilkan Calisir and David A. Hall The University of Manchester, Oxford Road, Manchester, M13 9PL, Lancashire, UK
18:00	Keynote	*Demonstration of lead-free piezo components* Guttorm Syvertsen-Wiig, Andreas B. Richter, Sophie Labonnote-Weber. Ceramic Powder Technology AS, Kvenildmyra 6, 7093 Tiller, Norway
18:30		Poster session
20:00 21:00		Dinner

Tuesday February 21th

Piezo2017 Session T1: Applications II

Chair: Nicolás Pérez

09:00	Invited talk	*Using photonic crystals to stop progresive waves in piezoceramic resonators* Francisco Montero de Espinosa Instituto de Tecnologias Físicas y de la Información Leonardo Torres Quevedo (ITEFI) C/ Serrano, 144 28006-Madrid, Spain
09:45		*Sodium Bismuth Titanate thick films fabricated by screen printing method for high temperature ultrasonic sensor* O. Gatsa (1,2), P. Combette (1,2), E. Rosenkrantz (1,2), D. Fourmentel (3), C. Destouches (3), and J.Y. Ferrandis (1,2). 1 University Montpellier, IES, UMR 5214, F-34000, Montpellier, France 2 CNRS, IES, UMR 5214, F-34000, Montpellier, France 3 CEA Cadarache, DEN/DER/SPEx/LDCI, St Paul lez Durance, France
10:00		*Bulk PZT Transformers Fabricated by Micro-Powder Blasting: Modeling and Experimental Results* Oliver M. Barham, Mona Mirzaei, Professor Don L. DeVoe University of Maryland, Dept of Mechanical Engineering, 2181 Glenn L. Martin Hall, Building 088, College Park, 20742, USA
10:15	Keynote	*Piezoelectric MEMS development in SINTEF* H. Ræder, F. Tyholdt, A. Vogl, T. Bakke, P. M. Rørvik and F. Lapique SINTEF, P.O.Box 124 Blindern, Oslo,Norway
10:45		Coffee break

Piezo2017 Session T2: Applications III

Chair: Erling Ringgaard

11:15		*Effects of the LGT crystal quality on the resonance frequency stability of Bulk Acoustic Waves Resonators* M. Allani, JJ Boy, X. Vacheret, N. Batis, T. Laroche, A. Nehari, K. Lebbou, C. Pecheyran, H. Cabane Institut FEMTO-ST, 26, rue de l'Epitaphe, BESANCON, 25000, France
11:30		*Piezoelectric Transistor Memory* M.G. Cain (1), A.Oladipo (2), D. Poelman and P. Smet (3), C. Felser, S. Parkin (4), F. Tyholdt (5), G. Martyna (6), I. Rungger and M. Stewart (7), J. Fompeyrine (8), L. Salminen, N. Hoffmann (9), N. Hildenbrand (10), T. Schmitz and S. Tiedke (11). 1. Electrosciences Ltd, 1 Osborn Road, Farnham, GU9 9QT, Surrey , UK 2. Bio Nano Consulting (London, UK), 3. University of Gent (Gent, Belgium) 4. Max Planck Institute (Dresden and Halle, Germany) 5. SINTEF (Oslo, Norway), 6. IBM TJ-Watson Research Centre (New York, USA), 7. National Physical Laboratory (Teddington, UK) 8. IBM Research (Zurich, Switzerland), 9. DCA (Turku, Finland), 10. Solmates (Enschede, The Netherlands), 11. Aixacct (Aachen, Germany)
11:45		*Elastooptic behavior in epitaxial films of perovskite oxide ferroelectrics* Alexandr Dejneka (1) and Marina Tyunina (2) 1. Institute of Physics CAS, Na Slovance 2, 182 21 Prague 8, Czech Republic 2. Microelectronics and Materials Physics Laboratories, University of Oulu, Finland
12:00		*Insight into processing, structure and properties of BiFeO3-SrTiO3 ferroelectric ceramics* M. Makarovic1,2, J. Walker3, A. Bencan1,2, B. Malic1,2 and T. Rojac1,2 1 Jozef Stefan Institute, Electronic Ceramics Department, Jamova cesta 39, 1000 Ljubljana, Slovenia 2 Jozef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia 3 Materials Research Institute, Pennsylvania State University, USA
12:15		*First-principles study of (Ba,Ca)(Ti,Zr)O3 solid solution* D. Amoroso (1,2), A. Cano (2) and Ph. Ghosez (1) 1) Physique Théorique des Matériaux, CESAM, Université de Liège (B5), B-4000 Liège, Belgium 2) ICMCB, UPR 9048, Université de Bordeaux, F-33600 Pessac, France
12:30 17:30		Lunch & free time for skiing or hiking

Tuesday February 21th		
17:30		Coffee break
		Winter School on Advanced Characterization of Piezoceramics **Session 3.** Chair: María Elena Montero Cabrera
17:30 18:30	Lecture 4	*Mechanical Characterization of Piezoelectric Ceramics* Kyle G. Webber Friedrich-Alexander Universität Erlangen-Nürnberg, Department of Materials Science. Erlangen, Bavaria, Germany.
		Piezo2017 Session T3: Modelling Chair: Franck Levassort
18:30	Keynote	*Virtual Instrument to obtain electrical model in piezoelectric elements used in Energy Harvesting* Francisco Javier Jiménez Martínez, Manuel Vázquez Rodríguez, David Alonso Sáez, José de Frutos Vaquerizo Universidad Politécnica de Madrid, Spain
19:00		*FEM modelling of interdigitated structures with respect to poling process* Ruichao Xu, Michele Guizzetti, Konstantin Astafiev, Erling Ringgaard Meggitt A/S, Kvistgaard, Denmark
19:15 19:30		*The Representation Of Coupling Interactions In The Material Properties Open Database (MPOD)* L. E. Fuentes-Cobas (1), D. Chateigner (2), G. Pepponi (3), S. Grazulis (4) (1) Centro de Investigación en Materiales Avanzados (CIMAV), Miguel de Cervantes 120, Complejo Industrial Chihuahua, Chihuahua 31136, Mexico (2) Normandie Université, IUT Caen, Université de Caen Normandie,CNRS UMR 6508 CRISMAT-ENSICAEN, F-14032 Caen, France (3) MiNALab, CMM-irst, Fondazione Bruno Kessler, 38123 Povo, Trento, Italy (4) Department of Mathematical Computer Science, Vilnius University, Faculty of Mathematics and Informatics, Naugarduko 24, LT-03225 Vilnius, Lithuania
20:00 22:00		CONFERENCE DINNER

Wednesday February 22th

		Piezo2017 Session W1: Advanced Characterization Chair: David Hall
09:00	Invited talk	*The influence of non-stoichiometry and chemical doping on the electrical properties of Na1/2Bi1/2TiO3 ceramics* Derek C Sinclair Functional Materials & Devices Group, Department of Materials Science & Engineering, University of Sheffield, Sheffield, UK.
09:45		*Influence of tetragonal platelets on the dielectric permittivity of 0.964Na1/2Bi1/2TiO3-0.036BaTiO3* Florian Pforr (1), Márton Major (1), Uwe Stuhr (2), Bertrand Roessli(2), Wolfgang Donner(1) 1. Institute of Materials Science, Technische Universität Darmstadt, 64287 Darmstadt, Germany 2. Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
10:00		*POLARIZATION AND DEPOLARIZATION EFFECTS ON STRESS DISTRIBUTION IN LEAD-FREE CERAMICS STUDIED BY RAMAN RESPONSE* Patricia Val Gómez, Adolfo del Campo García, Fernando Rubio Marcos, Jose Francisco Fernández Lozano, Alberto Moure Arroyo Electroceramics Department, Institute of Ceramics and Glass ICV-CSIC, Kelsen 5, 28049 Madrid, Spain.
10:15		coffee break
		Winter School on Advanced Characterization of Piezoceramics **Session 4.** Chair: J. J. Gervacio-Arciniega
10:45	Lecture 5	*Venice, Symmetry and Characterization of Functional Materials* Luis E. Fuentes-Cobas Centro de Investigación en Materiales Avanzados, S.C., Chihuahua, Chih. México.
11:45		**Farewell session**
12:30		BUS to MADRID (Chamartin Cercanías train station)

ABSTRACTS OF THE INVITED TALKS

INSIGHT INTO STRUCTURE, PROPERTIES, AND MOBILITY OF FERROELECTRIC DOMAIN WALLS

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As interfaces that can be displaced *in-situ,* ferroelectric domain walls are a source of continuous fascination. We have been studying during the past 5 years some of their properties and internal structure and learning how to control domain wall patterns and ultimately functionalize them. Among the obtained results are dense patterns of arrays of domains and domain walls having <10 nm width /periodicity (1, 2), controlled displacement of domain walls (3, 4, 5), charged domain walls with metallic conductivity inside the insulating matrix (6, 7) and their controlled creation and density (8, 9) and demonstrated reconfigurability (10). It has been found also that tailored bent neutral domain walls can be electrically conductive, and this metallic conductivity is sustained to ultra-low temperature (testifying the metallic nature of the conductivity) (11, 12). In addition, we have evidenced ferroelectric boundaries in non-ferroelectric, antiferroelectric materials (13), evidenced polarization rotation across wide walls (14), demonstrated ferroelectric switch for propagation of ferromagnetic domain walls at room temperature (15), and showed the possibility of elastic interaction between non-ferroelastic domain walls (16), promising new possibilities for domain-wall control.

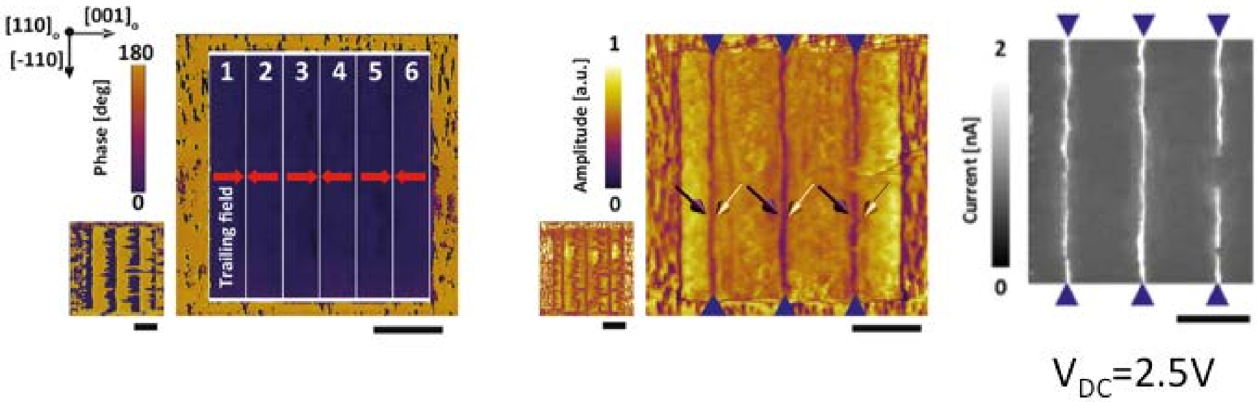

Fig. 1: Conductive charged domain walls, formed and reconfigured in $BiFeO_3$ films (10)

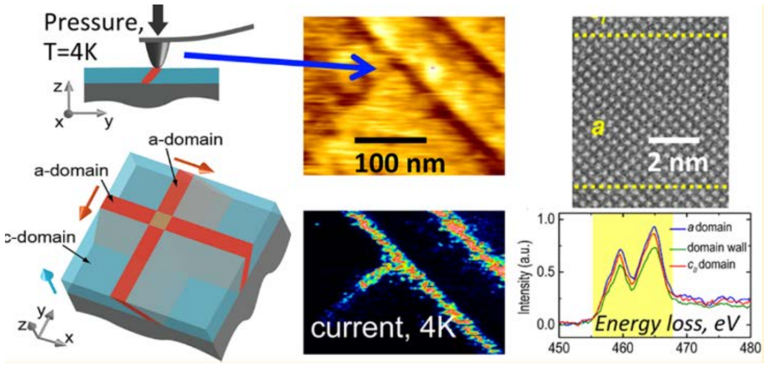

Fig. 2: Ultrafine domain, written by pressure at 4°K (left), shows conductivity (bottom, middle) and its confinement to the domain walls (bottom, right) (11).

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Brief CV Prof. Nava Setter.

Completed MSc in Civil Engineering at the Technion – Israel Institute of Technology and PhD in Solid State Science in Penn. State University, USA. After post-doctoral work at the Universities of Oxford and Geneva, she joined an R&D institute in Haifa (Israel) where she became the head of the Electronic Ceramics Lab in 1988. Since 1989 she has been directing the Ceramics Laboratory of EPFL, the Swiss Federal Institute of Technology in Lausanne (Switzerland) where she is a professor of Materials Science and Engineering. Starting Autumn 2016, she is also affiliated with the University of Tel Aviv, Israel. Her research interests include ferroelectrics and piezoelectrics, in particular the effects of interfaces, finite-size, and domain-wall phenomena, structure-property relations and the pursuit of new applications.

USING PHONONIC CRYSTALS TO STOP PROGRESSIVE WAVES IN PIEZOCERAMIC RESONATORS

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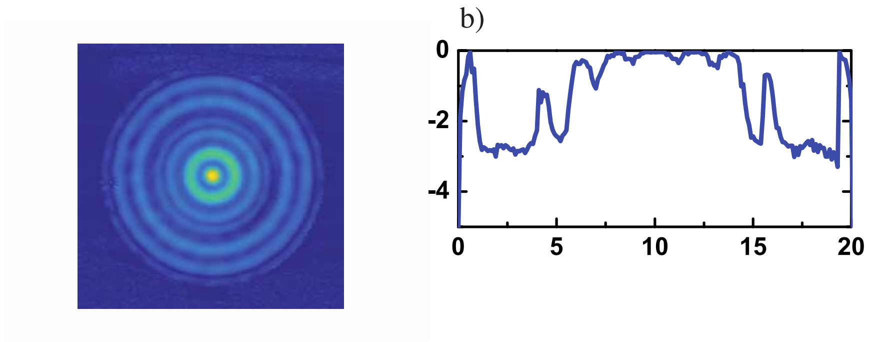
Piezoceramic resonators are the basic component of most ultrasonic transducers and its mechanical vibration profile at the resonance frequency constitutes an important issue in many applications. The dimensions and shape of a piezoceramic resonator define the vibration profile at a certain frequency due to the coupling of the contour waves. In the case of a disk polarized along the thickness direction, the plane wave travelling along the thickness and the plate waves coming from the cylindrical boundary are the two coupled wave fields. The thickness to diameter aspect ratio governs the resonance frequencies and the vibration profile. Thus, if a piston-like vibration surface is required, for either piezoelectric material characterization or ultrasonic transducer design, the lateral dimensions of a resonator should be many times smaller, or larger, than the thickness one. This is the case of transducers used in power ultrasonic, where a tall cylindrical shape, working at the first and lowest longitudinal mode, must be used to avoid the coupling with resonances related with the cylindrical shape [1].

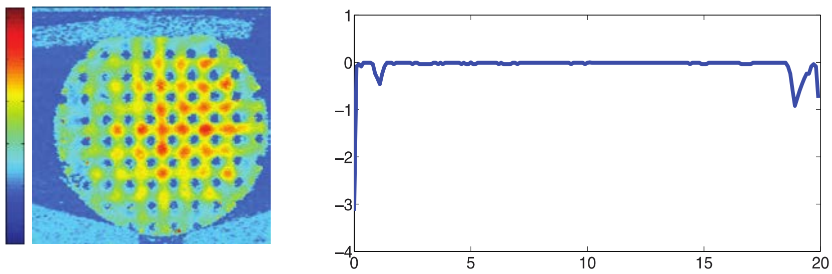
When planar are coupled with the thickness mode, a non-flat vibration emission surface is generated, producing a non-efficient transducer in terms of vibration or ultrasonic field emission. Consequently, filtering or cancelling the planar resonance modes is an important issue in many applications. Albeit, as it has been already mentioned, this can be done by an adequate control of the geometry of the resonators, it would be desirable to find a way to achieve this regardless the geometry and dimensions of the resonator. In this presentation we show that by using the principles of a phononic crystal, the radial modes of a piezoceramic resonator can be stopped independently of its lateral shape, producing, at certain frequency, a resonator with a regular and in-phase vibration surface capable to deliver high elastic and acoustic intensity.

