Electroceramics for End Users XII: PIEZO2023 with Ferroelectrics UK

Mazumdar-Shaw Advanced Research Centre
University of Glasgow
5 – 8 November 2023

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Piezo INSTITUTE The European Institute of Piezoelectric Materials and Devices
IOP Institute of Physics
I·M3
ROYAL SOCIETY OF CHEMISTRY
Engineering and Physical Sciences Research Council
UKRI UK Research and Innovation
Office of Naval Research GLOBAL Science & Technology

Welcome from the Co-Chairs

The conference series, Electroceramics for End Users, has been running for 20 years, principally under the auspices of the Piezo Institute, this year supported by UK Ferroelectrics.

The origins of the Piezo Institute are found in the European Poled Ceramics, “POLECER” network, launched in 2001 with the aim to identify key areas for development within polar electroceramics, coordinate R&D activities in the field, communicate results to industrial users, and support emerging technologies leading to new products that meet the latest environmental standards.

UK Ferroelectrics was founded in the same year with the aim to increase the opportunities for information exchange and collaboration between UK academic and industrial groups working with or using ferroelectric materials, with many members shared with the POLECER network. It is thus very timely for the two networks to come together again to share information at ECEUXII.

The technologies that the Piezo Institute and UK Ferroelectrics support are used in applications including medical ultrasound imaging and therapy, underwater sonar and infrastructure and structural maintenance. Further uses are found in areas as diverse as mobile phone communications, intruder detection and touchless robotics.

Medical ultrasound is of particular note as its implementation in the form of obstetric ultrasound was pioneered by Prof. Ian Donald, Regius Professor of Obstetrics and Gynaecology at the University of Glasgow. His paper, “Investigation of Abdominal Masses by Pulsed Ultrasound”, in The Lancet in 1958, used apparatus developed in the research department of Messrs. Kelvin Hughes Ltd., Glasgow, who “cooperated in the research with generosity and enthusiasm”.

Topics of particular contemporary interest include sustainability, with a specific interest in the removal of lead, as a toxic material, from many common piezoelectric devices.

Befitting the international nature of the conference, delegates this year come from across Europe, including Norway, France, Italy, Portugal, Germany, the Czech Republic and Romania, amongst others. We also welcome visitors from Japan, China and the USA and have an excellent representation from the UK, including Bath, Leeds, Sheffield, St Andrews and, of course, Glasgow.

We are fortunate to have use of the Mazumdar-Shaw Advanced Research Centre, “the home of collaborative research, innovation and discovery at the University of Glasgow.” This beautiful venue has the ambition to encourage creativity, support ideas from different disciplines and enable transformational programmes that unlock research that was previously out of reach.

Into the ARC this week we welcome ECEUXII delegates who are scientists and engineers from universities and industry at all stages in their careers, from undergraduate students to established professors and from early career industrial employees to senior directors. These individuals represent the electroceramics industry, itself made up of a healthy mixture including startup companies, established medium-sized companies and multinationals. All are welcome!

Sandy Cochran, Maxime Bavencoffe, Sebastiano Garroni and Laura Stoica
November 2023

Acknowledgements

The Organising Committee of ECEUXII is grateful for support from: the UK Engineering and Physical Sciences Research Council, part of UK Research and Innovation; the US Office of Naval Research – Global; the Piezo Institute; UK Ferroelectrics; the UK Institute of Physics; the Royal Society of Chemistry; and the UK Institute of Materials, Minerals and Mining. We are also grateful to the University of Glasgow for providing access to the Mazumdar-Shaw Advanced Research Centre.

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Winter School Programme

Sunday, 5th November

Start Time	End Time	Title	Tutor	Location
0850	**0900**	Opening of Winter School	Koko Lam	University of Glasgow, UK
0900	**1000**	Linear characterization of piezoceramics	Lorena Pardo	Materials Science Institute of Madrid, Spain
Break: 1000 - 1020				
1020	**1120**	Elaboration of lead-free piezoelectric thick films by aerosol deposition	Pascal Marchet	Institut de Recherche sur les Céramiques, Université de Limoges, France
Break: 1120 - 1140				
1140	**1240**	From suspensions to thick film structures	Danjela Kuscer	Jožef Stefan Institute, Slovenia
Lunch: 1240 - 1340				
1340	**1440**	Applications of electroceramics	Koko Lam	Glasgow University, UK
Break: 1440 - 1500				
1500	**1600**	Key issues for the design of efficient piezoelectric generators	Guylaine Poulin-Vittrant	CNRS - GREMAN, France
Break: 1600 - 1620				
1620	**1720**	Getting jiggy, using the inherent properties of a ferroelectric to deliver chemical change	Steve Dunn	London South Bank University, UK
1720	**1730**	Closing remarks	Koko Lam	University of Glasgow, UK
Close: 1730				

Oral Presentation Programme

Monday, 6th November

Welcome / Conference Opening: 0850 - 0900				
Plenary Session M1: Industry Presentations				
Chair: Laura Stoica				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
0900	**1000**	PLENARY: Ultrasound. Integrated. Everywhere.	Dave Hughes	Novosound Ltd., UK
1000	**1020**	INDUSTRY: Lithography-based additive manufacturing of piezoceramic materials	Julia Rabitsch	Lithoz GmbH, Austria
1020	**1040**	INDUSTRY: Applications, Performance and Industrialization of Textured PMN-PT-PZ Ceramics	Charles Mangeot	CTS Ceramics Denmark, Denmark
1040	**1100**	INDUSTRY: Piezoelectric properties of BNT-BT, processing, and potential applications	Tanya Einhellinger-Mueller	CeramTec GmbH, Germany
Break: 1100 - 1130				
Parallel Session M2A: Fundamentals of Piezo- and Ferroelectrics				
Chair: Ge Wang				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
1130	**1150**	Nonlinear piezoelectric response of Sm-doped $Pb(Mb_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ relaxor-ferroelectric ceramics	Tadej Rojac	Jozef Stefan Institute, Slovenia
1150	**1210**	Structural and Electrical Properties of $Sr_xNa_{1-2x}NbO_3$ Polycrystalline Ceramics	Thomas Hooper	University of Sheffield, UK
1210	**1230**	Dielectric behavior of lead-free ferroelectrics at Terahertz frequency	Man Zhang	University of Leeds, UK
1230	**1250**	INVITED: Bismuth ferrite solid solutions: new pathways to microstructural and functional property engineering	David Hall	University of Manchester, UK
Parallel Session M2B - Sponsored by ONR-G: Piezoelectric Materials				
Chair: Sarah Guerin				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
1130	**1210**	KEYNOTE: Piezoelectric polymers for energy, sensing and biomedical applications	Sohini Kar-Narayan	University of Cambridge, UK
1210	**1230**	Porous bacterial nanocellulose films as a matrix for piezoresponsive applications	Fernando Sá	Universidade de Aveiro, Portugal
1230	**1250**	Multiaxial Ferroelectricity and Piezoelectric Energy Harvesting from Organic Plastic Crystals	Malla Reddy	(IISER) Kolkata, India