Photonic and phononic materials are composite materials made of periodic distributions of embedded inclusions and the name phononic material or phononic crystal is used to refer materials for control phonons, sound and other mechanical waves. Phononic materials prevent propagation of waves in certain frequency ranges by making use of the fundamental properties of waves, such as scattering and interference, which can lead to the formation of band gaps, that is, a range of frequencies within which waves cannot propagate through the structure. The Floquet-Bloch theorem is the standard tool for the theory of formation of band gaps by a periodic array [2-6]. This approach also provides clear indications that the band gap around the Bragg diffraction frequency is indeed the reason why radial waves cannot propagate.

One of the advantages of working with piezoelectrics is that, contrary to usual materials where an external source of waves is required and the attenuation or phase shift is measured with Gain-Phase analyzer or other techniques, in phononic crystals built from piezoelectric materials, as proposed here, the propagating waves are originated by direct electric excitation of the material itself and no external sources of incoming waves is required. Even more, the direct piezoelectric effect also simplifies the detection of the different elastic effects since the pressure waves are a source of electric charge variations that are translated into electric signal, which can be easily analyzed.

FEM simulation, electrical impedance and interferometric measurements of different geometries are shown to demonstrate the usefulness of this design approach. Next figure shows the out-of-face vibration amplitude (a), and phase (b), of a pz27 20 mm diameter 1 MHz disc before and after making the phononic crystal with the drills [7].

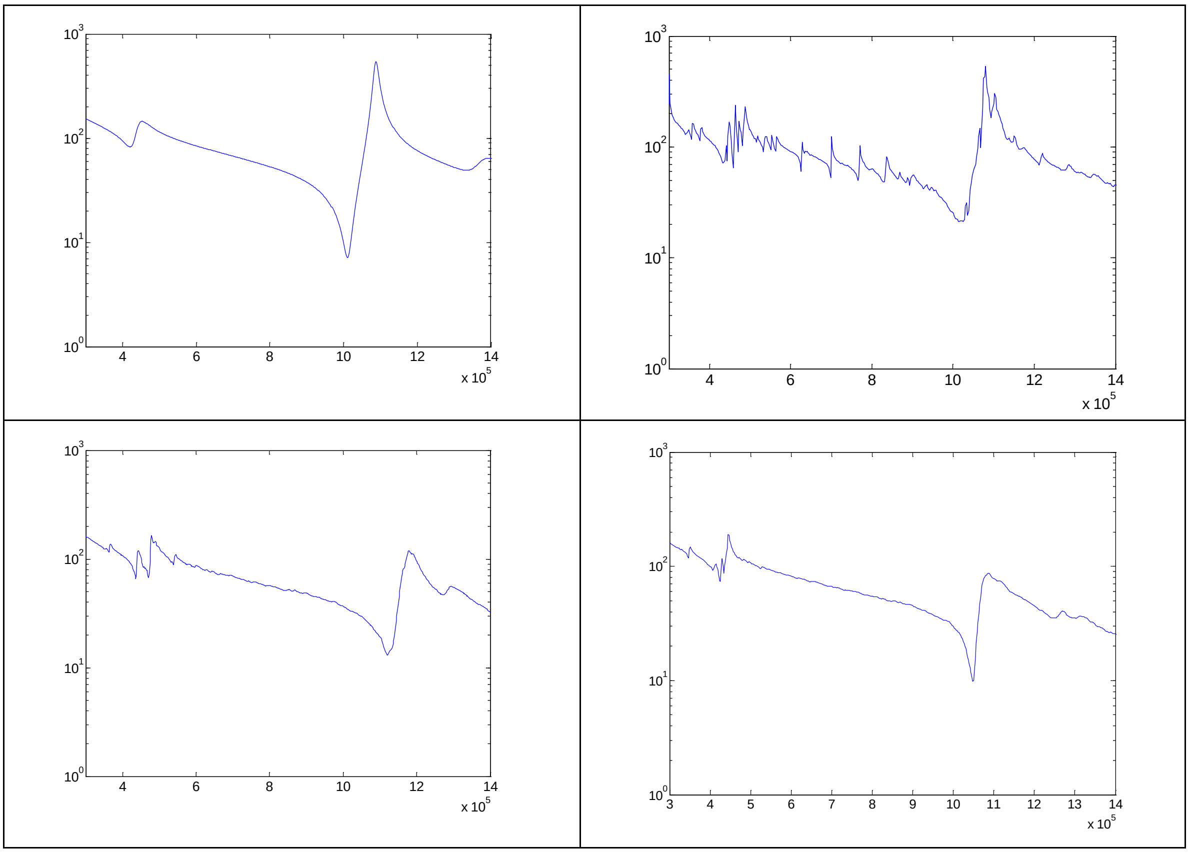




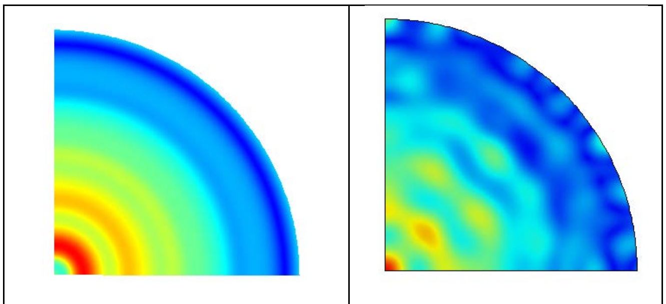
As an application, ultrasonic power transducers with phononic crystal sections have also been studied. Ultrasound piezoelectric power transducers are typically length resonators. The active part is a piezoceramic resonator and either one or two different metallic sections bonded or fixed by a screw (pre-stressed transducers). A different design is, for instance, that of the power transducers used for physiotherapy, which are made with only two sections: the piezoceramic resonator and the metallic capsule [8].

With the standard frequencies used –1 or 3 MHz-, the desired length-to-radial aspect ratio to have no interference between the thickness and the radial modes become not possible because the transducer acoustic aperture for practical and acoustic reasons is bigger than the transducer length. These acoustic constraints imply a length-to-radial aspect ratio very low and far from the desired figure and, in consequence, radial modes are always interfering with the main mode related with the length. Consequently, in this case the transducer emitting surface is far from the ideal piston-like behavior. Here, we use a phononic crystal design consisting of a periodic array of cylindrical voids drilled along the main vibrating direction in one or the two transducer components, that is, the piezoceramic and the capsule. This structure of holes produces a transducer capable of vibrating at its resonance frequency with a piston-like vibration surface, independently on its shape and dimensions.

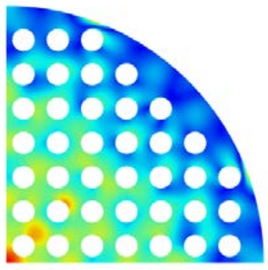
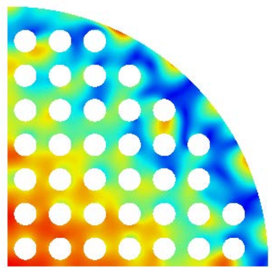
Next figure (a) shows the calculated module of the input electrical impedance of a transducer composed by a 2mm thickness pz26 piezoceramic disc with 30 mm diameter bonded to an aluminum disc with 3mm thickness and the same diameter. A monodimensional model – KLM- was used. The first thickness resonance observed corresponds to half a wavelength and the second, around 1 MHz, corresponds to the one wavelength resonance. The module of the input electrical impedance of the real transducer is also shown (b) showing the signature of the radial modes, not considered in the monodimensional model. When the piezoceramic is drilled following a phononic crystal approach (c) , radial modes signature disappear from 600 kHz to 1.2 MHz. . If, finally, both the piezoceramic and the aluminum sections are drilled with the same pattern, the frequency range where no impedance tracks broadens. In these last two cases the piezozeramic thicknes is 1.5mm to have the transducer resonance closer to 1 MHz. The Bragg conditions were calculated for 1 MHz.

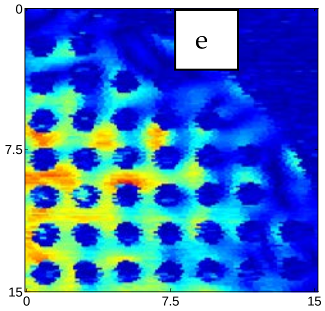


Finally, next figure shows FEM results of the out-of-face vibration amplitude of the transducer emission surface for four different cases: a) standard transducer, b) piezoceramic with holes , c) aluminum section with holes and d) both the piezoceramic and the aluminum sections with holes. In all the four models, the bottom piezoelectric disc face was grounded and the upper face was excited with an electric potential of 1V. A mechanical damping was introduced, as isotropic structural factor, of $1 + 2 \times 10^{-2}\, i$. Given the symmetry of the perforated disc, it is enough to consider only a quarter of the disc, provided that symmetry conditions are applied. A fine finite element mesh of about $h = 1.5 \times 10^{-4}$ m in the drilled domain and $h = 5 \times 10^{-4}\, m$ in the remaining domain, refined at all the boundaries, was considered. COMSOL Multiphysics® 4.4 was used. The experimental vibrometry of the real transducer corresponding to the last case (b) is shown in the last figure (e).



a)	b)

	
c)	**d)**



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Brief CV Prof. Francisco Montero de Espinosa

Researcher Professor since 2001, has 35 years of research experience with 118 research publications in SCI journals and more than 200 publications of meeting proceedings. He is the author of relevant articles as for instance, Nature(1), PRL(4), PRE(3),APL(3), JAP(1), Ultras(16), IEEE TRANS UFFC(9), Rheol(1), JRheol(1), JPH-D(3), MST(2). His scientific reputation in this field has led him to direct a large number of projects and research contracts. It is listed in the Essential Science Indicators, with 73 citations of his scientific papers in 2016, and around 1701 citations throughout his career (h index is 18). He has supervised 6 PhD students. He has also held management positions in the CSIC and the MEC as Head of the Physics and Mathematics section since 2006-2008, Vicepresident of Organization and Institutional Relationships and Chair of the Physics and Mathematics Committee, CNEAI.

NEW TRENDS ON THE SYNTHESIS OF PIEZOELECTRIC LEAD FREE MATERIALS

María Elena Villafuerte-Castrejón[1], Emilio Morán[2], Armando Reyes-Montero[1], Rodrigo Vivar-Ocampo[1], Jesús-Alejandro Peña-Jiménez[1], Salvador-Oliver Rea-López[1] and Lorena Pardo[3]

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[2]Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense,Madrid, Spain
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On the search for lead free materials with piezoelectric properties, the synthesis methods play a determinant role on their final properties. Synthesis and processing of these materials is not quite simple and some challenges are yet to be faced. Stoichiometric control, softer synthesis conditions, adequate grain size, ferroelectric domain size and distribution, sintering conditions and scalability for industrial transfer.

The most widely used piezoelectric is the PZT, but during the last two decades, due to environmental rules, the lead free materials have been intensely studied such as the featuring families with related perovskite structure: $BaTiO_3$ (BT), $Ba_{1-x}Ca_xTi_{1-y}Zr_yO_3$ (BCZT), $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) and $(K_{0.5}Na_{0.5})NbO_3$ (KNN). New trends on these methods involve the search of the most eco-friendly chemical way. In this work several routes to obtain these materials and their solid solutions with different cations are discussed.

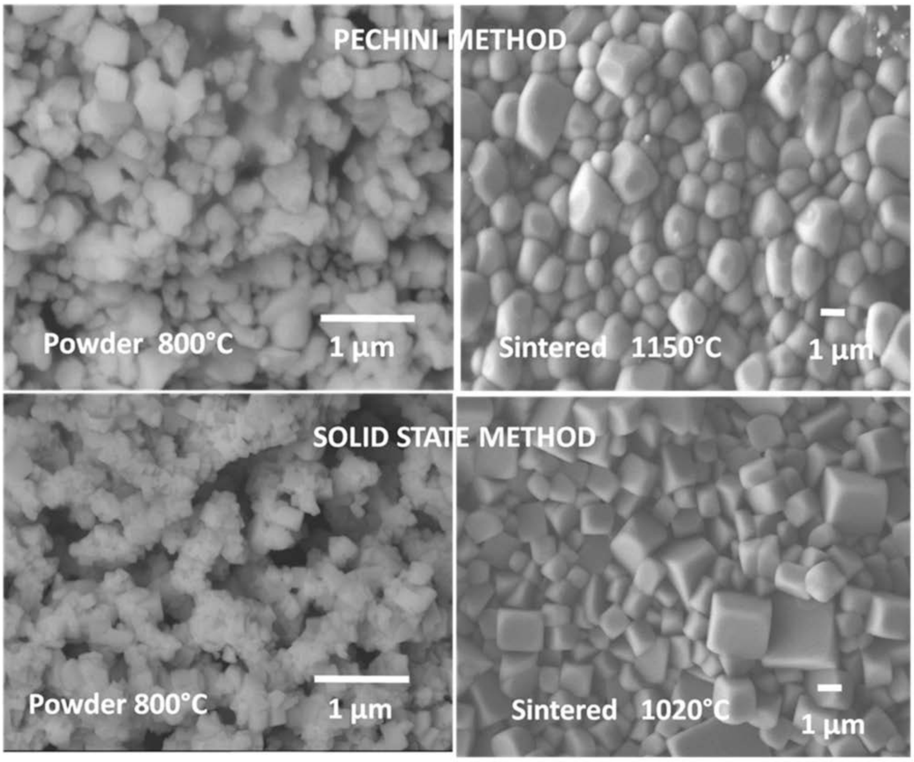

Fig.1. SEM micrographs of synthesized powder (by solid state route and Pechini method) and sintered ceramics of (1-x)Bi0.5Na0.5TiO3-xBa0.9Ca0.1TiO3 (x = 0.06) composition. Note the influence of the powder particle morphology on the ceramics' microstructure.

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Brief CV Prof. María Elena Villafuerte-Castrejón

MEV received the B.S. degree in Chemistry, the M. S degree in Inorganic Chemistry from Facultad de Química, Universidad Nacional Autónoma de México and the PhD degree in Science from Universidad Autónoma Metropolitana in México. She is working in Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, as"Investigador Titular" and as Professor in Facultad de Química. She won the "Reconocimiento Sor Juana Inés de la Cruz, UNAM" on March, 2005. Her research interest is ceramic materials, their synthesis, crystal chemistry characterization, optical and electrical properties as ferroelectricity and piezoelectricity.

THE INFLUENCE OF NON-STOICHIOMETRY, CHEMICAL DOPING AND MATERIALS PROCESSING ON THE ELECTRICAL PROPERTIES OF $NA_{1/2}BI_{1/2}TIO_3$ CERAMICS

Derek C Sinclair

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Precise control of electronic and/or ionic conductivity in electroceramics is crucial to achieve the desired functional properties as well as to improve manufacturing practices. It has been long known that low levels of non-stoichiometry in functional oxides, either associated with intentional element doping or unintentional element loss/gain during processing or impurities in raw materials can induce significant changes in functional properties. In particular, the presence of low levels of oxygen vacancies can play an important role in the functional properties. Two classical examples are $BaTiO_3$-based multilayer ceramic capacitors (MLCCs) with base-metal electrodes and $Pb(Zr,Ti)O_3$ (PZT)-based piezoelectric devices.

Here we will review our recent work on the structure-composition-property relationships of $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) materials based on a combination of A-site non-stoichiometry and chemical doping [1-5]. We will also emphasise the importance of controlling the powder processing methods required to ensure the desired electrical properties are obtained. Undoped NBT ceramics should be viewed as mixed ion-electron conducting materials where the magnitude of the bulk conductivity and oxide-ion transference number, t_{ion}, are heavily dependent on the nominal Na:Bi ratio in the starting composition. We have classified NBT ceramics into three categories; types I, II and III. Nominally Na-rich or Bi-deficient NBT ceramics (i.e. Na:Bi >1) are excellent oxide-ion conductors with high bulk conductivity and t_{ion} exceeding ~ 0.85 at 600 °C (Type I – oxide-ion conductors) whereas nominally Na-deficient or Bi-excess NBT ceramics (i.e. Na:Bi<1) are excellent dielectrics that are electrically insulating with t_{ion} < 0.10 at 600 °C (Type III, insulators). By chemical doping and/or starting compositions that are excessively Bi-rich, intermediate mixed ionic-electronic bulk conductivity is obtained with t_{ion} ~ 0.40 – 0.60 at 600 °C (Type II, mixed ionic-electronic conductors). A selection of compositions to illustrate this range of electrical behaviour are shown in the form of bulk electrical conductivity and t_{ion} in Figure 1 and as relative permittivity and tan δ in Figure 2.

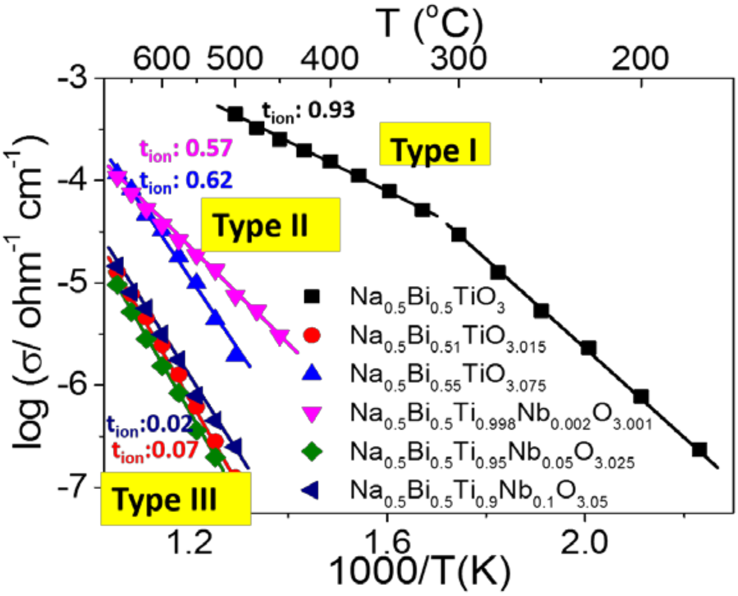

Figure 1. Arrhenius plot of bulk conductivity data from Impedance Spectroscopy measurements of various undoped and Nb-doped NBT ceramics. Also included are the corresponding t_{ion} values (at 600 °C) from emf measurements.

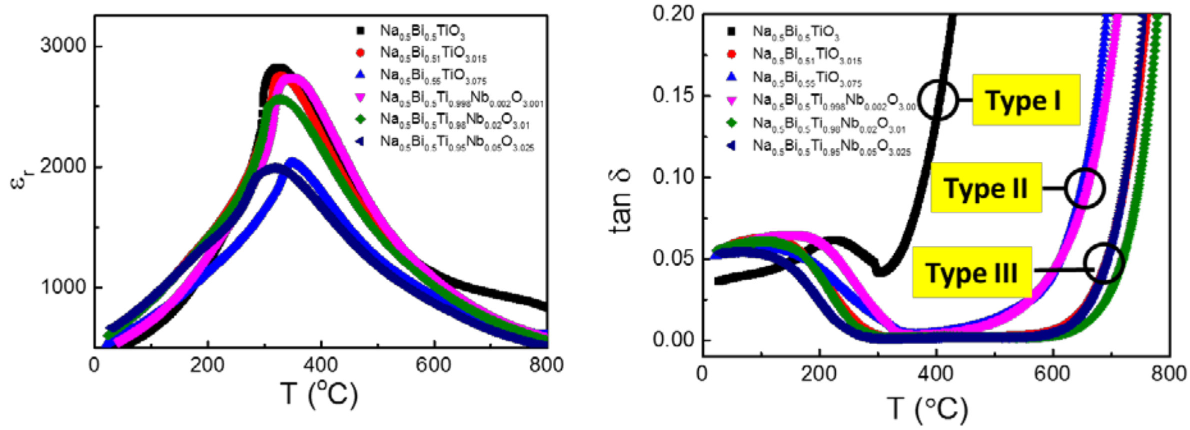

Figure 2. Temperature dependence of the relative permittivity, ε_r, and tan δ (both at 1 MHz) for the same undoped and Nb-doped NBT ceramics shown in Figure 1.

We attribute the source of the oxygen vacancies that are responsible for the high level of oxide-ion conductivity in nominally stoichiometric NBT (i.e. $Na_{1/2}Bi_{1/2}TiO_3$) ceramics to be associated with low levels of Bi_2O_3-loss during ceramic processing as given by the Kroger-Vink equation.

$$2Bi_{Bi}^{\times} + 3O_O^{\times} \rightarrow 2V_{Bi}''' + 3V_O^{\cdot\cdot} + Bi_2O_3$$

Acceptor dopants such as Sr for Bi or Mg for Ti significantly increase the oxide ion conductivity to promote solid electrolyte (Type I) behaviour whereas donor dopants such as Nb for Ti can suppress the oxygen vacancy concentration and exhibit excellent dielectric (Type-III) behaviour with tan δ < 0.02 at 600 ^{o}C. Such behaviour is desirable for NBT-based dielectric applications, eg as Pb-free piezoelectrics and/or as a solid solution member in temperature stable, high permittivity multilayer ceramic capacitors (MLCCs) operating at > 175 ^{o}C [6].

The defect chemistry of Type-III NBT ceramics is in strong contrast to that of $BaTiO_3$ and $Pb(Zr,Ti)O_3$ where acceptor doping on the Ti site, eg Fe^{3+}, Ga^{3+} can be used to create pinning defect centres that can transform them into so-called, 'hard' piezoelectric ceramics. In the case of Type-III NBT ceramics, acceptor doping on the Ti-site creates oxygen vacancies that are highly mobile and covert into Type-I NBT ceramics with as little as 0.5 at% acceptor doping. The results show NBT compositions can be tuned smoothly to exhibit t_{ion} from near unity to zero and confirm that the diffusion of oxygen vacancies in NBT is far superior to that in $BaTiO_3$ and $Pb(Zr,Ti)O_3$. The doping strategies that are therefore used to manipulate piezoelectric behaviour in other perovskite titanates are not applicable to NBT ceramics.

All NBT ceramics sintered in our laboratories are covered with sacrificial powder of the same composition in attempts to limit volatilisation of Na_2O and Bi_2O_3 to maintain the starting composition in the final ceramics. Sintering ceramics without sacrificial powders has no influence on the phase assemblage or bulk electrical properties of Type I ceramics (eg $Na_{0.48}Bi_{0.50}TiO_{2.97}$); however, Type II ceramics (eg $Na_{0.50}Bi_{0.52}TiO_{3.015}$) show evidence of Bi-rich secondary phases on the pellets surfaces that can be removed on polishing the ceramics. The electrical properties of the polished ceramics are consistent with Type-III as opposed to Type-II behaviour. These results suggest that sacrificial powder is important to limit Na_2O volatilization, especially in Bi-rich samples, Figure 3.

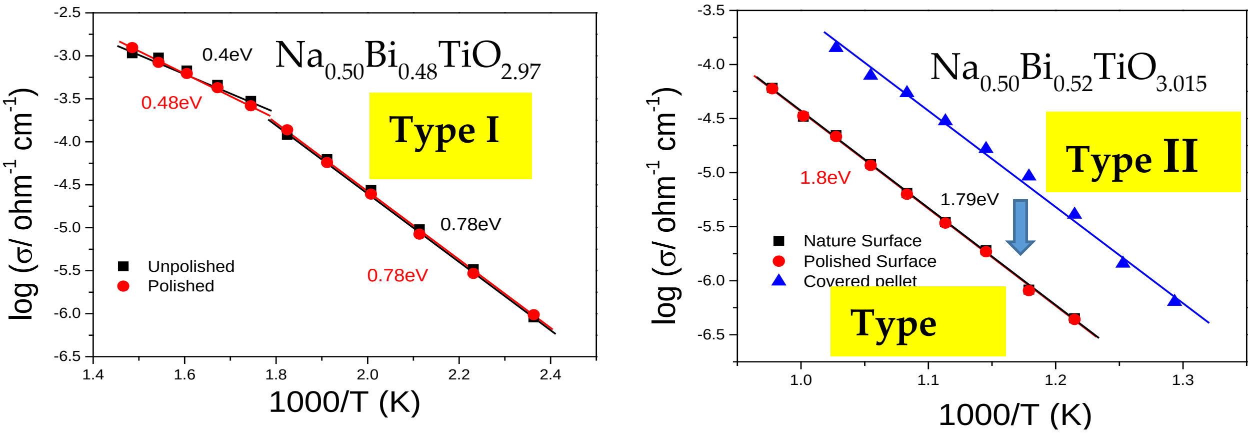

Figure 3. The influence of sacrificial powder used during sintering on the bulk conductivity of NBT ceramics.

The authors thank the EPSRC (EP/L017563/1) for funding.

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Brief CV Prof. Derek C Sinclair

Derek is currently Professor of Materials Chemistry at the University of Sheffield. He was appointed to the academic staff at the University of Sheffield in 1999 as a Lecturer in Functional Materials following from Lecturer appointments in the Department of Chemistry, University of Aberdeen (1994-99) and the Department of Materials Science, University of Leeds (1993-94). He obtained his BSc (1st Class Honours) and PhD (supervised by Professor Tony West) in Chemistry at the University of Aberdeen and held post-doctoral research appointments at the University of Aberdeen (with Profs Tony West and John Irvine) and the Interdisciplinary Research Centre for Superconductivity at the University of Cambridge (with Prof Paul Attfield), before joining the academic staff at Leeds in 1993. He's a recognised for his ability to probe the structure (crystal and defect)-composition-microstructure-property relationships of a wide range of functional oxides, spanning from polar dielectrics via mixed conductors to solid electrolytes.

WINTER SCHOOL LECTURES

WINTER SCHOOL

Simultaneously to the Electroceramics for End-users IX, **PIEZO2017**, conference and open to its attendees, we are organizing a JECS Trust funded Winter School on "Advanced Characterization of Piezoceramics". The proposed Winter School aims to discuss the role on piezoelectric ceramics processing and applications of the advanced characterization, microstructural, mechanical and electrical introducing both classical knowledge in these areas and novel techniques. The proposed program consists of three groups of activities: tutorials, student poster competition and a social event, which will be a chance for students and early-stage researchers to get to know each other and will provide the basis for networking and future collaborations in a relaxed atmosphere. Tutorials will be conducted by international experts that will provide unique insights for researchers and those interested in broadening their skills. This will take place on three Sessions on Sunday, Monday and Wednesday.

A number of grants were available for students to attend this Winter School. Grants will include a full student registration to attend the PIEZO2017 conference. The selection of the students was made according to the quality and relevance of the research of the abstract submitted to the conference, for which the student must be the presenting author. A letter from the scientific advisor stating the situation of the student will be requested to validate the application.

To obtain the certificate of attendance to the Winter School is necessary to attend all the Lectures, being the first of them given Sunday 19th February 2017 at 15:00.

There will be signature forms circulated to the Lecture's attendees to control the attendance.

Information of topics and CV of the Lecturers is giving in the following.

VENICE, SYMMETRY AND CHARACTERIZATION OF FUNCTIONAL MATERIALS

Luis E. Fuentes-Cobas

Centro de Investigación en Materiales Avanzados, S.C., Chihuahua, Chih. México.

The subject of the present tutorial is the structure-symmetry-coupling properties relationship in functional materials. Materials with coupling properties (e.g. piezoelectricity, magnetoelectricity) transduce one kind of physico-chemical stimulus (say, mechanical stress or magnetic field) into a response of a different nature (electric polarization). The use of synchrotron light diffraction in the investigation of matter symmetry at atomic-level is explained. As a motivational resource, the application of symmetry concepts to analyze a variety of Venice objects, from the Basilica di San Marco to paintings at the Guggenheim Museum, is explained. Several crystal physics concepts, e.g. symmetry versus anti-symmetry, direct versus reciprocal spaces, single- versus poly-crystals, polar- versus axial-vectors, are introduced by means of Venetian examples ranging from carnival masks to Murano glasses. Symmetry considerations allow understanding the infrared and Raman spectra of functional materials. In parallel with the mentioned topics, state of the art diffraction-scattering techniques for the investigation of materials structure are discussed. Recent investigations related with lead-free ferro-piezoelectrics illustrate the current scenario. Selected implications of structural symmetry on considered materials' properties are analyzed. The roles of space- and time-inversion symmetries in ferroic and multi-ferroic phenomena are commented.

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He obtained his B. Sc. (1970), M- Sc. (1977) and Ph.D. (1982) in Solid State Physics from Havana University, Cuba. He received a post-doc on neutron texture analysis at the Joint Institute for Nuclear Research, Dubna, Russia (1983 - 85). In Cuba he worked as Professor and Senior Researcher at Havana University and at the Cuban Academy of Sciences. In Mexico he works, since 1997, at the Physics Department of the Centro de Investigación en Materiales Avanzados, Chihuahua. His teaching and research activities have been centered on electromagnetic theory, crystallographic analysis by synchrotron light diffraction and the structure-properties relationship. He has made original contributions on the crystal physics of piezo- and magnetoelectric properties of polycrystals. Dr. Fuentes-Cobas coordinates the Materials World Modules-Mexico scientific education program (http://mwm.cimav.edu.mx) and the web page of the Material Properties Open Database project (http://mpod.cimav.edu.mx). He has been awarded in Russia, Cuba and Mexico for his research results.

MECHANICAL CHARACTERIZATION OF PIEZOELECTRIC CERAMICS

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Piezoelectric ceramics have enabled numerous technologies in many fields. Although there are a number of figures or merit, which are often application specific, reliability is a common requirement amongst all applications. These ceramic materials, however, are brittle with a fracture toughness approximately equivalent to window glass, making their implementation contingent of the application of compressive stresses or use outside of the dynamic range. In addition, many applications operate at elevated temperatures. For that reason, understanding the temperature dependent mechanical properties of perovskite ferroelectrics is critical.

The focus of this tutorial is on the macroscopic mechanical constitutive behavior of perovskite ferroelectrics, in particular ferroelasticity and field-induced phase transformations. The influence of crystal structure (phase boundaries), temperature, grain size, and substitution related defects will also be discussed. Following a brief introduction to general fracture mechanics concepts and terms, the role nonlinear mechanical behavior on the fracture of ferroelectrics will be introduced. The final section will introduce the mechanical properties of lead-free ferroelectrics. The phenomena responsible for the electromechanical response will be discussed as well as the likely impact on the fracture behavior. Suggestions for future studies and open questions will be presented.

Brief CV Prof. Kyle G. Webber

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X-RAY ABSORPTION STUDY OF FUNCTIONAL MATERIALS

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This tutorial is devoted to explaining the merits of the application of synchrotron radiation for studying the X-ray absorption fine structure (XAFS) in piezo- and ferroelectric materials. The XAFS phenomena are consequence of the X-ray photoelectric effect and the further behavior of the scattered electron. XAFS allows determining several features in the local order around atoms of crystalline materials. Chemical and physical properties, such as the interatomic distances, oxidation states, and the coordination number of atoms at the first few shells, are some of these features. The origin of the X-ray absorption edges of each element and its fine structure will be introduced as well. The difference between X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) effects and their applicability for the mentioned local order structure determinations in oxides will be explained. Finally, some of the works representing EXAFS and XANES applied to oxides, from the classical ones on PbTiO3 and BaTiO3 to modern functional materials, as chromium-iron maghemite and lead-free ferro-piezoelectrics, will be presented.

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Brief CV Prof. María Elena Montero Cabrera

She obtained her Bachelor in Physics (1972) at Havana University, Cuba, and her Ph. D. in Physical-Mathematical Sciences (1987) at the Joint Institute for Nuclear Research, Dubna, Russia.

Worked during 25 years in Cuba, at Havana University, in the Faculties of Physics and of Nuclear Science and Technologies. She was President of the Cuban Physical Society from 1994 to 1998. She has been member of the Pugwash Conferences on Science and World Affairs, recipient of the Nobel Peace Prize in 1995.

Currently works as Senior Researcher and professor at the Master and Doctor programs on Environmental Science and Technology at the Centro de Investigación en Materiales Avanzados (CIMAV) in Chihuahua, Mexico. Her main areas of research are X-ray diffraction and X-ray absorption fine structure on functional and environmental materials, as well as Environmental radioactivity, gamma-ray spectrometry, alpha-ray spectrometry by liquid scintillation and semiconductor detectors.

In her scientific research, for many years she has been employing beams in large facilities, such as neutrons in a nuclear reactor and X-ray in synchrotrons.