Lunch: 1250 - 1400				
Parallel Session M3A - Sponsored by The Piezo Institute: Photoferroelectrics and Piezocatalysts				
Chair: Steve Dunn				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
1400	**1420**	INVITED: Ferroelectric nanocomposites for enhanced solar energy conversion	Joe Briscoe	Queen Mary University of London, UK
1420	**1440**	$BaTiO_3$/Pt Hybrid Material for Enhanced Piezocatalytic H_2 Production	Guru Prasanna	London South Bank University, UK
1440	**1500**	Laser induced crystallization of ferroelectric glass ceramic for water cleaning applications	Chirag Porwal	IIT Mandi, India
1500	**1520**	Strain Mediated Photovoltaic Properties in Ferroelectric Nanocomposites	Emanuele Palladino	Queen Mary University of London, UK
1520	**1540**	Role of Structural and Orbital Characteristics on the Ferroelectric Photovoltaic Response	Shanmuga Priya	IIT Madras, India.
1540	**1600**	Opto-electronic control domain manipulation in ferroelectric oxides	Subhajit Pal	Queen Mary University of London, UK
Parallel Session M3B - Sponsored by ONR-G: Energy Harvesting				
Chair: Guylaine Poulin-Vittrant				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
1400	**1440**	KEYNOTE: Processing of Smart Porous Electro-ceramic Transducers (ProSPECT)	Chris Bowen	University of Bath, UK
1440	**1500**	Damage analysis of Functionally Graded Piezo Electric Materials (FGPM)	Jihed Zghal	Paris Nanterre University, France
1500	**1520**	Development of piezoelectric films based on PVDF and PVDF/ $BaTiO_3$ with enhanced performance for Energy Harvesting applications	Cintia Mateo	AIMEN Technology Centre, Spain
1520	**1540**	Relevant parameters to increase the harvested energy of a ZnO nanowires-based nanogenerator	Emmanuel Dumons	Université de Tours, France
1540	**1600**	A comprehensive energy flow model for piezoelectric energy harvesters: opening the black box	Zihe Li	University of Bath, UK
Break: 1600 - 1620				

Parallel Session M4A - Sponsored by UK Ferroelectrics: Advanced Characterisation				
Chair: Subhajit Pal				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
1620	**1640**	Towards spatially resolved measurements of thermal transport in ferroelectrics using Scanning Thermal Microscopy	Raymond McQuaid	Queen's University Belfast, UK
1640	**1700**	Understanding micro electrical contact measurements - an experimental and modelling study	Julian Dean	University of Sheffield, UK
1700	**1720**	Versatile electromechanical characterization of PVDF in changing environmental conditions	Markys Cain	Electrosciences Ltd., UK
1720	**1740**	The role of A site vacancies in the formation of temperature stable dielectrics in the $NaNbO_3$ - $La_{1/3}NbO_3$ solid solution	James Killeen	University of Sheffield, UK
1740	**1800**	In situ Characterisation of Ephemeral p-n junctions inside Ferroelectric Domain Walls	Kristina Holsgrove	Queen's University Belfast, UK
Parallel Session M4B: Lead Free Materials				
Chair: Tadej Rojac				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
1620	**1640**	Functional Inorganics Driven by Immiscibility	Yizhe Li	University of Manchester,
1640	**1700**	Revisiting the equilibrium symetries at the "MPB" of the BNBT solid solution system and their influence on the multifunctional properties	Lorena Pardo	Centro de Investigación en Materiales Avanzados, Mexico
1700	**1720**	High-performance BCZT Piezoelectric ceramics achieved by ultra-low temperature processing	Marzia Mureddu	University of Sassari, Italy
1720	**1740**	Evolution of structural, ferroelectric and piezoelectric properties of spark plasma sintered lead free KNN-Li/Ta ceramics	Damien Brault	Université de Tours / CNRS - INSA CVL, France
1740	**1800**	Insights into the early size effects of lead-free high-sensitivity piezoelectric $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ across the micron range	Harvey Amorín	ICMM - CSIC, Spain
Reception: 1800 - 2000				

Tuesday, 7th November

Start Time	End Time	Title	First Author	Contact Email
Plenary Session T1: Plenary Presentations				
Chair: Sandy Cochran				
0900	**1000**	PLENARY: Inside Piezoelectricity: the structural origins of electromechanical coupling	Andrew Bell	University of Leeds, UK
Plenary Session T1B: Industry Presentations				
1000	**1020**	INDUSTRY: Performance of KNN in resonant applications	Sandra Niederschuh	PI Ceramic GmbH, Germany
1020	**1040**	INDUSTRY: Research and development of lead-free ceramics for acoustic transducers	Ana Borta-Boyon	Thales Research and Technology, France
1040	**1100**	INDUSTRY: Applicability of Lead Free Piezoelectrics for Ultrasonic Evaluation	Peter Cowin	Ionix Advanced Technologies, UK
Break: 1100 - 1130				

Start Time	End Time	Title	Contact Author	Location
Parallel Session T2A: Piezoelectric Materials and Processing				
Chair: Sylvia Gebhardt				
1130	**1210**	KEYNOTE: Ferroelectric Ceramic Thick Films: Processing and Applications	Danjela Kuscer	Jožef Stefan Institute, Slovenia
1210	**1230**	Textured Lead-free Porous Piezoelectric Single Crystal-like Ceramics	Ajeet Kumar	University of Bath, UK
1230	**1250**	INVITED: Enhanced properties of relaxor-PT single crystals poled under an alternating current electrical field	Xiaoning Jiang	North Carolina State University, USA

Parallel Session T2B: Thin Films				
Chair: Kristina Holsgrove				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
1130	**1150**	Ferroelectric Properties of Halide Perovskite Molecular Semiconductor Thin Films	Lethy Jagadamma	University of St Andrews, UK
1150	**1210**	Solution deposition of magnetoelectric (1-x)$BiFeO_3$-x$PbTiO_3$ ferroelectric films on Ni-substrates	Lourdes Calzada	Instituto de Ciencia de Materiales de Madrid, Spain
1210	**1230**	Tailoring Grain and Domain Morphology in Ferroelectric Aurivillius Phase Thin Films via Controlled Supersaturation Conditions	Debismita Dutta	University College Cork, Ireland
1230	**1250**	Flexible Piezoelectric Nanogenerators based on Halide Perovskite Thin Films	Nirmal Raj	University of St Andrews, UK

Lunch: 1250 – 1345

Public Engagement Display led by Elmergue Germano,
UK EPSRC Centre for Doctoral Training in Future Ultrasonic Engineering

Plenary Session T3 - Sponsored by UK Ferroelectrics: Piezoelectric Material Applications				
Chair: Sebastiano Garroni				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
1345	**1445**	PLENARY: Piezoelectric materials as active biomedical implants – a "two-body problem"	Julia Glaum	NTNU, Norway

Short Break: 1445 - 1500

Parallel Session T3A - Sponsored by The Piezo Institute: Piezoelectric Composites				
Chair: Sakineh Fotouhi				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
1500	**1520**	Elaboration and evaluation of Ni/$BaTiO_3$ functionally piezoelectric graded material properties	Baraa Saidani	LEME, France
1520	**1540**	PVDF-BST-based Magneto-electric Flexible Composites	Roxana Patru	National Institute for Materials Physics, Romania
1540	**1600**	Curie temperature manipulation to improve die-lectric and piezoelectric properties of $BaZr_{0.15}Ti_{0.85}O_3$ ceramics	Lavinia Curecheriu	University of Iasi, Romania

Parallel Session T3B: Thick Films				
Chair: Markys Cain				
Start Time	**End Time**	Title	Contact Author	Location
1500	1520	Screen-printed lead-free, low-cost piezoelectric composites for posture monitoring	Zois Michail Tsikriteas	University of Bath, UK
1520	1540	Impact of a substrate layer on piezoelectric coefficients	Corentin Camus	LGEF at INSA de Lyon, France.
1540	1600	INVITED: Fabrication and Application of Piezoceramic Thick Film Sensors for Process Monitoring of Cutting Tools	Sylvia Gebhardt	Fraunhofer IKTS, Germany
Break: 1600 - 1640				
Parallel Session T4A: Processing of Piezoceramics				
Chair: Kyle Webber				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
1640	**1720**	KEYNOTE: $BaTiO_3$ ceramics by Cool-SPS at 600°C: Towards more sustainable lead-free ceramics?	Michael Josse	Universite de Bordeaux, France
1720	**1740**	Behind the enhanced electrical performance of Flash sintered potassium sodium niobate ceramics	Oleksandr Tkach	University of Aveiro, Portugal
1740	**1800**	INVITED: New Dielectric Ceramics with Ultralow Sintering Temperatures and Dielectric Loss for Passive Integration	Hong Wang	Southern University of Science and Technology, China
Parallel Session T4B - Sponsored by The Piezo Institute: Piezoelectric Materials				
Chair: Hamideh Khanbareh				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
1640	**1700**	INVITED: Piezoelectric Biomolecules for Lead Free, Reliable, Eco Friendly Electronics	Sarah Guerin	University of Limerick, Ireland
1700	**1720**	Piezoresponsive biocomposites	Paula Ferreira	University of Aveiro, Portugal
1720	**1740**	Micro and macro electromechanical characterization of chitosan films	Dayana Guzmán Sierra	University of Aveiro, Portugal
1740	**1800**	3D-printed Polymer Composite Devices Based on a Ferroelectric Chiral Ammonium Salt for HighPerformance Piezoelectric Energy Harvesting	Supriya Sahoo	Indian Institute of Science Education and Research, India
Break: 1800 - 1900				
Dinner / Ceilidh at Oran Mor, Byres Road: 1900 - 2300				