NUMERICAL CHARACTERIZATION OF PIEZOELECTRIC DISCS USING RESONANCE CURVES

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Piezoelectric materials characterization is a challenging problem involving physical concepts, electrical and mechanical measurements and numerical optimization techniques. Piezoelectric ceramics such as PZT belong to the 6 mm symmetry class, which requires five elastic, three piezoelectric and two dielectric constants to fully represent the material properties. If losses are considered the material properties are represented by complex numbers. The continuous improvement of the computer processing ability has allowed the use of a specific numerical method, the Finite Element Method (FEM), to iteratively solve the problem of finding the piezoelectric constants. Using their axis-symmetry, piezoelectric discs can be simulated in practical times.

The objective of this presentation is to present the basic concepts in the numerical characterization of 6 mm piezoelectric materials from experimental electrical impedance curves.

The basic strategy consists in measuring the electrical impedance curve of a piezoelectric disk, and then combining the Finite Element Method with an iterative algorithm to find a set of material properties that minimizes the difference between the numerical impedance curve and the experimental one. Different methods to validate the results are also discussed. Examples of characterization of some common piezoelectric ceramics are presented to show the practical application of the described methods.

Brief CV Dr. Nicolás Leonardo Pérez Álvarez

Engineering Assistant in Electronics – 1985, Universidad del Trabajo del Uruguay (UTU). Electrical Engineering – 1999, UdelaR (Universidad de la República - Uruguay). Magister in Physics – 2002, UdelaR. Doctor in Physics – UdelaR. Teaching experience for more than 25 years in university level courses. Institutions, UTU, UdelaR, Universidad ORT – Uruguay. Work as Project engineering for 8 years in automation and hardware design. More than 30 publications in international journals with cross review (among others, Smart Materials and Structures, Materials, Ultrasonics, IEEE TUFFC,…), more than 40 presentations in international congress and meetings. Current research interest in signal processing applied to acoustics, time reversal, wave focalization, materials characterization using acoustic techniques, piezoelectric ceramics, anisotropic materials, transducers, ultrasound applied to food industry and non-destructive evaluation.

IMPLEMENTATION OF ADVANCED MICROSCOPIES IN AN ATOMIC FORCE MICROSCOPE

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Over the last years, piezoresponse force microscopy (PFM) has become as the main technique to straightforwardly map and manipulate domains in ferroelectric materials at nanoscale level (D. Denning, Et al, Int. Mater. Rev. 6608, 1743280415Y.000, 2015) (S. Kalinin, Et al, Appl. Phys. Lett., 85, no. 5, 795, 2004). In this work, details of the instrumentation to obtain the dynamical response of the scanning probe microscopy (SPM) cantilever through controlling a lock-in amplifier by a computer with a software developed in LabView, is showed. By using the internal ac source of the lock-in is possible to obtain directly different material responses without the need of an expensive commercial module. The procedure is helpful and easy to implement for users that are interested into extend the capabilities of their atomic force microscope to carry out other techniques like piezoresponse force microscopy, atomic force acoustic microscopy and piezomagnetic force microscopy, to name a few. In order to illustrate the utility of the methodology proposed, resonance PFM, resonance-tracking PFM, resonance-tracking switching PFM, piezoresponse force microscopy non-linearities and discrimination of ferroelectric from non-ferroelectric responses measurements were conducted. Additionally, piezomagnetic force microscopy and atomic force acoustic microscopy characterizations with the same instrumentation were carried out.

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Brief CV Dr. J. J. Gervacio-Arciniega

At present Professor and Senior Researcher in the Department of Materials Physics at the Physics and Mathematics Faculty, Autonomous University of Puebla. Prior to this, he was Senior Researcher in the Department of Advanced Materials at Center of Nanoscience and Nanotechnology UNAM (México). He received a B.S. in Physics and mathematics science from Physics and Mathematics Faculty, Universidad Michoacana de San Nicolas de Hidalgo in 2006 and a M.S. and Ph.D. in Materials Science from Center for Research and Advanced Studies (CINVESTAV-México) in 2008 and 2012. In 2012, he joined the Center of Nanoscience and Nanotechnology CNyN-UNAM, as a postdoctoral researcher, where he worked on the implementation of piezoresponse force microscopy, magnetic force microscopy, atomic force acoustic microscopy, piezomagnetic force microscopy techniques and studies of local electromechanical properties of ferroelectrics. His primary research interests include developments for atomic force microscopy, local properties of materials, ferroelectric and multiferroic thin films.

ABSTRACTS OF PIEZO2017

PARAMETRIC STUDY OF A THIN PIEZOELECTRIC CANTILEVER FOR ENERGY HARVESTING APPLICATIONS

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Background, Motivation, Hypothesis and Objectives

Nowadays, bimorph piezoelectric cantilevers are commonly used in ambient vibrational energy harvesting. They are constituted of two thin layers of piezoelectric material separated by an inner shim material. To help the design process of these energy harvesting devices, analytical and numerical models have been developed. We here present a parametric study to determine the effective mechanical, piezoelectric and dielectric coefficients of a thinned piezoelectric layer. To this aim, a one-dimensional analytical model and a 3D finite element model are investigated.

Statement of Contribution/Methods

In this work, we mainly consider a 32mm x 4mm x 150µm layer of PZT material in free mechanical boundary conditions. The density ϱ was measured with a Kern© precision balance (Kern©, Balingen, Germany); the blocking capacitance C_0, the resonance fr and antiresonance fa frequencies were measured with a HIOKI IM3570 impedance analyzer (HIOKI E.E. CORPORATION, 81 Koizumi Ueda, Nagano 3861192 Japan). Thanks to those parameters, the electromechanical coupling coefficient k_{31} and several elastic, dielectric and piezoelectric coefficients (s_{11}^E, ε_{33}^T, d_{31}) of the piezoelectric layer were determined by using a 1D analytical admittance model in the length extensional mode. Then, in order to determine the sensitivity of the admittance module to all the coefficients of the compliance, dielectric and piezoelectric matrices, a 3D finite element model has been investigated.

Results, discussion and conclusion

Thanks to the good agreement between the 1D analytical approach and the 3D FEM simulation, the parametric study of all coefficients of the compliance, dielectric and piezoelectric matrices has revealed that besides the parameters determined using the 1D analytical model (i.e. s_{11}^E, ε_{33}^T, d_{31}), the electric impedance is essentially dependent on the s_{12}^E coefficient. The other coefficients have a very weak influence on the admittance in the length extensional mode. This work was financially supported by National Research Agency (ANR LabCOM "TMEMS" N° ANR14LAB5000401) and the French National Research and Technology Association (ANRT).

NON-RAYLEIGH DYNAMIC NON-LINNEARITY IN BARIUM TITANATE

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Perovskite oxide ferroelectrics possess excellent piezoelectric properties enabling the mainstream electromechanical applications of these materials. Most of devices operate under alternating electric or stress field, or in the dynamic mode. When the field is small for switching polarization and changing domain configuration, it causes a Rayleigh-type motion of domain walls, which gives the dielectric permittivity and piezoelectric coefficients being proportional to the field amplitude. Extensive research efforts are focused on increasing density and mobility of domain walls in order to enhance the Rayleigh-type performance and achieve the desired strong dynamic nonlinearity. Apart from the Rayleigh behavior, a quadratic field-dependence is valid for the dynamic response of random interacting dipoles: the dipoles reorient under applied field, and these flips of local polarization produce the nonlinear dynamic behavior. This non-Rayleigh increase of permittivity is rare: it occurs in such relaxors as $PbMg_{1/3}Nb_{2/3}O_3$, where the long-range spontaneous ferroelectric polarization and domains do not exist, but, instead, polar nano-clusters host local polarization. Here we experimentally demonstrate extraordinary non-Rayleigh dynamic nonlinearity in normal ferroelectric barium titanate. A hysteresis-free quadratic field dependence of the dynamic dielectric response is observed in the absence of mobile domain walls in epitaxial films. The nonlinear response is related to nano-sized entities revealed by analysis of the dielectric relaxation. The entities are ascribed to fluctuations of polarization caused by local lattice inhomogeneities in the films. The lattice inhomogeneity causing polar entities can be introduced by controlled nano-structuring in bulk and thin-film samples. This strategy of enhancing dynamic response through creating inhomogeneity can enable routes to high-performance ferroelectrics. Besides its importance for the field of ferroelectric thin films, the found extraordinary elastically induced dynamics can significantly contribute to understanding of bulk ferroelectric relaxors and piezoelectrics, especially lead-free ones.

ALIGNED POROSITY PYROELECTRICS FOR ENERGY HARVESTING

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Energy harvesting continues to receive the increasing amounts of industrial and academic interests since it provides a route for the realisation of autonomous and self-powered low-power electronic devices. Pyroelectric materials are of particular interest since they have the ability to operate with a high thermodynamic efficiency for converting temperature fluctuations into useable electrical power. Pyroelectric energy conversion offers a novel way to convert waste heat into electricity by alternatively heating and cooling a pyroelectric material and has attracted much interest in areas such as low-power electronics and battery-less wireless sensors. For pyroelectric harvesting applications, the main requirements include high pyroelectric coefficient, high figures of merit, low dielectric constant and low dielectric loss. Efforts on improving performance often focus on dense materials which undergo chemical modifications or utilise the single crystal materials. Due to the complexity of developing new formulations with high cost, and the low Curie temperature and poor mechanical properties of single crystals, the applications of pyroelectric harvesting materials are currently limited. Our previous work has indicated that a porous structure whose permittivity and thermal capacitance is decreased has beneficial consequences for energy harvesting applications if the pyroelectric coefficient is not reduced significantly. The porosity also has the potential to decrease the heat capacity which leads to an improvement of the thermal response; however, porosity can also decrease the electrical resistivity and pyroelectric coefficient. This complex relationship between pyroelectric, dielectric and thermal properties means that there is potential to tune the porosity to achieve the optimum response for a given application. Freeze casting, which has the ability to produce an aligned pore structure with low production cost, oriented pore channels and improved mechanical strength, dielectric and thermal properties, will be exploited in this research.

3D PRINTING OF FERROELECTRIC DEVICES USING STANDARD FUSED DEPOSITION MODELLING METHOD

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3D printing is an additive manufacturing technology to build up complex structures which are difficult to produce by several other processing techniques. So called 3-3 ferroelectric composite structures can be build up by this technique easily. A regular pattern of continuous ferroelectric skeleton structures in all three dimensions can be fabricated by 3D printing and thermal treatment e.g. debinding and sintering. In this study fused deposition modelling or fused filament fabrication method using thermoplastic monofilament PZT-polymer composite material was used to build PZT skeleton structure. Based on existing thermoplastic injection moulding and extrusion knowhow three different kinds of binders were used for the additive manufacturing process. After precoating and mixing processing steps, the 52 vol% PZT feedstock was extruded into endless filaments with a diameter of 3mm. Conventional 3D FDM machine was used for the printing process. Rheological characterisation to correlate shear thinning behaviour with printability was done. A certain shear thinning behaviour is necessary to be able to print the feedstocks with common used Bowden Extruder technology. After printing and sintering, the width of junctions and bridges as well as the thickness of the printed grid like structured disks were investigated for different printing conditions and polymeric binders. As expected, the different rheological behaviours of the feedstocks resulted in different printing results. The shrinkage after sintering of the disc diameter for all samples was not influenced by printing parameters or binder systems. After sintering a d33-value up to 300 μC/ could be achieved. The samples which were printed at higher temperature showed a correlation between the piezoelectric constant and the shrinkage of the thickness. With an increased shrinkage, the piezoelectric constant increased. Finally offset closed porous structures were printed and a much higher polarisation of the closed porous structures, in comparison to dense ceramics, could be achieved.

PLZT X/90/10 CERAMICS FOR ENERGY STORAGE

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The importance of antiferroeletric materials is related to antiferroeletric to ferroelectric field induced transition which provide the physical foundation for a large broad range of applications especially for energy storage capacitors. Lead lanthanum zirconate titanate $(Pb_{1-x}La_x)(Zr_{0.90}Ti_{0.10})_{1-x/4}O_3$ (denoted as PLZT x/90/10) ceramics have recently received increasing interest due to its compositional dependent phase boundary region between rhombohedral and orthorhombic phase. These ceramics show tailored antiferroelectricity whereas the stability of antiferroeletric phase, reversibility and irreversibility of AFE to FE induced transition and electric field necessary to induce the transition from AFE to FE may be tuned by La modification. PLZT AFEs have a high Curie temperature (~170 ^oC) which means that the antiferroeletric phase may exist in a wide range of temperature. Therefore these ceramics could be potential candidates for high energy-storage capacitors. In this study, we have focused on how the individual phases (ferroelectric or antiferroeletric) as well as their phases coexistence influence the energy storage properties. Particularly, we have evidenced that there is a linear relationship between the amount of ferroelectric phase presented in the ceramics and the EAF critical field necessary to induce the transition between antiferroeletric and ferroelectric phase. Furthermore we demonstrated that, while the PLZT system evolves from a FE state to an AFE state as a function of La content and from an AFE state to a FE state depending on the applied electric field, the recoverable energy (Wre) and loss energy (Wloss) range between two limits whose lower and higher values are obtained for PLZT composition in AFE state and FE state, respectively. The energy storage value (Wre) range from 0.819 J/cm3 (for PLZT 2/90/10 and electric field of ~30 kV/cm) to the highest value of 1.85 J/cm^3 (for PLZT 3.5/90/10 and electric field ~65 kV/cm).

PIEZOELECTRIC BASED ICE PROTECTION SYSTEM - PRELIMINARY MODELLING AND EXPERIMENTAL RESULTS

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There are number of negative effects of ice accretion on the aircraft structures that may seriously compromise safety of aircraft operation. E.g. ice accretion may change smooth flow of air over the wing, leading to severe decrease in lift and increase in drag forces, it also may cause damage to external equipment such as antennas. Therefore, Ice Protection Systems (IPS) are of critical importance for aircraft, being one of the major safety ensuring systems on board. Increasing demands upon the aviation Industry to reduce emissions and associated net passenger mile costs are forcing designers of new aircraft to turn their attention towards more-electric aircraft (MEA) solutions. It is, therefore, anticipated that new platforms will increasingly utilise alternative electrically based technologies for IPS. Whilst large airframes have the capacity to generate significant levels of electrical power, compatible with Electro-thermal power requirements, this is not the case on smaller airframes e.g. Business Jets. Existing technologies that can provide viable Ice Protection at low electrical power employ Electro-Expulsive (EEDI) and Impulsive (EIDI) concepts for the electro-mechanical de-Icing of surfaces. These concepts however, exhibit a number of drawbacks, such as reliability, slow reaction, and change in airfoil shape. One of the possible solutions that is widely investigated in this area is based on piezoelectric effect. The present work is focused on a development of an alternative ISP on the basis of piezoelectric effect, making such systems compatible with small airframes. An extensive FEM modelling of piezo-based IPS for simplified aircraft structures (flat plates) and airfoil type structures has been performed, estimating shear stresses that can be achieved at the metal - ice layer interface. Comparing to the data available in the literature, such modelling has been performed not only for the steel based structures, but also for aluminum based structures, also considering different types of piezoelectric actuators (hard- and soft-PZT based). An icing system (simplified wind tunnel system) has been developed internally on the basis of available climatic chamber and a successfully tested for different types of aircraft structures. Finally, first prototype of a piezoelectric based IPS has been demonstrated, showing successful de-icing of two different types of ice (rime ice and glaze ice) on steel and aluminum based structures.

PROCESSING OF STRONTIUM DOPED SODIUM POTASSIUM NIOBATE THICK FILMS OBTAINED BY ELECTROPHORETIC DEPOSITION

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Piezoelectric energy harvester is a device that converts the environmental available mechanical energy into electrical energy. The harvested energy can be used to power wireless, autonomous microsystems or macroscale devices. With the aim to prepare a cantilever-type piezoelectric energy harvester, the processing of sodium potassium niobate-based thick films by electrophoretic deposition (EPD) and consequent sintering was studied. The powder with the nominal composition $(K_{0.5}Na_{0.5})_{0.99}Sr_{0.05}NbO_3$ (KNNSr), prepared by the solid state synthesis at 800°C, was electrosterically stabilized in absolute ethanol with poly(acrylic acid-comaleic-acid) (PAM). The suspension containing 1 vol.% of KNNSr was stable and had a conductivity of 22 µS/cm and a zeta potential of -50 ± 5 mV. The powder was deposited on square-shaped platinized alumina substrates with dimensions 8×8 mm2 at a constant current density of 15,6 A/m^2, an inter-electrode distance of 3 mm, and a deposition time of 90 s. The scanning electron microscopy (SEM) analysis of as-deposited layers revealed that the surface of the layer was uniform and any processing defects are observed. The thickness of the as-deposited layers, measured by optical profilometer, was around 45 µm. The shrinkage temperature curve of KNNSr powder compact showed that the sample started to shrink at 1040 °C and had shrinkage of 12.3 % at 1140 °C. The melting of the KNNSr powder compact was observed at 1150 °C. Based on these results, KNNSr layers were sintered at 1075 °C, 1100 °C and 1120 °C during two hours in air. In this presentation, effects of the sintering temperature on the density, structure, microstructure and dielectric properties of KNNSr thick films will be presented and discussed.