Wednesday, 8th November

Parallel Session W1A - Sponsored by UK Ferroelectrics: Capacitor Materials				
Chair: Man Zhang				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
0900	**0920**	Strategies for Optimising Energy Storage Properties in Electroceramics	Ge Wang	University of Manchester, UK
0920	**0940**	Antiferroelectric-like Tetragonal Tungsten Bronzes for Capacitor Applications	Kerry A. McMahon	University of St Andrews, UK
0940	**1000**	Lead-free $BiFeO_3$ and $AgNbO_3$-based ceramics for dielectric energy storage capacitors	Zhilun Lu	University of Leeds, UK
1000	**1020**	Dielectric behavior of high entropy ferroelectrics	Haixue Yan	QMUL, UK
Parallel Session W1B: Lead-free Materials - Applications				
Chair: Koko Lam				
Start Time	**End Time**	**Title**	**Contact Author**	**Location**
0900	**0920**	Enhanced piezoelectric properties and ageing behavior in highly aligned porous bismuth ferrite-barium titanate ceramics.	Bastola Narayan	University of Bath, UK
0920	**0940**	Design, Testing, and Comparative Analysis of Lead-Free KNN-NTK and PZT Piezoceramics in a Time-of-Flight Flowmeter Application	Baltramiejus Andrijaitis	CTS Corporation, Czech Republic
0940	**1000**	Development of Pb-free ceramics for various piezo applications	Pravin Varade	IIT Bombay, India
1000	**1020**	Qualification of Modified $(Ba,Sr)(Sn,Ti)O_3$ for Electrocaloric Components Fabrication	Christian Molin	Fraunhofer IKTS, Germany
Break: 1020 - 1100				
Plenary Session W2 - Sponsored by ONR-G: Thick Films				
Chair: Maxime Bavencoffe				
Start Time	**End Time**	**Title**	**Contact Author**	
1100	**1200**	PLENARY: Unlocking the Piezoelectric Response of Ceramic Thick Films	Kyle G. Webber Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany	
Panel Session W3 - Sponsored by UK Ferroelectrics: The Future				
1200	1255	**Electroceramics - the Next 10 Years** **Chair - James Roscow, with Hong Wang, Markys Cain and Kyle Webber**		
Conference Close / Goodbye: 1255 - 1300				
Lunch: 1300 - 1400				
University of Glasgow Lab Tours: 1400 - 1600				

Poster Presentations

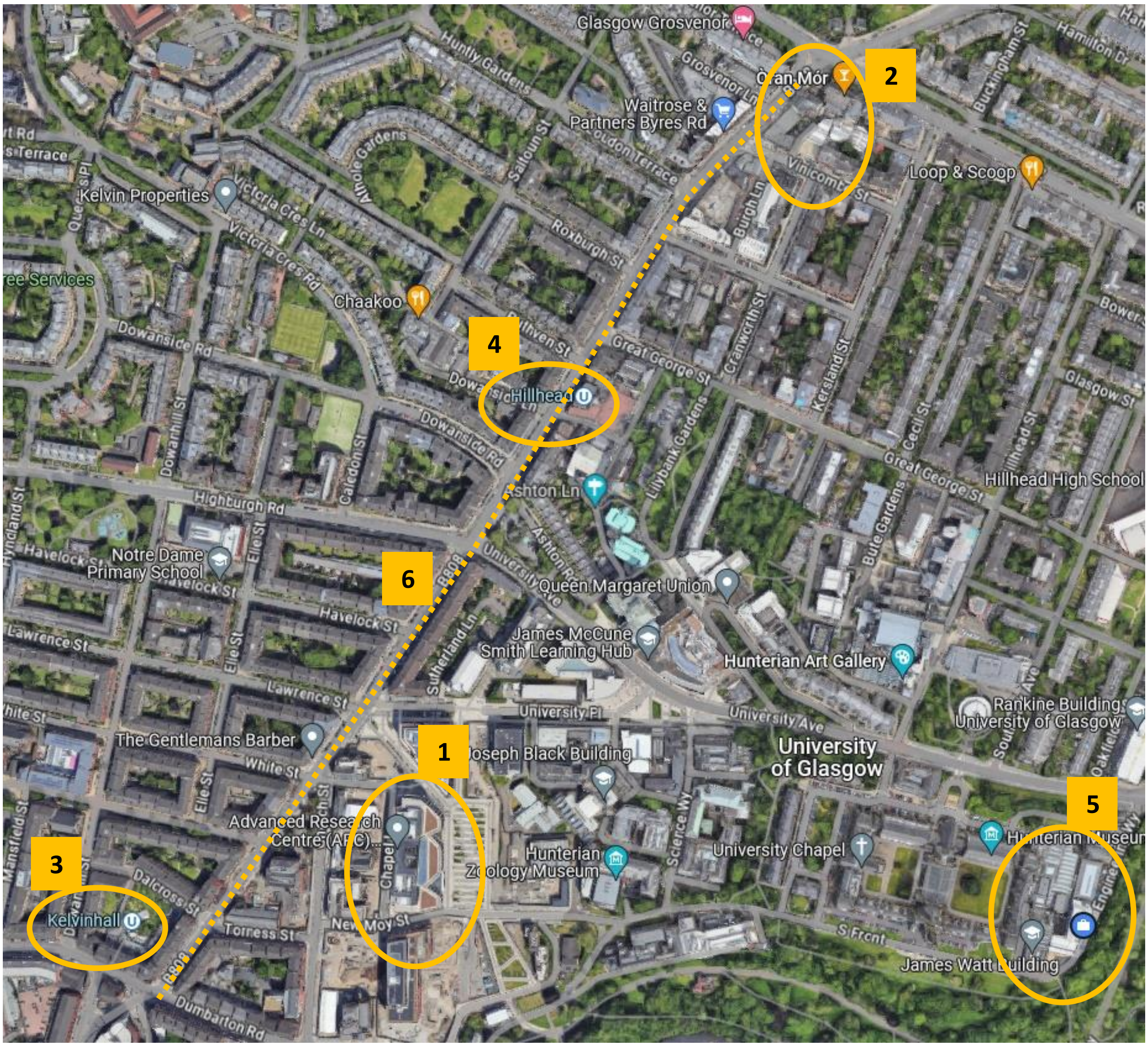
All posters will be displayed from Monday to Wednesday