Exploring the Potential of Bismuth Sodium Titanium Thick films for Microelectronic Applications

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Lead free piezoelectric materials have been a significant focus of research in the last decade in the field of electroceramics. One of the most promising lead free materials with a high Curie temperature (> 250 °C) and fairly good piezoelectric coefficients (d_{33} ~130 pC/N) is $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) - $BaTiO_3$ (BT) solid solution. BNTBT has been intensively investigated from a structural and performance point of view. For commercial applications, thin and thick film coatings of piezoelectric material are of prime interest. Moreover, the thick films show properties close to the bulk counterpart, which makes them suitable for miniaturization of devices. Thick films of BNTBT are of industrial importance for various electronic applications, such as, miniaturised capacitors, sensors and actuators. In addition, the deposition of BNTBT thick films onto metal and insulating substrate is of great interest because of the possibility of integration of dielectric and piezoelectric layers with semiconductors and metallic structures for different applications such as transducers and actuators. In this context, electrophoretic deposition (EPD) and screen printing (SP) techniques were employed to obtain BNTBT thick films. The BNTBT powders were synthesised by a solid state method and characterized to ensure stability of colloidal suspensions and allow forming of the thick films. The BNTBT thick films obtained by EPD with the application of 60 V DC bias between two platinum electrodes for variable times had thicknesses ranging from 10 to 45 µm, whereas, the thickness of SP BNTBT films on an alumina substrate varied from 6 µm to 18 µm, corresponding to 1 layer to 3 layer deposition. The BNTBT sintered film on the alumina substrate showed the formation of Al/Ti containing secondary phases. To minimize the formation of secondary phase various strategies were adopted such as sintering in an inert atmosphere and the use of a metallic interlayer. The thick films obtained were characterised using X–Ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The electrical properties were measured using a LCR meter and Piezo Force Microscope (PFM). The present studies provide a way to optimize the processing conditions to obtain BNTBT thick films for microelectronics applications.

HIGH PIEZOELECTRIC RESPONSE AND EVOLUTION OF FERROELECTRIC PROPERTIES OF SINGLE CRYSTALS GROWN IN $BaTiO_3$-$CaTiO_3$-$BaZrO_3$ PSEUDO-TERNARY SOLID-SOLUTION

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Ferroelectric and piezoelectric materials attract much attention due to their application in actuators, transducers and sensors. The industry market is dominated by lead-based compounds, such as $Pb(Zr,Ti)O_3$ (PZT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$-PbTiO3 (PMN-PT). However, driven by environmental issues caused by their hazardous synthesis and recycling, the demand for lead-free piezoelectrics has been increased. An excellent piezoelectric constant of 620 $pC.N^{-1}$ was reported in (1x)$BaTi_{0.8}Zr_{0.2}O_3$-x$Ba_{0.7}Ca_{0.3}TiO_3$ (with x=0.5) (BCTZ) polycrystalline ceramics, making them as promising alternatives to lead-based materials. Moreover, it is highly expected that BCTZ piezoelectric single crystals can exhibit significantly higher properties than their polycrystalline ceramics owing to the absence of grain boundaries and their macroscopic anisotropy. As previously predicted, a piezoelectric constant of about 1500-2000 $pC.N^{-1}$ is anticipated in the vicinity of the optimal composition $Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O_3$. In this work, we review different attempts of crystal growth by Top Seeded Solution Growth method of BCTZ by varying zirconium content. Chemical analysis and electrical characterizations are presented and compared to those of corresponding ceramics. The compositional dependent electrical performance is investigated and similarities with PZT system are pointed out. As main results, a cross-over from relaxor to ferroelectric state in the whole BCTZ solid solution is evidenced. Polycrystals grown on iridium rod with compositions close to the optimal one displayed good electromechanical properties; d^{31} piezoelectric coefficient up to 285 $pC.N^{-1}$ was measured by the resonance method and d^{33} up to 496 $pC.N^{-1}$ by the Berlincourt method. Such promising results make expect higher piezoelectric coefficients on orientated single crystals.

TEXTURATION OF LEAD-FREE BATIO3 BASED PIEZOELECTRIC CERAMICS

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Piezoelectric ceramics have been integrated for a long time in a wide range of devices, particularly in ultrasonic applications such as underwater sonar systems, medical imaging and most of them use $Pb(Zr,Ti)O_3$ (PZT) materials. However, due to health care and environmental problems, lead content must be reduced in such applications [1]. Among the few lead-free materials families which can be considered for the replacement of PZT [2, 3], barium titanate based materials ($BaTiO_3$) appear as interesting because of its piezoelectric properties at room temperature and capacity to be modulated by doping, even if Curie temperature is not very high (120°C). However, ceramics are generally limited by their isotropic nature. For this reason, texturing process have been developed in order to improve/optimize their electromechanical properties. The aim of the present study is thus to obtain textured BaTiO3 based materials by using the templated grain growth process (TGG) and to measure their piezoelectric properties. Doped and undoped BaTiO3 powders were prepared by classical solid state route while BaTiO3 templates of different morphologies were elaborated by a molten salts process. The templates and matrix particles were then dispersed in the appropriated solvent using dispersing agent together with suitable binder and plasticizer. The slurry was then tape casted on plastic film and then dried. The green sheet was cut, stacked, pressed and then sintered at the appropriated temperature in order to obtain thick samples. Thin sintered samples (200 – 300 m) were also elaborated using only one sheet. This process allowed obtaining highly oriented materials (texturation degree 70 to 90) with interesting piezoelectric properties.

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Self-poling of BiFeO3 thick films induced by the annealing through the ferroelectric-to-paraelectric phase transition

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Perovskite bismuth ferrite – $BiFeO_3$ (BFO) – has been shown to have great potential for many applications due to a number of attractive properties, such as its multiferroic nature at room temperature, high Curie temperature, and high remanent polarization. Thus, various piezoelectric devices, for example, sensors, actuators and transducers, can be prepared using an active layer of BFO-based materials integrated onto substrates as thick films. But, the processing of the BFO thick films is challenging due to readily occurring chemical reactions between the substrate, electrode and BFO layer. However, not only is it challenging to prepare high-quality BFO thick films due to processing issues, but it is problematic to pole the material due to its high coercive field and high electrical conductivity. The results of this study suggest an alternative way of poling BFO films by sintering (annealing) at a temperature above the ferroelectric-paraelectric phase transition (TC), overcoming the obstacle of poling the BFO ex-situ using large external electric fields. BFO thick films were prepared by screen-printing a Bi_2O_3-Fe_2O_3 mixture on a Pt-electroded alumina substrate and sintering the films at different temperatures. Direct and converse piezoelectric d_{33} coefficients of as-sintered films were measured. The phase composition and microstructure of the BFO thick films were characterized by roomtemperature and high-temperature X-ray diffraction analysis and analytical microscopy. The BFO thick films sintered above TC exhibited a d_{33} of 18 pC/N; in contrast, the films sintered below TC revealed a low piezoelectric response with d_{33} of 3 pC/N. Thus, it was observed that a significant self-poling effect only appears in cases when the films are heated and cooled through the ferroelectric-to-paraelectric phase transition (TC 820 ^{o}C). These self-poled films exhibit a microstructure with randomly oriented columnar grains, thus distinctly different from that of the samples sintered ust below the TC with equiaxed grains. In the selfpoled films, a compressive strain gradient along the film thickness was observed. The origin of the strain gradient and its role in the self-poling effect will be discussed in detail.

Acknowledgements

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Highly-Sensitive Pressure Detection by AlN Piezoelectric Thin Film on a Flexible Substrate

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This research work reports on detection of ultra-small applied forces of 20 μN with AlN piezoelectric thin films on flexible aluminum discs (100 μm thick and 10mm diameter). Forces of 20-350 μN were applied on the samples by a controlled air flow. The AlN films were grown to a thickness of about 470nm by a reactive sputtering process. Different preferred crystallographic orientations of the AlN crystals relative to the film plane are obtained by variations of the growth temperature. High sensitivity and linearity to applied forces are obtained in films that consist of a mixture of c-axis and a-axis orientations of AlN crystals relative to the film plane. However, a less force sensitivity is found in the case of only c-axis or a-axis oriented AlN crystals in films having the same physical dimensions, as compared to the mixed oriented crystals. The effect of elastic bending the substrate on the pressure detection sensitivity is also studied. The results show an optimum elastic bending for improved force detection sensitivity by about 50%. The AlN films could detect sound waves travelling in an atmospheric environment without any bridging medium. The AlN films was found to be highly sensitive to temperature changes in the range of room temperature and 60^{o}C.

SOLUTION-DERIVED SODIUM POTASSIUM NIOBATE THIN FILMS: INFLUENCE OF DONOR DOPING ON MICROSTRUCTURE AND FUNCTIONAL PROPERTIES

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Potassium sodium niobate, $K_{0.5}Na_{0.5}NbO_3$ (KNN) is an environment friendly lead-free alternative to highly efficient lead-based piezoelectrics. Recurring problems of KNN ceramics are related to processing and they include low densification and difficulties to control the microstructure. Aliovalent doping, such as strontium doping in low amounts, has been found as one of the approaches to enhance densification, reduce the grain size, which both contributed to improved functional response. It was shown that in solution-derived KNN thin films the microstructure depends on the fraction of alkali excess in the coating solution and rapid thermal annealing conditions, i.e., temperature and time; either finegrained (grain size << film thickness) or columnar with grains of cuboidal shape [Kupec et al., 2012]. Furthermore, the films with columnar microstructure exhibited strong leakage, which was not the case for the films with fine grains [Kupec et al., 2015]. The aim of this work was to study if and to what extent the donor doping influences the microstructure of KNN thin films, and consequently dielectric, ferro- and piezoelectric properties of such films in view of their possible application in energy harvesting. Liquid precursors of $(K_{0.5}Na_{0.5})_{1-y}Sr_yNbO_3$ (KNN-ySr) thin-films, where the Sr-dopant content was set at y = 0, 0.005, 0.01, were prepared from potassium and sodium acetates and niobium ethoxide in 2-methoxyethanol solvent with 5 mol% of potassium acetate excess. Strontium was introduced as acetate. The approximately 250 nm thick KNN-ySr thin films on Pt/TiOx/SiO2/Si substrates were obtained by rapid thermal annealing at 650 ^{o}C for 5 min. According to X-ray diffraction analysis, all synthesized thin films crystallize in pure perovskite phase. The surface and cross-section microstructure analysis, performed by the field emission scanning electron microscopy, reveals that the films consist of equiaxed grains, the average size of which gradually decreases from about 90 nm for undoped KNN to a few tens of nm by increasing the Sr-dopant content. In the contribution we discuss the influence of the chemical modification on the functional response, i.e., dielectric properties versus frequency and temperature, polarisation – electric field dependence, leakage current and piezoelectric response of the as-prepared films.

TUNING FERROELECTRIC PROPERTIES OF $BiFeO_3$-$BaTiO_3$ CERAMICS VIA ISOVALENT AND DONOR SUBSTITUTION USING La^{3+}

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Among the various BiFeO3-based solid solutions investigated, $BiFeO_3BaTiO_3$ (BF-BT) has received considerable attention due to the observation of weak ferromagnetism at room temperature and a high ferroelectric TC in the region of 620°C. However, in common with other BF-based pseudo binary systems, the presence of high leakage current, associated with reduction of Fe^{3+} and generation of oxygen vacancies, is a serious issue for BF-BT. To address this issue, our research is investigating the influence of small amounts of La^{3+} as either an isovalent or donor substitution for Bi^{3+} or Ba^{2+} respectively. The composition 0.75BF-0.25BT was selected for modification with La^{3+}, due to its proximity to the MPB in this system.

It is shown that both types of substitution provide the means to suppress the reduction, resulting in lower leakage current and dielectric loss. Although highly resistive ceramics were produced by conventional solid state sintering in air, the ferroelectric hysteresis loops of donor substituted ceramics display pronounced constriction, with low remanent polarisation. Microstructural studies have indicated that the constriction effect in the P-E loops is linked to the development of chemical and microstructural heterogeneity in the form of core-shell structures. The grain cores show evidence of ferroelectric domains while the shell region appears to be more disordered and lacks a clear domain pattern. It is demonstrated that air-quenching is an effective way to reduce the thickness of the shell region, which enhances the domain switching behaviour. In contrast, isovalent substitution of La^{3+} for Bi^{3+} yields a relatively homogeneous microstructure and well-saturated P-E loops in conventionally-sintered ceramics.

In conclusion, the substitution of La^{3+} for Bi^{3+} or Ba^{2+} in 0.75BF-0.25BT ceramics, as an isovalent or donor dopant respectively, has provided beneficial effects on the functional properties and interesting microstructural features that could be exploited in electromechanical transducers and actuators.

CRYSTAL STRUCTURE, MICROSTRUCTURE AND PIEZOELECTRIC PROPERTIES OF CA/ZR CO-SUBSTITUTED BATIO3 LEAD FREE PIEZOCERAMICS

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Recently, lead free piezoelectric ceramics have attracted worldwide attention to reduce the amount of hazardous substances in electronic devices. In the present study, solid solutions of Ca and Zr co-substituted $BaTiO_3$ ($Ba_{1-x}Ca_xTi_{1-y}Zr_yO_3$; x = 0.13 and y ≤ 0.15) piezoceramics have been investigated systematically by semi-wet method. X-ray diffraction patterns of all specimens show the single phase formation. A tetragonal structure with P4mm symmetry was confirmed by Rietveld method and Raman spectra. Surface morphology of all these samples are dense, uniform and homogeneous except for y = 0.15. Dielectric properties showed sharp phase transition at Tc, corresponding to FE to PE transition for x/y = 0.13/0, phase transition became quite diffused with increasing y. More interestingly, the piezoelectric charge and planar coupling coefficients (d_{33}~ 367 pC/N and k_p ~39%) also reached to maximum for the composition y = 0.10, which makes it a potential leadfree candidates for piezoelectric applications.

DEMONSTRATION OF LEAD-FREE PIEZO COMPONENTS

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Today, more than 98% of the piezoceramic components are based on lead-containing materials (PZT), and technical and market frameworks are designed for this material, limiting access for lead-free materials. Even though RoHS and REACH regulations are pushing towards PZT replacement, the lack of lead-free materials supply has been a major slowing factor during the transition phase. Additionally, lead-free materials offer other advantages such as lower density, which opens up for new applications or improved products, and the possibility of replacing expensive electrodes with low-cost nickel. The state of the art process used to produce PZT materials, solid-state synthesis, is not suitable for lead-free piezoceramics, mainly due to evaporation of volatile species and poor sinterability. Therefore, substantial effort is needed to develop and modify production- and processing technologies to qualify lead-free piezoceramic components and devices. Moreover, proven reliability and consistency over time - of both materials and components are key technological barriers to overcome in order to commercialize lead-free piezoelectric devices.

Here we present a scalable synthesis route, spray pyrolysis, capable of produce tons of lead-free piezoceramic materials. The process yields homogeneous materials, stoichiometric control and sub-micron particles with excellent sinterability. Despite the properties and quality offered, component production protocols developed for solid-state powders cannot be directly applied to spray pyrolysed materials. Cerpotech and partners are developing components using spray pyrolysed powders and existing industrial manufacturing platforms to verify the performance and consistency of the materials and components to develop competitive products.