Session	Presentation Number / Title	Contact Author	Location
P1: Advanced Characterisation	**P1.1** Spatially Resolved High Voltage Kelvin Probe Force Microscopy: A Novel Avenue for Examining Electrical Phenomena at nanoscale	Amit Kumar	Queen’s University Belfast, UK
	P1.2 Investigating electrothermal properties of domain walls using Scanning Thermal Microscopy	Lindsey Lynch	Queen’s University Belfast, UK
	P1.3 Development of a microbridge device for thermal conductivity measurements for ferroelectrics	Yeekin Tsui	Queen’s University Belfast, UK
	P1.4 Multiple Innovations in Characterizing Piezoelectric Materials	Sakineh Fotouhi	University of Glasgow, UK
	P1.5 Non-Contact Characterisation of Piezoelectric Materials	Anna Alexandrou	University of Glasgow, UK
P2: Capacitor Materials	**P2.1** Investigation of Structural, Microstructural and Dielectric Properties of Nd-substituted Bismuth Ferrite Ceramics	Dibakar Das	University of Hyderabad, India
	P2.2 High Resolution Spatial Mapping of the Electrocaloric Effect in a Multilayer Ceramic Capacitor using Scanning Thermal Microscopy	Olivia Baxter	Queen’s University Belfast, UK
	P2.3 Lead-Free $BiFeO_3$ – $CaTiO_3$ Ferroelectric Ceramics for High-Temperature Energy Storage Application	Dibakar Das	University of Hyderabad, India
	P2.4 Bismuth potassium titanate - bismuth ferrite based high energy density ceramic capacitors	Yubo (Martin) Zhu	University of Sheffield, UK
P3: Fundamentals of Ferroelectrics	**P3.1** Revisiting the "Giant" electric field induced strain in Sr-doped $K_{0.5}Na_{0.5}NbO_3$	Muhammad Wasim	Sheffield Hallam University, UK
	P3.2 Are there antiskyrmions in barium titanate?	Jiří Hlinka	Czech Academy of Sciences, Czech Republic
	P3.3 Behaviour of ferroelastic and ferroelectric domains in $AgNbO_3$ under temperature and stress influence	Xi Shi	Friedrich-Alexander-University Erlangen-Nürnberg, Germany
P4: Lead-free - Materials and Applications	**P4.1** Stability of Electromechanical Properties in Co Modified Aurivillius $CaBi_4Ti_4O_{15}$ at Elevated Temperature	Supratim Mitra	Banasthali Vidyapith, India
	P4.2 The Effect of A-site Vacancies on the Thermodynamic Stability of $Sr_{2.2}Na_{0.6}$+x$Nb_{5-x}Ti_xO_{15}$ Ceramics	Sadi Ege Parim	The University of Sheffield, UK
	P4.3 Ferroelectric hardening in $BiFeO_3$-$BaTiO_3$ ceramics	Lecheng Zhang	University of Manchester, UK
	P4.4 Electroelastic Database of Doped Barium Titanate Ceramic for Transducer Applications	Franck Levassort	Université de Tours / CNRS -INSA CVL, France
	P4.5 Lead-free Piezoceramic Materials for Transducer Applications	William Schulz	University of Leeds, UK
	P4.6 Piezoelectrics for high temperature transducers	Jiajun Shi	University of Manchester, UK

P5: Photoferroelectrics and Piezocatalysis	**P5.1** Accurate Band Alignments for Complex Heterojunctions from First Principles: The Case of α-Fe_2O_3/$BaTiO_3$ Interface	Jorge Ontaneda	Queen Mary University of London, UK
	P5.2 Quantification of phase and amplitude response by piezoresponse force microscopy	Subhajit Pal	Queen Mary University of London, UK
	P5.3 Effect of corona poling on piezocatalytic degradation using ferroelectric nanoparticles	Abinaya Krishnamurthy	London South Bank University, UK
	P5.4 Examination of piezoelectric properties of polymeric graphitic carbon nitride (g-C_3N_4) and potential for pollutant degradation and hydrogen peroxide generation	Akalya Karunakaran	University of Bath, UK
	P5.5 Planetary ball milling induced piezocatalysis for dye degradation using $BaTiO_3$ ceramics	Vishal Singh Chauhan	Indian Institute of Technology Mandi, India
P6: Piezoelectric Composites	**P6.1** Ice Templated Lead-Free Porous Ferroelectric Ceramics and Composites for Hydrostatic Applications	Alex Tezcan	University of Bath, UK
	P6.2 Swimming microrobot based on piezoelectric materials	Qingping Wang	University of Bath, UK
	P6.3 Development and characterization of high-performance PVDF-based piezoelectric films	Ignacio Ezpeleta	AIMEN Technology Centre, Spain
	P6.4 The effects of cooling rate on the microstructure-piezoelectric performance of porous freeze-cast ferroelectrics	Nguyen Vo-Bui	University of Bath, UK
P7: Energy Harvesting	**P7.1** Piezoelectric energy harvesting from pressure ripples in hydraulic systems	Jingqi Liu	University of Bath, UK
	P7.2 High Performance Near-Room-Temperature Pyroelectric Energy Harvesting Characteristics of Ferroelectric-Semiconductor Composites	Shanmuga Priya	Indian Institute of Technology Madras, India
	P7.3 Improved Piezoelectric Performance in PVDF Bimorphs of Opposite Polarization Orientations	Yonatan Calahorra	Israel Institute of Technology, Israel
	P7.4 Piezoelectric Energy Harvesting By Employing Biocompatible Ferroelectric Molecular Cu(II) Complexes	Rajashi Haldar	Indian Institute of Technology Bombay, India
	P7.5 $BaHf_xTi_{1-x}O_3$ thin films: from sol-gel synthesis to piezoelectric energy harvester	Maxime Bavencoffe	Université de Tours / CNRS - INSA CVL, France
P8: Processing of Piezoceramics	**P8.1** Modulating Grain Size and its Impact on the Properties of $Ba_{1-x}Sr_xTiO_3$ Ceramics	Roxana Patru	National Institute for Materials Physics, Romania
	P8.2 Properties of PZT and KNN electro-ceramics sintered by SPS without post-annealing	Hélène Debéda	Univ. Bordeaux / CNRS - INP, IMS, UMR 5218, France
	P8.3 Tunable BNT particles morphology through topochemical microcrystal conversion synthesis	Ruxue Yang	Imperial College London, UK
	P8.4 Finite element modelling and characterization of cold sintering process for electroceramic materials.	Kamalpreet Singh	University of Bath, UK

P9: Thick Films	**P9.1** Development and implementation of multifunctional materials for printed electronics in harsh environment	Elsa dos Santos	Univ. Lyon / CNRS - INSA Lyon, LGEF, France
	P9.2 Piezoceramic Thick Films on Porous Substrates as Ultrasonic Transducers	Sylvia Gebhardt	Fraunhofer IKTS, Germany
	P9.3 Effect of post-annealing on microstructure and electrical properties of piezoelectric thick films grown by Aerosol Deposition	Anass Chrir	CNRS Institute of Research for Ceramics, France
	P9.4 Aerosol deposition of $Na_{0.5}Bi_{0.5}TiO_3$-$NaNbO_3$ thick films	Juncheng Pan	University of Manchester, UK
	P9.5 Effects of quenching on the structure and electrical properties of $Na_{0.5}Bi_{0.5}TiO_3$-$NaNbO_3$ Ceramics	Juncheng Pan	University of Manchester, UK
P10: Ultrasonics and Acoustics	**P10.1** Co-design and AI for Innovation in Ultrasonic Transducers for Underwater Sonar	Katie Wilkie	University of Glasgow / Strathclyde, UK
	P10.2 A Simple Design Tool for Single-Element Piezoelectric Ultrasonic Transducers	Maxime Bavencoffe	University of Tours / CNRS - GREMAN UMR 7347, France
	P10.3 Magnetoelectric Bulk Acoustic Resonators for the Ultra High Frequency (UHF) Band	Mahdieh Shojaei Baghini	meLab, University of Glasgow
	P10.4 Ultrasound Non-Destructive Evaluation/Testing using Capacitive Micromachined Ultrasound Transducer (CMUT)	Mohamed Abdalla	University of Glasgow / Strathclyde, UK
	P10.5 Characterization of buried interfaces in optical thin films using ultrafast acoustics	Pavel Mokrý	Institute of Plasma Physics of the CAS, Czech Republic
P11: Ferroelectrics and Other Materials	**P11.1** Demonstration of a Tunable Acoustic Metamaterial, Employing a 3D Printable Magnetic Membrane as the Active Mechanism	Alicia Gardiner	University of Glasgow / Strathclyde, UK
	P11.2 Ultrahigh Relative Clamped Dielectric Permittivity of PMN-PT Ceramics by the Modification of Samarium	Koko Lam	Hong Kong Polytechnic University, Hong Kong
	P11.3 Microwave Synthesis of PMN-PT ceramics	Parveen Paliwal	DIT University - Dehradun, India
	P11.4 Modelling of metamaterial response in a gyroid ferroelectric actuator	Guilherme Selicani	Technical University of Denmark, Denmark
	P.11.5 Advances in Electroceramics: An Industrial Perspective	Jim Bennett	Ceramtec UK Ltd, UK

Map of the Neighbourhood



1. Advanced Research Centre
2. Oran Mor, Conference Dinner
3. Kelvin Hall Underground
4. Hillhead Underground
5. James Watt School of Engineering
6. Byres Road, Glasgow, G12

ECEUXII - www.gla.ac.uk/schools/engineering/research/conferences/eceuxii/

The ARC - www.gla.ac.uk/research/arc/

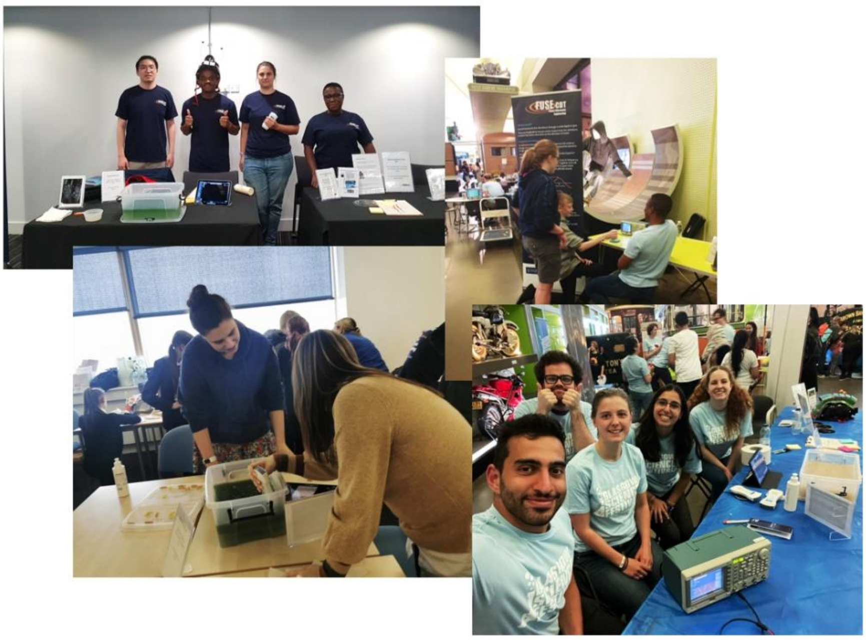
Glasgow University - www.gla.ac.uk

Organizing Committee

General Chair	Sandy Cochran, University of Glasgow
PIEZO2023 Co-chair	Maxime Bavencoffe, INSA Centre Val de Loire
PIEZO2023 Co-chair	Sebastiano Garroni, University of Sassari
Ferroelectrics UK Co-chair	Laura Stoica, Thales UK Ltd
Finance Chair	James Roscow, University of Bath
Publicity Chair	Hamideh Khanbareh, University of Bath
Winter School Chair	Koko Lam, University of Glasgow
Website Leads	Sakineh Fotouhi, University of the West of England Weihuan Kong, University of Glasgow
Public Engagement Lead	Elmer Germano, University of Glasgow

Public Engagement Showcase

FUSE CDT Future Ultrasonic Engineering

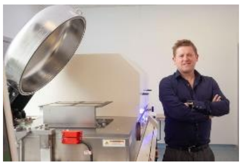


Students from the Centre for Doctoral Training in Future Ultrasonic Engineering, hosted at the Universities of Glasgow and Strathclyde, will showcase their public engagement activities during lunch on Tuesday, 1250 – 1345.

Plenary Speakers

Inside Piezoelectricity: the structural origins of electromechanical coupling
Prof. Andy Bell, University of Leeds, UK

Andrew Bell was educated at the University of Birmingham, UK (BSc Physics, 1978) and the University of Leeds (PhD Ceramic Science and Engineering, 1984). He has been Professor of Electronic Materials at the University of Leeds, School of Chemical and Process Engineering since 2000. He previously spent almost 15 years in industrial research posts and 4 years as a Senior Scientist in the Ceramics Laboratory at EPFL, Switzerland. He has undertaken research on a wide range of topics in ferroelectric and dielectric materials, encompassing basic science, materials processing, structural & electrical characterization and device physics, including pyroelectric materials and devices, microwave dielectrics and piezoelectrics. He has published over 200 papers with a total of more than 6000 citations.From 2000 onwards, his research focussed almost exclusively on piezoelectric materials, particularly on those with capabilities beyond those of PZT. In 2011 he founded Ionix Advanced Technologies Ltd to exploit the new high temperature piezoelectric compounds emerging from his research group. Prof. Bell was elected a Fellow of the Royal Academy of Engineering in 2016 and was elevated to Fellow of IEEE in 2019. He was awarded the Verulam Medal of the Institute of Materials in 2014. He has received the IEEE's Ferroelectrics Recognition Award (2012) and Robert E Newnham Ferroelectrics Award (2022). He is currently the 2023 IEEE-UFFC Distinguished Lecturer in Ferroelectrics.



Ultrasound. Integrated. Everywhere.
Dr Dave Hughes, Novosound Ltd., UK.

A high-growth entrepreneur and physicist, Dr Dave Hughes has over 12 years' experience researching ultrasound for medical, dental and industrial applications. During his time as a Research Fellow at the University of the West of Scotland (UWS), Dave invented Novosound's core IP which led to the creation of Novosound in April 2018 – the first spin-out company to emerge from UWS. Dave Hughes has developed from an academic to a successful company director, overseeing the technical direction and vision of Novosound. Under his leadership, Novosound has grown rapidly to become an award-winning global business, working across diverse industry sectors and markets including oil & gas, aerospace, energy and medical. Dave holds a visiting professorship at UWS and was named Institute of Directors (IoD) Scotland Director of the Year 2020 in the start-up category. Since 2018 Novosound has grown from six people to 30+. Key customers have included international energy company Uniper and, in the aerospace sector, BAE Systems and GE Aviation. More recently Novosound has taken exciting steps in the wearable and healthcare sector with work in the dental imaging market and a digital healthcare R&D project with a Nasdaq-listed tech group.

Piezoelectric materials as active biomedical implants – a "two-body problem"

Julia Glaum, NTNU, Norway

Julia Glaum received her Diploma in Physics from the Justus-Liebig-Universität Gießen, Germany in 2006 and her PhD in Materials Science from the Technische Universität Darmstadt, Germany in 2010. After a Postdoctoral stay at UNSW Sydney, Australia, she moved to the Norwegian University of Science and Technology (NTNU) in 2015. Here, she is now heading a research group with its main focus on functional materials for biomedical applications. Her main research activities stretch from the development of materials and components suitable for *in-vivo* applications to studies on material stability and reliability under physiological conditions. Furthermore, she is the leader of the Synergy Group "Biomedical Materials Science" that merges research and educational efforts in biomedical materials science at NTNU.

Unlocking the Piezoelectric Response of Ceramic Thick Films

Kyle G. Webber Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Kyle G. Webber is Professor of Ceramics and Head of the Institute of Glass and Ceramics in the Department of Materials Science and Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany. Since 2020, he is the Director of the International Research Training Group IGK2495 "Energy Conversion Systems: From Materials to Devices", with is a joint international project with Nagoya Institute of Technology, Japan. He received a B.Sc. in Marine Systems Engineering from Maine Maritime Academy in 2003, where he obtained a US Coast Guard license for a 3rd Assistant Engineer, and a M.Sc. and Ph.D. in Mechanical Engineering from the Georgia Institute of Technology in 2005 and 2008. His primary research focus is electromechanical properties of functional ceramics, field-induced phase transformations, and lead-free ceramic/ceramic composites. He was an Emmy Noether Research Fellow of the German Research Foundation and was awarded the IEEE UFFC Ferroelectrics Young Investigator Award in 2017. He has authored or co-authored more than 140 refereed publications in the field of electroceramics.