TEMPERATURE DEPENDANCE OF PIEZOELECTRIC PROPERTIES IN LEAD-FREE CERAMICS

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As a result of more than a decade of active research worldwide three families of lead-free materials have emerged as potential candidates for replacing lead-based piezoelectrics. Promising lead-free families are those based on $BaTiO_3$ (BT), $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) and $(K,Na)NbO_3$ (KNN). The properties in these materials are good enough to start replacing PZT-based materials for applications operating near room temperature. However, many harsh environments including oil well drilling, aerospace, automobile and power plant engines require actuators to sustain electromechanical strains at elevated temperatures, which is big challenge for all prominent lead-free materials. The focus of our work is to compositionally engineering lead-free materials for high temperature applications. So far we have studied different systems based on $K_{1/2}Bi_{1/2}TiO_3$, $BiFeO_3$ and $(K,Na)NbO_3$. Amongst which $K_{1/2}Bi_{1/2}TiO_3$-based materials have shown promising properties for actuator applications with temperature stable electromechanical strains of 0.16 % (6 kV/mm) from RT to 300 °C. In-situ measurements on $BiFeO_3$ and $(K,Na)NbO_3$-based systems have shown that electromechanical properties are strongly temperature dependent in these ceramics despite high values of TC.

SODIUM BISMUTH TITANATE THICK FILMS FABRICATED BY SCREEN PRINTING METHOD FOR HIGH TEMPERATURE ULTRASONIC SENSOR

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Sodium Bismuth Titanate (NBT), chemical formula $Na_{0,5}Bi_{4,5}Ti_4O_{15}$, is a material that has high Curie temperature, average piezoelectric (d33), coupling (k33) coefficients that make it an ideal candidate for application at elevated temperatures. This kind of new material may constitute a possible solution for measurements in Materials Testing Reactor (MTR). In the near past, IES (Institut d'Électronique et des Systèmes) in collaboration with CEA (Commissariat à l'Énergie Atomique et aux Énergies Alternatives) have developed the first ultrasonic sensor that has been tested in MTR [1]. However its working temperature was limited on 200°C. IV generation of nuclear reactors, in its first phase, requires an increasing of operation temperature up to 350°C. In this work, we investigate the material properties. The samples have been fabricated by screen printing method, fired, polarized, characterized by its dielectric (ε_{33} = 172), resistivity (ϱ = 3.26×10^{12} Ohm·cm), piezoelectric (d_{33} = 13 pC/N), ferroelectric and pyroelectric behaviors. Obtained data establish a promising background for this material in high temperature piezoelectric applications.

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BULK PZT TRANSFORMERS FABRICATED BY MICRO-POWDER BLASTING: MODELING AND EXPERIMENTAL RESULTS

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Background / Motivation

Conventional cm-scale piezoelectric transformers are key components for power electronics applications including AC/AC and AC/DC conversion, galvanic isolation, and voltage rectification. Previous research has led to bulk devices as small as 2 cm in diameter and ~1 mm thick, with voltage gains ranging from 2 – 40 and efficiencies between 60 – 98 %.

Statement of Contributions and Methods

Miniature bulk radial mode piezoelectric transformers are fabricated from 127 µm thick bulk PZT sheets, with aluminum electrodes deposited by evaporation and photolithographically patterned on one side of the device. A dry-film photoresist layer is used to selectively mask the PZT during micro-powder blasting with 25 µm sized alumina particles, to define structural features. Transformers with PZT anchor widths as small as 200 µm are achieved using this process. Experimental Results Voltage gains as high as 2.4 are achieved for a 4 mm diameter radial mode device supported by folded-beam tethers, with an output power density of 51.3 Wcm^{-3}, corresponding to an output power of 80 mW at 5 V input when driving a 1 MΩ output load. Additionally, axial extension mode devices are fabricated on the micrometer scale, proving the manufacturing process at micrometer dimensions. A numerical model utilizing electrostatic, structural mechanics, acoustic and electrical circuit physics is used to predict device performance and compared to an analytical model.

Discussion and Conclusions

Experimental results indicate that through the use of micro-powder blasting, significantly smaller bulk piezoelectric devices can be fabricated with similar voltage gain numbers to devices several orders larger by volume, enabling advances in micro-robotic and other small-scale systems for end users. The effect of tethering the vibrating disc transformer is investigated to determine its effect on efficiency; additionally, at larger output loads FEA and analytical results become less accurate; possible causes and approaches are discussed.

PIEZOELECTRIC MEMS DEVELOPMENT IN SINTEF

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SINTEF is an independent research institute that has experience with making piezoMEMS devices since 2002. Our competences cover the whole process from idea and design, through materials development and process integration to device fabrication to packaging. SINTEF develops piezoMEMS in-house and in collaboration with our customers and partners but also has a key strategy to be a developer of new devices (www.piezomicrosystems.com). SINTEF has a proven track record of successful concepts, devices and projects like e.g. the T-Lens currently being commercialized by poLight (www.polight.com) and the StreetHopper by Polewall (www.polewall.com). A key to success in piezo MEMS has been to both have deep material and MEMS competence that has resulted in successful PZT and MEMS process integration. The SINTEF labs are also very flexible compared to a production foundry and are thus ideal for development and testing of new materials and processes. The continuing research in material science and fabrication processes at SINTEF ensures continued development of state-of-the-art technology. This is done in collaboration projects like the H2020 program. Recently started developments include thin films of lead-free KNN and relaxor materials such as PMN-PT. SINTEF has two commercial PZT deposition tools based on PLD (pulsed laser deposition) and CSD (chemical solution deposition) and is hence well equipped for deposition of thin film piezoelectrics and other functional materials up to 200 mm wafers.

EFFECTS OF THE LGT CRYSTAL QUALITY ON THE RESONANCE FREQUENCY STABILITY OF BULK ACOUSTIC WAVES RESONATORS.

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In the time and frequency domain, we need ultrastable crystal resonators embedded in ultrastable oscillators (USO), working at 10 MHz and exhibiting excellent short term stabilities. Up to now, the quartz crystal fulfills its function. But, Langatate piezoelectric crystal (La3Ga5.5Ta0.5O14) seems to allow better performances (higher quality factor, greater robustness to the effects of radiation…). The applications of this domain require high quality material with reproducible properties. LGT crystal is grown by Czochralski method. Its physicochemical properties and specificities of this growth process induce defects. They can react as ionic and electronic charge carriers and generate conductive losses, particularly at high temperatures, which limit the potential use of LGT crystal in certain applications. In view to define the best LGT ingot zone for the best Q.f product of a given acoustic resonance (around 10 MHz), we have realized the cartography of impurities distributions and we have studied the chemical homogeneity along the growth axis by femtosecond laser ablation ICPMS coupling. Other analysis methods as IR, UV-vis and ESR spectroscopies, chemical etching to reveal etch pits and dislocations, optical method using crossed polarizers to study the homogeneity of the refractive indices. Moreover, the electrical conductivity of samples cut in different parts of the LGT boule along its growth axis was measured, before and after high temperature annealing. At least, Y-cut resonators have been designed and manufactured to study the quality of the chosen frequency resonance, particularly its Qfactor, directly linked to the stability of the USO.

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Electrosciences announces the start of a multinational project funded by the European Commission under the H2020 ICT Programme.

Computer clock speeds have not significantly increased since 2003, creating a challenge to invent a successor to CMOS technology able to resume the improvement in clock speed and power performance. The key requirements for a viable alternative are scalability to nanoscale dimensions - following Moore's Law - and simultaneous reduction of line voltage in order to limit switching power. Achieving these two aims for both transistors and memory allows clock speed to again increase with dimensional scaling, a result that would have great impact across the IT industry. PETMEM is a European partnership amongst Universities, Research Institutions, SMEs and a large company that will focus on the development of new materials and characterization tools to enable the fabrication of an entirely new low-voltage, memory element. This element makes use of internal transduction in which a voltage state external to the device is converted to an internal acoustic signal that drives an insulator-metal transition. Modelling based on the properties of known materials at device dimensions on the 15 nm scale predicts that this mechanism enables device operation at voltages an order of magnitude lower than CMOS technology (power is reduced two orders) while achieving 10 GHz operating speed.

ELASTO-OPTIC BEHAVIOR IN EPITAXIAL FILMS OF PEROVSKITE OXIDE FERROELECTRICS

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Perovskite oxide ferroelectrics are known for their excellent piezoelectric properties enabling numerous applications. Strong piezoelectric effects coexist with remarkable optical behavior in these materials. Such ferroelectrics are wide bandgap insulators exhibiting high transparency and large refractive index in broad optical spectral range. Moreover, the refraction in these materials can be tuned by electric or stress field. Changes of refractive index under stress or strain, or piezo-optic phenomena create a basis for many optical devices employing ferroelectric crystals. Nevertheless, modern technologies require thin films instead of bulk crystals. The optical properties of high-quality single crystal-type ferroelectric films are practically unexplored. Here we report on elasto-optic behavior in epitaxial films of perovskite oxide ferroelectrics: $SrTiO_3$, $BaTiO_3$, $KNbO_3$, $(K,Na)NbO_3$, $NaNbO_3$, $PbTiO_3$, $Pb(Zr,Ti)O_3$, and $(Pb,Sr)TiO_3$. Optical properties of these materials were measured with spectroscopic ellipsometry technique in a wide spectral range. The high sensitivity of this technique allows a measurement of very thin films (only a couple of nanometers thick) giving access to their fundamental physical parameters (crystalline structure, polarization, surface roughness etc.). As a result, we demonstrate huge epitaxial strain-induced variations in refraction. The results will be discussed in terms of effects of strain and polarization on band structure of the films.

INSIGHT INTO PROCESSING, STRUCTURE AND PROPERTIES OF $BiFeO_3$-$SrTiO_3$ FERROELECTRIC CERAMICS

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Among lead-free piezoceramic candidates, bismuth ferrite ($BiFeO_3$, BFO) has attracted a considerable attention due to its high Curie temperature (Tc ~830 °C) and multiferroic nature at room temperature. However, a number of shortcomings have prevented the use of this material in practical applications, particularly the complicated processing and high electrical conductivity. One of the possible solutions to overcome these problems is to incorporate other ABO3 perovskites in solid solutions with BFO. In addition, these BFO-ABO_3 systems are of great interest due to the possibility to exhibit a morphotropic phase boundary (MPB), where the electromechanical properties could be enhanced.

Here, we studied the incorporation of $SrTiO_3$ (ST) into a solid solution with BFO (BFO-ST) due to the possibility to exhibit yet unexplored MPB between a polar and non-polar phase, where the piezoelectric properties are enhanced through polarization extension mechanism, which is often ignored in the literature. The system was investigated in terms of processing and structural, microstructural and functional properties. Our study revealed that the conventional solid state synthesis is not a suitable method for the synthesis of the BFO-ST ceramics as it results in the formation of a significant amount of Bi-rich, sillenite phase segregated at the grain boundaries and grain junctions. For this reason, we propose an alternative processing route, i.e., mechanochemical activation-assisted synthesis, which resulted in ceramics with good level of chemical homogeneity and without the presence of the sillenite phase. Measurements of the dielectric permittivity in the frequency range 10^6-10^{-2} Hz showed that these ceramics exhibit elevated electrical conductivity, which was successfully reduced by doping the system with a small amount (0.1 wt.%) of MnO_2. We observed typical ferroelectric hysteresis loops in the whole (x)BFO-(1-x)ST compositional series with high remanent polarization, i.e., 30-50 $\mu C\ cm^{-2}$. A weak compositional enhancement of the piezoelectric d_{33} coefficient was observed with a maximum d_{33} value of 73 pC N^{-1}. Finally, in strong contrast to unmodified BFO ceramics, we show that BFO-ST ceramics exhibits weak aging, which is discussed in terms of domain-wall pinning effects.

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VIRTUAL INSTRUMENT TO OBTAIN ELECTRICAL MODEL IN PIEZOELECTRIC ELEMENTS USED IN ENERGY HARVESTING

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The Virtual Instrument designed and described in this work is used to obtain a linear electrical model of piezoelectric elements used in Energy Harvesting with periodically mechanical excitations. The methodology followed to obtain the electrical model is described and the Virtual Instrument is explained. All this is particularized to perform a Road Traffic Energy Harvesting application. The piezoelectric elements are stimulated by the Test Bench, patented by POEMMA R&D GROUP, that is be able to simulate a vehicle passages under a specific speed and flow rate of traffic. Also hardware for collecting and storing energy with different topologies has been designed. The Virtual Instrument of this work allows the following actions: to set up the test parameters, to control the Test Bench and the hardware for collecting and storing, to measure and process the response signals of device under test, and finally, to calculate and obtaining of linear electrical model of the chain formed by piezoelectric elements – Rectifiers – Capacitors. Using this model is possible to scale the number of elements, and the optimal topology needed to harvest the required energy by a specific electrical load.

FEM MODELLING OF INTERDIGITATED STRUCTURES WITH RESPECT TO POLING PROCESS

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FEM (Finite Element Method) modelling software such as COMSOL Multiphysics can be a powerful tool for modelling of the behaviour and response of piezoelectric materials and devices. Devices based on piezoelectric crystals are particularly well suited, because the polarization magnitude in crystals is predetermined defined by cut direction. In the case of polycrystalline piezoelectric ceramic materials, the overall polarization vector in the material is not oriented in one single direction nor is constant all over the material. Therefore, a poling process, where a strong electrical field is applied across the material to align the dipole domains in one particular direction on a macroscopic level, should be performed. In this paper poling process and performances of SAW (surface acoustic wave) devices with interdigitated electrodes have been investigated through FEM simulations. SAW devices have found a number of applications in physical and chemical sensing. Two poling configurations of SAW piezoelectric ceramic devices have been compared: a standard one having a polarization perpendicular to the substrate and a second one with a more complex polarization but easier for manufacture. The latter one can be achieved by applying a high electric potential to one of the interdigital electrodes while grounding the other one. The standard SAW device and the interdigital poled SAW device have been modelled using the Piezoelectric Devices Module in COMSOL. In order to correctly model the interdigital poled SAW device the poling process has also been modelled by simulating the resulting electric field from the applied voltage on the electrodes. The electric field magnitude was mapped to the polarization magnitude according to the virgin hysteresis curve of the piezoelectric ceramic, while the orientation of the polarization has been aligned in the direction of the simulated electric field. The module of the transfer function between the transmitting IDT (interdigital transducer) and the receiving IDT provides the proper sensitivity comparison of the two SAW devices. It has been shown that COMSOL Multiphysics can used to model not only piezoelectric devices but also the poling process in the case of piezoelectric ceramic materials, which is of utmost interest for users and designers of piezoceramics. In this paper, the focus has been mainly on SAW devices, but it can be applied to any piezoelectric ceramic based devices with non-trivial polarization pattern.

THE REPRESENTATION OF COUPLING INTERACTIONS IN THE MATERIAL PROPERTIES OPEN DATABASE (MPOD)

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The Material Properties Open Database (MPOD) is a functional element of the web-based open databases system linked with the International Union of Crystallography (IUCr). MPOD delivers single-crystal tensor properties in several representations, ranging from numerical matrices to 3D printing. Longitudinal moduli surfaces can be displayed in computers as well as in smart cell phones. MPOD was initiated by D. Chateigner in 2010. Properties are stored as ".mpod" files. IUCr formatting standards (CIF) are followed. The original published paper containing the data is cited. Structural and experimental information is also registered and linked. The MPOD system includes a physical properties dictionary with pertinent constitutive equations. "Coupling properties", i.e. piezo-effects and magnetoelectricity, represent interactions linking different subsystems in a material. Currently, piezoelectricity occupies a significant fraction of cases in MPOD. The implications of crystal symmetry in piezoelectricity are systematically taken into account. Matrices' elements and longitudinal moduli surfaces are checked for consistency with the Neumann Principle. Magnetoelectric axial tensors introduce exciting features into MPOD. Color-symmetry and time-inversion considerations add complexity and interest to the task of systematizing the reception, validation and representation of this remarkable coupling property. The representation of polycrystals' properties symbolizes a forthcoming challenge to the MPOD international group. The MPOD presentation includes a real-time demonstration of the database possibilities. Funding from Project CONACYT 257912 is acknowledged.

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FIRST-PRINCIPLES STUDY OF $(BA,CA)(TI,ZR)O_3$ SOLID SOLUTION

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High-performance piezoelectrics are key components of various smart devices and, recently, it has been discovered that $(Ba,Ca)(Ti,Zr)O_3$ (BCTZ) shows enhanced piezoelectric properties. Within this framework, by means of a theoretical approach based on Density Functional Theory (DFT), different chemical compositions of the multifunctional BCTZ solid solution have been investigated, focusing on the energetics and lattice dynamical properties. Our goal is to understand better the microscopic mechanisms involved in the large electrochemical response of BCTZ in order to rationalize the search of optimal compositions.