Keynote Speakers

Piezoelectric polymers for energy, sensing and biomedical applications

Sohini Kar-Narayan, University of Cambridge, UK

Sohini Kar-Narayan is a Professor of Device & Energy Materials in the Department of Materials Science at the University of Cambridge, where she leads an interdisciplinary research group working on functional nanomaterials and devices for energy, sensing and biomedical applications. She received her PhD in Physics from the Indian Institute of Science, Bangalore, in 2009, and was awarded a prestigious Royal Society Dorothy Hodgkin Fellowship in 2012. Prof. Kar-Narayan received the Royal Society of Chemistry Peter Day Prize in 2023. She was recognised as one of the Top 50 Women in Engineering of 2021 by the Women's Engineering Society, and was elected Fellow of the Institute of Materials, Minerals & Mining (IoM3) in 2022. She was the recipient of a World Economic Forum Young Scientist Award and a European

Research Council (ERC) Starting Grant in 2015, and an ERC Consolidator Grant in 2023. She is a Co-Founder and Director of ArtioSense Ltd., a spin-out from the University of Cambridge that seeks to commercialise a microfluidic force sensing technology for applications in orthopaedic surgery, which was awarded the Armourers & Braisiers' Venture Prize Award in 2022. She is an Associate Editor of the journal Applied Materials Today.

Processing of Smart Porous Electro-ceramic Transducers (ProSPECT)
Chris Bowen, University of Bath, UK

Christopher R. Bowen was born in Beddau, U.K., in 1968. He received the B.Sc. degree (Hons.) in materials science from the School of Materials, University of Bath, Bath, U.K., in 1990, and the Ph.D. degree from the Department of Materials, University of Oxford, Oxford, U.K, in 1994. In 1998, he joined the University of Bath, where he is currently a Professor. He has authored over three monographs, 260 papers, chapters in monographs, conference proceedings, and abstracts. His current research interests include the manufacture and characterization of ferroelectric ceramics and piezoactive composites for sensor, actuator, and energy harvesting applications.

Ferroelectric Ceramic Thick Films: Processing and Applications
Danjela Kuscer, Jožef Stefan Institute, Slovenia

Danjela Kuscer received the Ph.D. degree from the University of Ljubljana, Ljubljana, Slovenia, in 1999. She is currently a Senior Researcher with Electronic Ceramics Department, Jožef Stefan Institute, Ljubljana, Slovenia, and an Associate Professor with Jožef Stefan International Postgraduate School, Ljubljana. Her research topics include synthesis of complex-composition ceramic materials, mainly piezoelectrics and ferroelectrics for electronic applications, formulation and characterization of suspensions, processing and patterning of thick film structures, and structural and microstructural characterization of materials. She is the author or coauthor of 130 publications, 150 technical reports, five patents, and one patent applications.,Dr. Kuscer was a member of the Organizing Committee of four international conferences. She is also a member of association MIDEM-Societey for Microelectronics, Electronic Components and Materials, Slovenian Chemical Society, and the International Society of Electrochemistry. She received the National Puh Recognition for achievements in research of ceramics in 2015 and awards Excellent in Science in 2016 in the field of technical science. She has been involved in about 20 projects. Since 2011, she has been an Associate Editor of the field technology and materials in journal Informacije MIDEM.

$BaTiO_3$ ceramics by Cool-SPS at 600°C: Towards more sustainable lead-free ceramics?
Michaël Josse, University of Bordeaux, France

Michaël Josse is Associate-Professor (HDR) at the University of Bordeaux and the Institute of Condensed Matter Chemistry of Bordeaux (CNRS UMR 5026) since February 2005, and is the author of more than 50 publications and 100 communications. A Solid State Chemist at heart, he obtained his PhD from University Blaise Pascal (Clermont-Ferrand) on the crystal chemical and magnetic properties of terbium fluorides. Upon joining ICMCB, he first explored the crystal chemistry of ferroelectric « Tetragonal Tungsten Bronze » (TTB) ferroelectrics oxides. He provided empirical evidences that the anionic framework and its aperiodic modulations are central to the dielectric behaviour of TTB materials. He initiated their growth in single crystals (by the flux method) and thin films (by sputtering) forms, and revealed metastable ferroelectric phase in some TTBs. In 2012, he initiated the development of Cool-SPS, at first for the sintering of thermos-dynamically fragile materials, and latter obtained the first molecular ceramic. By relying on the specificities of SPS, on Nowadays, Cool-SPS, central to his current activities, is now applied to a wide range of materials, from molecular to refractory ones, and specifically to some important functional oxides.

Invited Speakers

Ferroelectric nanocomposites for enhanced solar energy conversion
Joe Briscoe, Queen Mary University of London, UK

Prof Joe Briscoe completed an MSci at the University of Durham (Grey College) in Natural Sciences with a masters thesis focused on doping of ceramic zinc oxide. Following this he undertook a PhD at Cranfield University in nanostructured quantum dot photovoltaics. Upon completion of his PhD, Prof Briscoe moved to Queen Mary where he worked on the development of a new type of nanostructured piezoelectric energy harvesting device using ZnO nanorods, and the investigation of ferroelectric materials as novel photocatalysts for the production of fuels (solar fuels / artificial photosynthesis) and the degradation of pollutants. He also worked on a number of projects developing emerging photovoltaic technologies, such as hybrid organic-inorganic lead halide perovskites, organic photovoltaics (OPVs) and dye-sensitised solar cells (DSSCs). He became a Lecturer at QMUL in 2017, Senior Lecturer in 2020, Reader in 2021 and Professor in 2023. Prof Briscoe's current research is focussed on investigating a range of new materials, structures and material combinations for use in nanostructured, low-cost photovoltaics (PVs), photocatalysis/ photoelectrocatalysis (PEC) and piezoelectric energy harvesting, with a particular focus on the use of polar (ferroelectric, piezoelectric) materials within these devices. He was awarded an ERC Consolidator Grant in 2020 to develop novel solar energy devices based on photovoltaic/ photocatalytic-ferroelectric nanocomposite thin films. He has also developed a novel approach to the post-treatment of perovskite solar cells using aerosol treatment, and started a spin-out, AeroSolar in 2022 to commercialise this process.

Bismuth ferrite solid solutions: new pathways to microstructural and functional property engineering
David Hall, University of Manchester, UK

David Hall is a Reader in Materials Science (Ceramics) in the Department of Materials and Henry Royce Institute at the University of Manchester, UK. His research interests include nonlinear dielectric and piezoelectric properties of ferroelectric ceramics, in-situ diffraction techniques for determination of electro-mechanical actuation mechanisms, high temperature lead-free ferroelectrics, energy storage dielectrics, and the manufacture of both protective and functional ceramic coatings by powder aerosol deposition.

Enhanced properties of relaxor-PT single crystals poled under an alternating current electrical field

Xiaoning Jiang, North Carolina State University, USA

Dr. Xiaoning Jiang is a Dean F. Duncan Distinguished Professor of Mechanical and Aerospace Engineering and a University Faculty Scholar at North Carolina State University. He is also an Adjunct Professor of Biomedical Engineering at North Carolina State University and University of North Carolina, Chapel Hill, and an Adjunct Professor of Neurology in Duke University. Dr. Jiang received his Ph.D. degree from Tsinghua University (1997) and his Postdoctoral training from the Nanyang Technological University and the Pennsylvania State University (1997-2001). He was the Chief Scientist and Vice President for TRS Technologies, Inc. prior to joining NC State in 2009. Dr. Jiang is the author and co-author of two books, 6 book chapters, 24 issued and pending US Patents, more than 170 peer reviewed journal papers and over 140 conference papers on piezoelectric ultrasound transducers, ultrasound for medical imaging and therapy, drug delivery, ultrasound NDT/NDE, smart materials and structures and M/NEMS. Dr. Jiang serves as the Vice President for Technical Activities in IEEE Nanotechnology Council (NTC). He was the Co-Editor-in-Chief of IEEE Nanotechnology Magazine (2020 - 2021) and an IEEE NTC Distinguished Lecturer in 2018 and 2019. Dr. Jiang is an ASME Fellow, a SPIE Fellow and an IEEE Fellow.

$BaTiO_3$ ceramics by Cool-SPS at 600°C: Towards more sustainable lead-free ceramics?

Sylvia E. Gebhardt, Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden, Germany

Sylvia E. Gebhardt is head of the group Multifunctional Materials and Components of the Fraunhofer Institute for Ceramic Technologies and Systems (IKTS) in Dresden, Germany. She studied Material Science at the Technical University Bergakademie Freiberg, Germany and at Leeds University, UK. She received the Diploma degree in 1996 and was awarded a Ph.D. degree in 2000 for her thesis on development and characterization of fine-scaled 1 3 piezocomposites for ultrasonic transducers. Her research interests are focused on material synthesis of complex ferroelectrics like lead free piezoelectrics, electrocaloric materials, antiferroelectrics, PTC thermistors, and others. Topic of particular interest is the development innovative technologies for the manufacture of ceramic components like screen printing of piezoceramic thick films for sensors, actuators, and ultrasonic transducers, multilayer fabrication for electrocaloric cooling components and high-power capacitors, micromolding for high frequency ultrasonic transducers, as well as fiber spinning and composite fabrication for medium and low frequency ultrasonic transducers.

New Dielectric Ceramics with Ultralow Sintering Temperatures and Dielectric Loss for Passive Integration

Prof. Dr. Hong Wang, Southern University of Science and Technology

Hong Wang is a chair professor and dean of Graduate School at the Southern University of Science and Technology. Prior, she was a professor at Xi'an Jiaotong University from 2002 to 2017. She received her BS, MS and PhD degrees in electronics materials and devices from Xi'an Jiaotong University. Her main research interests include dielectric materials, multifunctional composites, and dielectric measurements. She has (co)-authored over 370 peer-reviewed papers, 45 patents, and has delivered more than 70 invited talks in international academic conferences. She received 2023 IEEE Ferroelectrics Recognition Award. She is a Fellow of

IEEE. She was the chair for the Asian Electroceramic Association (AECA) and has been a member of AECA since 2005. She serves as an associate editor for IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control and editorial board members for the Journal of Advanced Ceramics, Journal of Materiomics, the Journal of Chinese Ceramic Society, and IET Nanodielectrics.

Piezoelectric Biomolecules for Lead Free, Reliable, Eco Friendly Electronics

Sarah Guerin, University of Limerick, Ireland

Dr Sarah Guerin is the PI of the newly established Actuate Lab in the Department of Physics. She currently works on both in silico and ex silico engineering of biomolecular crystals, primarily for application areas in eco-friendly sensing and pharmaceuticals. Dr Guerin has been successful in securing €2M of funding from Science Foundation Ireland and the European Research Council for the development of organic piezoelectric device components. She currently works with a large number of international research groups as a world-leader in computationally predicting the electromechanical properties of novel molecular crystals. She has been awarded the British Association of Crystal Growth Young Scientist of the Year Award and the IEEE Dilip Das Gupta Memorial Award.

Industry Speakers

Dave Hughes, Novosound
Ultrasound. Integrated. Everywhere.

Julia Rabitsch, Lithoz
Lithography-based additive manufacturing of piezoceramic materials

Charles Mangeot, CTS
Applications, Performance and Industrialization of Textured PMN-PT-PZ Ceramics

Tanya Einhellinger-Müller, Ceramtec
Piezoelectric properties of BNT-BT, processing, and potential applications

Sandra Niederschuh, PI Ceramic
Performance of KNN in resonant applications

Peter Cowin, Ionix Advanced Technologies
Applicability of Lead Free Piezoelectrics for Ultrasonic Evaluation

Ana Borta-Boyon, Thales TRT
Research and development of lead- free ceramics for acoustic transducers

Session M1: Plenary and Industry

Ultrasound. Integrated. Everywhere.

Dave Hughes

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Ultrasound is a prevalent method for imaging and measurement. It involves sending sound pulses through an object and collecting the returning echoes to 'see inside'. The most well-known use of ultrasound is in maternity wards and hospitals worldwide. However, it is also used in industrial applications for non-destructive testing (NDT); where the same technology is used to monitor the status of high-value equipment for wear and tear (Aerospace), detect corrosion in pipelines (Oil and Gas), and fracture detection in turbine blades (Wind Farms and Renewable Energy). Independent market research shows a clear need for more effective and lower-cost solutions in ultrasound imaging and measurement. Current sensor materials have several drawbacks. Of most concern, they are brittle, meaning they can't be made to shape the object being imaged (for example, in NDT where small diameter pipes are being inspected). This leads to insufficient measurement data and repeated work for the NDT technicians to gain a complete insight to the object under test. A pliable sensor that flexes to the shape of the surface under test will revolutionise NDT in asset management through cost-saving and lifetime extension. The resolution of the ultrasound system (which gives rise to image quality and measurement accuracy) is related to how thin you can make the piezoelectric material. Imaging small objects (such as carbon fibre layers in NDT, teeth and gums in Dentistry, or micro-vascular tissues in Veterinary/Medical Imaging) requires high resolution, which is not possible with current technology to produce a cost-effective ultrasound system due to the difficulty and high cost of fabricating high resolution (very thin, 0.01mm) sensors. In this presentation, Dr Dave Hughes, Founder and CEO of Novosound, will demonstrate how thin film piezoelectric materials solve this manufacturing problem by introducing a breakthrough method of manufacturing high-resolution ultrasound sensors that are low-cost and flexible enough to curve around objects. This is enabled by Novosound's printable ultrasound sensor technology using additive manufacturing via thin film technology and driven by their system and software expertise. Covering the Novosound vison of 'Ultrasound Integrated Everywhere', Dr Hughes will also talk about the University Spin-Out journey from academic researcher to award-winning commercial business with global traction and impact, and some lessons learnt and challenges faced along the way!

Lithography-Based Additive Manufacturing of Piezoceramic Materials

Dr. Martin Schwentenwein[1*] and Julia Rabitsch[1]

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Lithography-based additive manufacturing (AM) technologies utilize photopolymerization to create objects by solidifying a liquid resin through exposure to light. The resin is composed of monomers, a photoinitiator, and ceramic particles at a high solid loading. The solidification process involves radical polymerization, which is initiated by light exposure. Lithography-based techniques offer several advantages, including the ability to create highly precise and complex parts with superior surface quality compared to other AM methods. The process follows an indirect approach, where a green part is first produced. This green part is a composite of ceramic particles which are evenly dispersed in a photopolymer matrix acting as a scaffold. In a subsequent thermal post-processing step, the green part undergoes debinding and sintering to transform it into a final dense ceramic component. While lithographic AM of oxide ceramics for structural applications is well-established, the use of functional ceramics in this printing technique is relatively new. The absorption of light and the higher refractive indices exhibited by many piezoelectric ceramics pose challenges. This study focuses on demonstrating the precise printing of test designs and components using lithography-based AM with functional ceramics and evaluating their properties. Two different types of piezoceramic materials were investigated: classical lead-zirconate-titanate (PZT) and lead-free potassium-sodium-niobate (KNN). The results showed that the 3D printed components exhibited comparable properties to their conventionally manufactured counterparts. The measured d33 values for PZT and KNN were 650 and 100 pC/N, respectively. In conclusion, the experimental data demonstrate that AM, particularly lithography-based AM, is a viable method for fabricating functional ceramic components with piezoelectric properties similar to those achieved through conventional manufacturing processes.