At first, a comprehensive study of the four parent compounds has clarified the energy landscape and the competitions at play between various phases. Then, a description of BCTZ based on the Virtual Crystal Approximation (VCA), has revealed strong competitions between different ferroelectric phases when increasing the stoichiometry of Ca and interesting trends of the main observables, such as polarization and piezoelectric coefficient. Complementary calculations on supercells are also provided. At variance, it has been found that VCA is not accurate to reproduce the energetics and ferroelectricity of the system when increasing the Zr stoichiometry, whereas the standard DFT approach based on supercells more properly works. A better understanding of the environment required to activate ferroelectric distortions in BCTZ is provided by a simple model based on $BaZrO_3/BaTiO_3$ superlattices. This first analysis allows us to predict that appealing ferroelectric and piezoelectric properties characterize a wide-range of compositions of BCTZ and that more advanced DFT-based studies are required to completely describe the physics of this system

INFLUENCE OF TETRAGONAL PLATELETS ON THE DIELECTRIC PERMITTIVITY OF $0.964Na_{1/2}Bi_{1/2}TiO_3$-$0.036BaTiO_3$

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Among the lead-free ferroelectrics, (1-x)$Na_{1/2}Bi_{1/2}TiO_3$-x$BaTiO_3$ is one of the most promising material systems. The dielectric properties around the morphotropic phase boundary at x = 0.06 were cited as d_{33} = 125 pC/N and $\varepsilon_{33}^T/\varepsilon_0$ = 580. These values are comparable to those of commonly used lead-containing ferroelectrics. However, the atomistic mechanisms leading to the relaxor properties are still unclear. In diffuse X-ray and neutron scattering experiments, information about the nanostructure of a single crystal can be obtained from the scattering intensity between Bragg reflections. Previous diffuse x-ray scattering experiments performed by our group on the rhombohedral $0.96Na_{1/2}Bi_{1/2}TiO_3$-$0.04BaTiO_3$ revealed features related to the local octahedral tilting order and planar defects separating different tilt domains. These features react strongly to the application of an external electric field and their temperature dependence is clearly correlated with the dielectric permittivity. Due to the higher oxygen sensitivity of the neutron scattering method, we have complemented our X-ray scattering experiments with a diffuse neutron scattering study [1]. Our results show the coexistence of multiple tilt systems over a wide temperature range and a strong temperature dependence of the respective domain sizes. On this basis, we propose a model of the nanostructure featuring chemically pinned tetragonal platelets in a rhombohedral matrix. The different tilt domains are separated by a cubic intermediate phase. Furthermore, a clear correlation between the thickness of the tetragonal platelets and the dielectric permittivity could be identified.

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POLARIZATION AND DEPOLARIZATION EFFECTS ON STRESS DISTRIBUTION IN LEAD-FREE CERAMICS STUDIED BY RAMAN

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The increasing interest in the development of lead free potassium/sodium niobates (KNN) ceramic materials as a promising substitutes of lead oxide based ferroelectrics, represented by lead zirconate titanate (PZT), is due to its ferroelectric and piezoelectric properties that depend on several aspects such as the stabilization of tetragonal phase and the presence of secondary phases, mainly conditioned by the synthesis process. The dependence of the phase structure with the doping content modifies the dielectric and piezoelectric properties of a ferroelectric material and are attributed to the contributions associated with the lattice distortion and domain wall movement (and reorientation) in polycrystalline ceramics [1,2]. Polarization and depolarization processes produce changes in stress states of ceramic grains. In this sense, confocal Raman spectroscopy at room temperature has been shown as an effective tool to study these microstructural aspects of piezoelectric materials. This work shows profiles of stress distribution (assessed from measurements of Raman shift) on KNN samples along the polarization direction. The effects of charge accumulation, polarization defects near the electrode are discussed. Polarization and depolarization cycles are also studied in order to understand how these processes affect the crystal structure and residual stresses across an orthorhombic-tetragonal phase transition.

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Piezoelectric microelectromechanical systems (piezoMEMS) offer a wide range of benefits compared to other approaches of generating micromechanical motion, such as thermal or electro/magnetostrictive techniues ref1. For this reason the technology has lately found its way into several commercially available devices, including inkjet printer heads, ultrasound transducers and gyroscopesref1. However, the effect of realistic and harsh operating conditions on the lifetime, fatigue and failure mechanisms of piezoMEMS devices has not yet been thoroughly investigated. Here we present initial studies of dominant failure mechanisms in piezoMEMS devices when actuated in realistic and harsh operating conditions with specific focus on humidity.

$PbZr_{0.48}Ti_{0.52}O_3$ (PT)-based piezoelectric micromirrors were fabricated at SITEF MiaLabref2 using SITEFs standard chemical solution deposition (CSD), pulsed laser deposition (PLD) and sputtering techniques. Both CSD and PLD-based devices were actuated at frequencies representative to normal device operation in 2-atmosphere with relative humidity levels from 0 to 90 and temperatures from 25°C to 100°C. The lifetime and dominant failure mechanisms for devices both with and without Al2O3-passivation deposited by atomic layer deposition (ALD) were studied. The presentation will focus on both the cause of identified failure mechanisms and suggested means for improving lifetime and reliability of these micromirrors. Key words: PT, piezoelectric MEMS, mechanical fatigue

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VALUATION OF VARIATIONS IN PIEZOELECTRIC CONSTANTS AFTER AGING PROCESS

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Piezoelectric ceramics properties change with time. Aging effects are the diminishing of dielectric constants, dielectric losses and coupling factors, whereas the elastic stiffness increases. In this work, the evolution of elastic, piezoelectric and dielectric constants are evaluated after five years of aging. To compute the ten parameters, the piezoelectric model is adjusted to minimize the difference between Finite Element simulations and experimental data. Here we present the results for the PZT27 from Ferroperm. Three different geometries were studied, thickness 2 mm with diameters 10, 20 and 30 mm. An average is obtained from ten samples of each size. The evolution of the energy consumed by the sample for radial and thickness modes are also evaluated. Results presented here allow the evaluation of the aging process over each parameter in the piezoelectric model.

PIEZOELECTRICAL PROPERTIES OF BNBT CERAMICS VIA SELF-SWITCHING PFM

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One of the most extensively studied lead-free ferro-piezoelectrics is (1-x) $(Bi_{0.5}Na_{0.5})TiO_3$ + x$(BaTiO_3)$ (BNBTx) by solid solution. Current explanation for the relaxor behavior of BNBTx ceramics can be found in the coexistence of three phases if the studied composition is in the vicinity of the so-called Morphotropic Phase Boundary (MPB), which is found to exist for x= 5.5 to 7. Piezoresponse force microscopy (PFM) has been established as an effective tool for the characterization of domain structure and domain switching behavior of ferroelectric materials. In PFM measurements the amplitude of the acquired signal is proportional to the effective longitudinal piezoelectric coefficient, d_{33}.

Submicrometer structured BNBT4 and BNBT6 ceramics were obtained by sol–gel auto-combustion nanopowders by hot-pressing (700–950 °C) and subsequent recrystallization (1000–1050 °C) [1, 2]. Bulk BNBTx samples were characterized by scanning probe microscopy (MFP-3D Infinity, Asylum Research Inc., USA) under the Dual AC Resonance Tracking Self-Switching PFM (DARTSS PFM) mode to study its piezoelectric properties. Piezoresponse signal was obtained from BNBTx samples applying 30 -100 V_{AC} with triangular waveform cycles to the samples using Ti/Ir coated Silicon tips with a nominal spring constant of 2 N/m and a resonance frequency of 70 kHz. Piezoelectric deformation-applied voltage (D-V) "butterfly" loops measures were converted to piezoelectric hysteresis loops according to the law of converse piezoelectric effect to know the local effective piezoelectric d_{33} coefficient [3-5]. Values of d33 from 100 to 130 pm/V were obtained, in accordance with the values acquired by Berlincourt-meter, reported in [1, 2]. The amplitude and phase images, as well as the corresponding "butterfly" and hysteresis loops will be displayed in the presentation.

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CHARACTERIZATION OF LEAD FREE PIEZOELECTRIC CERAMIC

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The components and materials used in the industry must meet safety conditions and be friendly with the environment. In the case of piezoelectric ceramics, the use of lead as a primary element is discouraged. New lead free piezoelectric materials are developed to comply with new. For low deformations, the constitutive equations are linear, and the symmetry group 6mm. To adjust this model five elastic, three piezoelectric and two dielectric constants are needed. The identification of these parameters can be made by minimization the difference between a Finite Element Simulation (FEM) and the experimental impedance curves. In this work, the results of the first complete set of parameters for a BNBT6 Lead-Free piezoceramic ($Bi_{0.5}Na_{0.5}$, 0.94Ba, $0.06TiO_3$), with density 5760 kg/m^3 is obtained from FEM optimization. These preliminary results are obtained from a sample with 0.83 mm thickness and diameter 13.42 mm. The order of the obtained parameters are c_{11} = 108 GPa, e_{33} = 7,6 N/m2 and ε_{33} = 400. These first results must be validated using several equal samples, different geometries and mechanical measurements.

EFFECT OF TA ON STRUCTURE, MICROSTRUCTURE AND PROPERTIES OF K0.5NA0.5NBO3 CERAMICS SINTERED BY VARIOUS TECHNIQUES

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PZT and its derivatives exhibit a wide range of piezoelectric properties allowing their applications in transducers, actuators and sensors. However, due to the toxicity of lead for human health and environment, many studies are carried out on lead-free piezoelectric materials.

Among these materials, $(K,Na)NbO_3$ (KNN)-based solid solutions are promising candidates owing to their high dielectric, piezoelectric and mechanical characteristics shown by Saito et al. in 2004, followed by numbers of publications. However, reaching high density in this system appears difficult and remain an issue to overcome in order to consider applications. Tantalum substitution on the niobium site is effective in improving the piezoelectric properties but decreases significantly the grain size and also the densification of the ceramics.

In this study, $K_{0.5}Na_{0.5}Nb_{1-x}Ta_x$ (KNNT) (with x = 0.00, 0.05, 0.10, 0.20, 0.30, and 0.50) ceramics are prepared using conventional and spark plasma sintering techniques. XRD phase identification reveals an evolution from orthorhombic to tetragonal perovskite phase with the increase of tantalum amount. This result is confirmed by Raman spectroscopy. SEM observation and energy dispersive X-ray spectrometry analysis reveal a composite aspect of the ceramics showing some discontinuities in the solid solution. Enhancement of the piezoelectric properties is observed for both sintering techniques under tantalum effect but spark plasma sintering process leads to a significant improvement of the density up to 96 % and thus of the properties. High relative permittivity (ε_r = 805), piezoelectric charge coefficient (d_{33} = 160 pC/N) and piezoelectric coupling coefficient (k_p = 46 %) are obtained from the KNN ceramics substituted by tantalum.

HOMOGENIZED ELECTROELASTIC MODULI OF 1-3 PIEZOCOMPOSITE WITH VARIOUS PILLAR SHAPES

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Due to their enhanced properties with respect to conventional piezoelectric ceramics, 1-3 piezocomposite materials (i.e. piezoelectric rods aligned in a polymer matrix) have been predominant in transducer applications and the determination of their effective electroacoustic tensor has been the subject of numerous investigations. A model is proposed to predict the complete electroelastic moduli of 1-3 piezocomposites. The main aim of this model is to deliver precise effective elastic, dielectric and piezoelectric parameters while taking into account the real geometry of the composite. Various piezoelectric pillar shapes and spatial distribution were tested to assess the effect on the effective parameters. In order to homogenize the composite, slowness surfaces of bulk waves were computed in the large wavelength approximation using Finite Element method (ATILA Sofware). These numerical results were fitted using relations deduced from Christoffel's equation for wave propagation in piezoelectric media which takes into account the symmetry class of the composite. Moreover, these model predictions are discussed and compared with a fast Fourier transform [1] and a matrix method [2]. Computation was done with PZT4 and epoxy resin with volume fractions ranging from 10% to 70% for square, circular and triangle-shaped pillar geometries. A "staggered row" geometry with square pillars is also investigated. For all cases, the complete electroelastic moduli was obtained and successfully compared to the numerical estimates obtained with the FFT method. Our model and FFT based predictions yield identical results whilst matrix method results are in good agreement except for some parameters. For varying pillar geometry, related thickness mode coefficients are seen to be in agreement but notable differences appear for other coefficients (related to transverse modes) when the volume fraction reaches 70%. These results will allow to tend toward an optimization process to deliver new configurations for high values of several parameters such as e31 for energy harvesting applications.

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Modeling of the mechanical response of piezoelectric structures from millimeter to micrometer

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Background, Motivation, Hypothesis and Objectives:

With the development of micro and nanotechnologies, the research in the field of piezoelectric materials and new micro-electromechanical devices are getting much more inter-related. In this context, integrated structures based on piezoelectric thin films are widely investigated and their characterization become a crucial issue in the development of new applications. Previous works have addressed the development of experimental techniques to characterize the mechanical response of a piezoelectric thin film laid down a substrate. To support these investigations, 3D modeling based on the finite element method has been developed.

Statement of Contribution/Methods:

To complete our experimental approach, a numerical study based on the finite element method is carried out: 3D modelings of piezoelectric samples from bulk materials to thin films are examined. For each considered sample, a time dependent analysis and a frequency domain study are performed. From the simulations we obtain information on the effective piezoelectric coefficient, d33, of the active electro-material and on its impedance that are compared to experimental values.

Results, discussion and conclusion:

The ability to predict the mechanical response of piezoelectric samples from finite element modeling has been demonstrated and compared to experimental data. However, the difference between the modeling and the experiment increases as the size of the piezoelectric film decreases from millimeter to micrometer. It is experimentally known that thin films have different parameters when compared to bulk materials and this differences have to be taken into account as well as other effects such as substrate clamping or electrode size.

Optimization of synthesis of Bi4Ti3O12 platelets for templated grain growth of ceramics

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Nowadays, piezoelectric materials are used in a large number of devices and ultrasonic applications, such as underwater sonar systems and medical imaging. The most popular material used for this purpose is $Pb(Zr,Ti)O_3$ (PZT), which represents a number of health and environmental problems due to the lead content [1]. So the current efforts are concentrated in the elaboration of lead-free piezoelectric materials with competitive properties compared to those of PZT. One of the attractive possibilities for this goal is the templated grain growth (TGG) of ceramics [2]. The fabrication process consist in the shaping, by tape-casting, and then sintering of a slurry containing templates, which are oriented by viscous forces, giving then a textured material with improved properties compared to those of an isotropic ceramic [3]. Thus one of the key points of this method is the synthesis of suitable anisotropic templates with high aspect ratio, allowing their orientation during tape casting process. For the synthesis of anisotropic $BaTiO_3$ templates, we selected a twostep synthesis, taking $Bi_4Ti_3O_{12}$ as intermediate compound [3]. Indeed, $Bi_4Ti_3O_{12}$ is (i) intrinsically highly anisotropic, (ii) can be easily obtained in platelets form and (iii) can be converted into $BaTiO_3$ platelets by a topochemical conversion. The secondary phases present in the final product can play an important role in the final properties of the sintered material [4]. Thus the aim of this study is to optimize the elaboration process of this precursor, by changing synthesis parameters. $Bi_4Ti_3O_{12}$ was synthesized by a molten salts process, using different amounts of Bi2O3, different salt: oxide ratios and several synthesis temperatures. The obtained material was then washed and characterized by XRD and SEM. After optimization of the synthesis parameters, the molten salt process allows obtaining $Bi_4Ti_3O_{12}$ templates with an excellent purity, a plate-like morphology and a main size around 50 µm.

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Reduction of PbO loss in PZT-cobalt ferrite composites through quite-fast sintering and its quantification by means of XRD analysis.

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Nowadays, considerable efforts have been devoted to design and control the fabrication of multifunctional materials in order to fulfil the needs of modern technology for novel sensors, microwave devices, energy harvesting, photovoltaic technologies, solid-state refrigeration, data storage recording technologies and multiferroic random access multistate memories (MFRAM) [1]. Particulate ceramic composites are low cost, simple production technology, higher strain mediated magnetoelectric coupling (since electric order phase/magnetic phase interface density can be higher) and easy control of electrical and magnetic properties if the ferroelectric phase and the ferromagnetic one are mixed in a favourable proportion under the percolation threshold of the ferromagnetic phase. A great research effort is in progress to improve the fabrication of PZT–CoFe2O4 (PZT–CF) composites due to the excellent piezoelectric properties showed by the PZT material class and the large magnetostrictive coefficient of the CF. Unfortunately, during the sintering process particulate PZT-CF composites, side reactions do occur that are detrimental to the properties of the so-obtained material. In this study, we have avoided such reactions and PbO loss by setting a quite-fast sintering process [2]. The extent of PbO loss was determined by means of XRD analysis of the densified samples taking into account the amount of ZrO2 and the variations of the perovskite's tetragonality [2]. The calculated PbO loss values are in agreement with the final density and the microstructure of PZT-CF composites. In particular, microstructural characterization showed that CF grain size distribution can be mono- or bi-modal, and CF overgrowth was found to affect the coercivity of the material [3].

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DIGITAL IMAGE CORRELATION FOR PIEZOELECTRIC STRAINS CHARACTERISATION

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Piezoelectric materials are widely used in sensors, actuators or even energy harvesting applications. Designing such devices properly requires to fully control the material constitutive laws. This is especially true since new piezoelectric systems are progressively asked to work in harsh environmental conditions (high electric field, stress or temperature). Consequently, material characterisation is a crucial step for piezoelectric systems design. However, the characterisation of piezoelectric electromechanical behaviour is difficult due to the possible heterogeneity of materials and to the complexity of boundary conditions. In this context, Digital Image Correlation (DIC) is a promising tool since it is a full-field strains measurement method. In addition, this field measurement is carried out for the longitudinal and transversal strains simultaneously and thus, gives access to test conditions (strains homogeneity) and sample in-plane properties. In this work, a 2D DIC bench was developed to characterise piezoelectric electro-mechanical behaviour with the capability of mastering test conditions. The proposed experimental set up uses a long distance microscope uestar M100 and a low speed 9 megapixels camera. This equipment was chosen to focus on millimetre thickness sized sample characterisation. In these conditions, we show how boundary conditions and material properties homogeneity influence the characterisation process.

Keywords: piezoelectric strain strain field electro-mechanical behaviour ferroelectric 2D-DIC.

INFLUENCE OF KBT ON THE STRUCTURAL AND ELECTRICAL PROPERTIES OF BCZT CERAMICS

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Barium titanate ceramics modified by calcium and zirconium dopants, denoted BCZT, exhibit promising piezoelectric properties with a piezoelectric charge coefficient, d33, in the region of 600 pC/N being reported at room temperature. The functional properties of such materials are affected by temperature-instability, due to the occurrence of polymorphic phase transformations and a relatively low Curie temperature. The need for high sintering temperatures for densification of BCZT is also a serious concern, particularly when considering the compatibility with certain substrates for thick film deposition. It has been proposed that the incorporation of bismuth-based perovskite compounds, such as $BiFeO_3$ and $Bi(Mg_{0.5}Ti_{0.5})O_3$ into BCZT could both increase the temperature-stability of properties and improve the sintering behavior. The aim of the present study was to determine the effects of adding $(K_{0.5}Bi_{0.5})TiO_3$ (KBT) into BCZT solid solutions having 2 different calcium titanate contents. The effects of increasing KBT content, in the range from 0 to 10 mol%, on phase transition behaviour, densification, microstructure, dielectric, ferroelectric and piezoelectric properties of these ceramics were systematically investigated. Examination of XRD patterns obtained at room temperature reveal broadening of the {111}pc and splitting/overlapping of the {200}pc diffraction peaks, suggesting that both rhombohedral and tetragonal phases co-exist at room temperature. The results of dielectric permittivity-temperature measurements demonstrate that the incorporation of KBT into solid solution with BCZT suppresses the Curie peak, associated with the tetragonal to cubic transformation, strongly and shifts the lower temperature anomaly, associated with the rhombohedral to tetragonal transformation, to below room temperature. Ferroelectric hysteresis measurements show significant increases in polarization and coercive field at low KBT contents, but a subsequent loss of remanent polarization values for KBT contents above 5%. It is also demonstrated that the addition of KBT enhances the densification behavior of these materials.

EFFECT OF DC BIAS AND PO2 ON THE CONDUCTIVITY OF UNDOPED-BATIO3 AND Y-DOPED BATIO3 CERAMICS

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Equilibrium electrical conductivity of of both $BaTiO_3$ and Y-doped $BaTiO_3$ Ceramics were studied in terms of Y_2O_3 substitution for A, B, AB sites. Samples of $BaTiO_3$ with low concentrations (x=0, 0.0001, 0.001 and 0.01) of Y_2O_3 were synthesized from powders. (Acceptor, self and donor compensations)-doped $BaTiO_3$ powders of formulas: $BaTi_{1-x}Y_xO_{3-x/2}$, $Ba_{1-x}Ti_{1-x}Y_{2x}O_3$, $Ba_{1-x}Y_xTiO_3$ were prepared by solid state method. Pellets were sintered by conventional sintering (CS) which heated in air and fired at 1000°C–1550°C and either quenched or slow-cooled to room temperature. Structural and microstructural properties were studied by XRD, SEM, EDX, Raman and IS. The electrical conductivity of both $BaTiO_3$, $BaTi_{1-x}Y_xO_{3-x/2}$ and $Ba_{1-x}Ti_{1-x}Y_{2x}O_3$ Ceramics shows nonohmic, low-field characteristics. The electrical conductivity increases with time on application of a small dc bias voltage. The conductivity increase is reversible on removal of the dc bias. This effect appears to be caused by departures from local electroneutrality in the defect structure of nonstoichiometric $BaTiO_3$ which are reduced by electron transfer on application of a dc bias, leading to a more conducting, low-level excited state in which holes associated with underbonded oxygens, presumably as O^- ions, are the principal charge carriers. Ceramics gradually return to their ground state in two stages on removal of the dc bias and the conductivity decreases. Oxygen-deficient sample quenched from 1400°C is n-type with increasing the conductivity and a decrease in activation energy whereas, p-type was observed for sample quenched below 1400°C or slow cooled. As overall, samples show a decrease in resistance with increasing dc bias voltage and an increase in resistance with decreasing pO2. The decrease in conductivity with decreasing pO2 is consistent with p-type conduction mechanism.

STRUCTURAL, DIELECTRIC, PIEZOELECTRIC AND FERROELECTRIC PROPERTIES OF PSZT- PMNN CERAMICS

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We report our studies on structural, dielectric, ferroelectric and piezoelectric behavior of $Pb_{1-x}Sr_x[(Zr_{0.52}Ti)0.95(Mn_{1/3}Nb_{2/3})_{0.05}]O_3$,(PSZT- PMnN) ceramics with x = 0.0, 0.025, 0.050 and 0.075 prepared by a semi-wet route. X -ray diffraction (XRD) patterns have been recorded at room temperature, which reveals that PSZT-PMN ceramics are single phase in nature. Rietveld analysis of the powder diffraction data shows the presence of a morphotropic phase boundary (MPB) of PSZT-PMN ceramic near the composition $x \geq 0.050$. The structural change takes place from tetragonal with P4mm space group to rhombohedral with R3c space group at $0.050 \leq x \leq 0.075$. Raman spectroscopy studies also confirm the existence of MPB for $x \geq 0.050$. It has been shown that at room temperature dielectric, ferroelectric and piezoelectric response are maximum for the composition with x = 0.050. It has been shown that the transition temperature decreases significantly with increasing of Sr^{2+} substitution in PZT-PMN ceramic. The impedance spectroscopy study shows the presence of both bulk and grain boundary effect in PSZT-PMN material and also shows Negative Temperature Coefficient of Resistance (NTCR). The bulk conductivity exhibits Arrhenius type thermally activated hopping process which is supported by the AC conductivity behavior as a function of frequency and temperature.

Phase transformations and chemical heterogeneity in KNNS-BNKZ piezoceramics

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Potassium sodium niobate-based ceramics are a promising type of leadfree piezoceramics that could potentially be used for high temperature applications due to their possession of relatively high Curie temperatures as well as high piezoelectric charge/strain and voltage coefficients. Recently, novel KNN-based ceramics have been developed by forming solid solutions of $K_{0.48}Na_{0.52}Nb_{0.95}Sb_{0.05}O_3$ with $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}ZrO_3$ (KNNS-BNKZ); Promising piezoelectric properties, with a d_{33} in the region of 500 pC N-1 at room temperature, were attributed to the coexistence of rhombohedral and tetragonal phases. However, the nature of the coexisting phases and the temperature-dependence of functional properties is still unclear from previous research. The aim of this investigation was to determine the influence of BNKZ on the crystal structure and functional properties of KNN, by preparing (1-x)KNNS-(x)BNKZ ceramics with x=0.01 and 0.02, using the conventional mixed-oxide method.

High resolution synchrotron X-ray powder diffraction (SXPD) measurements reveal that the addition of BNKZ into KNNS ceramics at levels of 1 and 2 mol% leads to an increase of the rhombohedral-tetragonal and a reduction of the orthorhombic-tetragonal transition temperature. The phase transformation regions are also significantly broadened, leading to the coexistence of phases over wide ranges of temperature. By combining the results of the SXPD measurements with microstructural examination using SEM, evidence is also found for the occurrence of chemical heterogeneity, which could provide an additional means to control the functional properties. The structural observations are correlated with changes in the dielectric properties, obtained as permittivity-temperature plots, and variations in the polarisation and coercive field values, obtained from measurements of the ferroelectric hysteresis loops as a function of temperature. Results obtained for the nonlinear dielectric and piezoelectric properties of these materials will also be discussed

DIELECTRIC, ELASTIC AND PIEZOELECTRIC COEFFICIENTS INCLUDING ALL LOSSES OF LEAD-FREE $BA_{1-x}CA_xTI_{0.9}ZR_{0.1}O_3$ CERAMICS

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$Ba_{1-x}Ca_xTi_{0.9}Zr_{0.1}O_3$ (BCTZ) solid-solution system is attracting a great deal of interest nowadays as lead-free ferro-piezoceramics. Recently it was possible to achieve homogeneous and dense ceramics with optimum electric performance using moderate synthesis and sintering temperatures [1]. Moreover, the electrical characterization is accomplished with a set of independent piezoelectric, elastic and dielectric coefficients by means of different symmetry modes: radial, thickness and shear. BCTZ materials shows a temperature and frequency dependence to dielectric permittivity as well as ferroelectric and piezoelectric characteristics. These aspects must be taken into consideration when designing transducers [2]. A number of alternative methods of analysis for the complex impedance curve, at resonance of piezoelectric ceramics, were developed in the last twenty years in order to obtain material parameters in complex form [3]. The automatic iterative method developed at Spanish CSIC was implemented for all the resonances and resonator shapes needed for the determination of all piezoelectric ceramic materials including losses, namely: radial and thickness extensional resonances of thin disk, thickness poled; Shear resonance of a plate, thickness poled; and length extensional resonance of a long bar resonator, length poled. 3-D modeling carried out by Finite Element Analysis (FEA), based on the matrix of material properties obtained with such a characterization method was used as quality criteria of this [4]. Measurements of material parameters at resonance were performed on ceramic shear plates, thickness-poled, and results were discussed in terms of the loss mechanisms of the ceramic.

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$Ba_{1-x}Ca_xTiO_3$ MICROWAVE-ASSISTED HYDROTHERMAL SYNTHESIS

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This communication reports the microwave-assisted hydrothermal synthesis of $Ba_{1-x}Ca_xTiO_3$ (BCT) and their piezoelectric properties. Using this synthetic method we can obtain materials in shorter period of time compared with conventional methods [1]. Particularly, under microwave irradiation we can isolate the desired phase in few minutes instead some days (*i.e.*, employing conventional solid state methodologies) [2].

X-ray diffraction (XRD) of the as-prepared material exhibits few low-intensity patterns corresponding to the $CaTiO_3$ impurity. This implies phase segregation and, thus, absence of solid solution. Nevertheless, a posterior conventional thermal treatment at 1000 ºC for a short period of time (2 h) originates the desired solid solution ($Ba_{0.9}Ca_{0.1}TiO_3$) (fig. 1), which crystalizes in the symmetry group *P*4*mm* with the ratio c/a = 1.0044. The high reactivity is related with the nanometric character of the obtained particles, with diameters in the range of 20-30 nm (calculated applying the Debye-Scherrer formulae). After thermal treatment, particles becomes larger (from 20-30 to approximately 80 nm; fig. 2). Piezoelectric properties of the sintered pellets, with different solid solutions for BCT and distinct amounts of Ca (x = 0.05, 0.1, 0.15 and 0.2), have been recently studied and the result processing is in progress. However, It is expected that the better piezoelectric properties comes from the phases with c/a ratio > 1 [3].

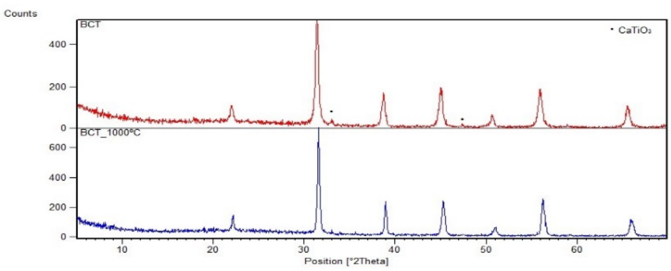

***Fig. 1**: XRD patterns of BCT before and after the thermal treatment*

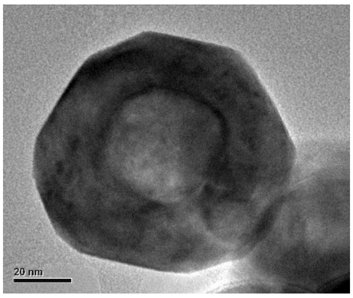

***Fig. 2**: TEM image from a* $Ba_{0.9}Ca_{0.1}TiO_3$ particleafter the thermal treatment

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GROWTH AND CHARACTERIZATION OF GE-CONTAINING QUARTZ CRYSTALS

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Objectives. The objective of investigation was developing of reliable laboratory method for growing of Ge-containing quartz crystals. Previous experimental and theoretical works [1-4] allow to consider the Gecontaining quartz crystals as perspective piezoelectric material which can lead to improvement of known and to creation of new more effective electronic devices working at increased and high temperatures.

Methods. The crystals of high germanium α-quartz were grown using hydrothermal method of temperature gradient at temperatures from 240 to 700°C and pressures from 30 to 150 MPa in autoclaves 280-1500 ml. The aqueous solutions of NH4F were used as mineralizers. The mixture of alpha quartz and germanium oxide was served as nutrient. Duration of runs was from 1 to 3 months.

Results. The results of the experimental work have shown that major factors influencing formation of homogenous crystals, are mineralizer concentration in aqueous solutions, germanium oxide content in nutrient, temperature, and crystallographic directions of as growth crystals. The same factors determine growth rates of crystals, their morphology and degree of germanium distribution. The most homogenous crystals with the GeO_2 content of 10-14 wt. % were grown in fluoride solution on seeds parallel to prism x {11-20}, pyramid s {11-21}, negative z {01-11} and positive r {10-11} rhombohedra faces at temperatures 520-600°C and pressure 70-150 MPa.

Discussion and conclusions. This study have allowed to develop a reliable laboratory method of growth of quartz with the GeO_2 content Ð¾f 10–14 wt. % in hydrothermal fluoride solutions as well to define conditions of maximum capture and uniform distribution of germanium in as grown crystals.

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LEAD-FREE STRONTIUM AND LITHIUM DOPED BISMUTH SODIUM TITANATE CERAMICS FOR HIGH POWER ENERGY STORAGE

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Above depoling temperature Td, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) shows relaxor ferroelectric behaviour which is good for high power energy storage in capacitances. The Td of BNT is above 100 °C. To use BNT for energy storage application, the BNT-based materials should show relaxor behaviour at room temperature. In this paper, single phase Li and Sr cosubstituted BNT ceramics were prepared. The materials show relaxor ferroelectric loops at room temperature with energy density up to 0.6 J/cc, which can be attributed to the phase transitions produced by chemical pressure that was induced by co-substitution at A-site in BNTbased ceramics.

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