Keywords: 3D printing, stereolithography, ceramics, piezoelectric

Applications, Performance and Industrialization of Textured PMN-PT-PZ Ceramics

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CTS, in collaboration with scientists at the Applied Research Laboratory (ARL) at Penn State, is developing textured piezoelectric materials providing performance superior to ceramics at a cost lower than single crystals. Textured materials find applications within the defence industry, such as for Anti-Submarine Warfare applications, as well as the medical field, typically high intensity focused ultrasound (HIFU). These textured materials are fabricated using a Mn-doped PMN-PT-PZ composition located along the tetragonal/pseudo-cubic phase boundary. An engineered slurry comprised of barium titanate templates and PMN-PT-PZ matrix powder is tape cast to form thin sheets that are laminated together to form green stacks that are between 1 and 10 mm thick. The tape casting process aligns the (001) planes of the barium titanate templates parallel to the surface of the cast tape. Parts sintered in a PbO rich atmosphere achieve a dense matrix followed by templated growth around the $BaTiO_3$ templates, creating a ceramic material with a high level of orientation. Variations in material properties according to thickness suggest that an improved control of the sintering profile and atmosphere is required. The dielectric constant, d_{33} coefficient and Lotgering factor for approximately 1 mm thick samples were 1800, 950 pC/N and 0.998, respectively. Recent efforts focused on reliably scaling up to parts that are 9 mm thick and achieved dielectric constants of 1400, d_{33} in the 560 pC/N range, and Lotgering factors >0.99, with further improvements to come. Another development aspect is the production of near net shape textured parts. Research is ongoing using additive manufacturing and alternative forming methods in order to further optimize the manufacturing process.

Keywords: piezoceramic, PMN-PT-PZ, textured, templated grain growth

Piezoelectric Properties of Bnt-Bt, Processing, and Potential Applications

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The development of Piezoceramics, which do not contain lead has been a main focus of universities and companies for at least the last two decades. This is mostly due to the laws implemented in the EU to avoid certain substances, in this case lead, in the supply chain of electronic equipment and automotive applications. In contrast to certain other applications, lead is a main constituent of the piezoelectric materials based on PZT and one of the main reasons for the unique properties. Despite the quite large research, no real substitution has been found. The most promising materials are still based on Potassium -Sodium-Niobate (KNN) and Bismuth-Sodium-Titanate-Barium-Titanate (BNT-BT). Still, the properties are inferior to PZT and the powder processing routes are mostly more expensive, which makes the production highly cost-intensive. The use of KNN is, according to recent investigations into the Lifecycle (LCA), not beneficial to the environment either. But interestingly, some properties of lead free Piezoceramics differ quite strong from PZT in a way, which could be used in some applications. BNT-BT for example, has a very strong anisotropy between the planar and longitudinal effect. This could be exploited in applications which require strong thickness mode oscillation in combined with lower losses due to mechanical friction caused by planar mode oscillation. In this presentation the current state of the art for BNT-BT based ceramics will be presented. Comparisons are drawn with PZT and the next steps to generate more data on reliability and reproducibility of leadfree materials from a production point of view will be discussed.

Keywords: lead free piezoceramic, bismuth-sodium-titanate - barium-titanate, BNT-BT

Session M2A: Fundamentals of Piezo- and Ferroelectrics

Nonlinear Piezoelectric Response of Sm-Doped Pb($Mb_{1/3}Nb_{2/3}$)O_3–$PbTiO_3$ Relaxor-Ferroelectric Ceramics

Matija Arzensek[1], Urh Tos[1], Silvo Drnovsek[1], Hana Ursic[1], Mirela Dragomir[1], Mojca Otonicar[1], Sarūnas Svirskas[2], Maja Koblar[1] and Tadej Rojac[1*]

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Lead-based relaxor ferroelectric perovskites, exemplified by the Pb($Mg_{1/3}Nb_{2/3}$)O_3–$PbTiO_3$ (PMN–PT) solid solution, are a group of multifunctional materials with exceedingly large piezoelectric and dielectric properties, making them not only scientifically curious but also technologically important. The most recent breakthrough was the discovery of the extraordinary enhancement of the piezoelectric response of PMN–PT ceramics when doped with rare-earth ions, particularly with Sm, resulting in piezoelectric coefficients (~1500 pC/N) getting closer to those measured in single crystals of undoped PMN-PT. The initial explanation of the origin of the large response was based on the particular effect of Sm dopant in inducing local structural heterogeneities that promote polarization rotation under applied field. However, soon after, several other reports followed with diverse, sometimes contradicting explanations. In this study, using nonlinear converse piezoelectric measurements alongside harmonic and Rayleigh analysis, we attempted to separate the different reversible and irreversible nonlinear contributions to the piezoelectric response of Sm-doped PMN–PT (Sm content range 0–3 mol% and PT content range 25–35 mol%). The results suggest that the origins of the large response are multiple and therefore, depending on the Sm concentration, different microscopic mechanisms have to be considered to explain the enhanced piezoelectric response. We believe that our study provides some useful information in the on-going quest on the complex origins of the piezoelectricity of relaxor-based ferroelectric materials.

Keywords: relaxor, ferroelectric, piezoelectricity, PMN–PT, rare earth doping

Structural and Electrical Properties of $Sr_xNa_{1-2x}NbO_3$ Polycrystalline Ceramics

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Sodium niobate ($NaNbO_3$) is a material of interest both academically as a vessel for understanding the phenomenology of antiferroelectric materials, and more recently technologically as a foundation material for energy storage applications [1]. Despite the phase diagram of $SrNb_2O_6$ and $NaNbO_3$ being constructed in the late 1970s [2], very few studies have been conducted to probe the perovskite region of this phase diagram with nomenclature $Sr_xNa_{1-2x}NbO_3$. Arguably, the most comprehensive study of this material has been carried out by Torres-Pardo et al. [3], however the composition space was limited from x = 0.10-0.20. Here, a wider study on A-site deficient $Sr_xNa_{1-2x}NbO_3$ (x = 0.00 - 0.25) polycrystalline ceramics has been carried out to screen any useful material properties. Despite complexity in the microstructural evolution of these materials due to the formation of $NaNb_3O_8$ liquid phase, the crystallographic and dielectric properties show much clearer trends. The introduction of Sr^{2+} stabilize the ferroelectric Q-phase, decrease the ferroelectric-paraelectric phase transition whilst promoting relaxor-like behaviour, and above x = 0.00 shows increasing conductivity and tanδ values associated with predominantly electronic conduction. Despite A-site vacancies typically being associated with p-type behaviour, here progressively n-type behaviour is observed due to the increased tendency to lose under-bonded oxygens and reduce Nb^{5+} to Nb^{4+}.

Keywords: sodium niobate, dielectric properties, impedance spectroscopy

References:

[1] MH. Zhang, H. Ding, S. Egert. *et al*. *Nat. Commun.* 14 (2023) 1525

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Dielectric Behavior of Lead-Free Ferroelectrics at Terahertz Frequency

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Development of new devices based on ultrafast response of polarization in ferroelectrics needs novel dielectric characterization method at high frequency. The advent of terahertz (THz) technology has now allowed to characterize the high frequency dielectric properties of different ferroelectrics including perovskite structured $Bi_{0.5}Na_{0.5}TiO_3$ ceramic, Aurivillious phase $Ca_{0.99}Rb_{0.005}Ce_{0.005}Bi_2Nb_2O_9$ ceramic and perovskite-layer-structured (PLS) $La_2Ti_2O_7$ single crystal [1-3]. Intense THz pulses were used as a high-frequency electric field to investigate ultrafast switching in $Bi_{0.5}Na_{0.5}TiO_3$. Transient atomic-scale responses, which were evident as changes in reflectivity, were captured by THz probing. The high-energy THz pulses induce an increase in reflectivity, associated with an ultrafast field-induced phase transition from a weakly polar phase (*C*c) to a strongly polar phase (*R*3c) within 20 ps at 200 K. This phase transition in $Bi_{0.5}Na_{0.5}TiO_3$ was confirmed using X-ray powder diffraction and by electrical measurements. By characterizing the dielectric properties of a poled (less domain walls) and unpoled $Ca_{0.99}Rb_{0.005}Ce_{0.005}Bi_2Nb_2O_9$ ceramic, it was found that the dynamics of domain walls are different at kHz and THz frequencies. At kHz frequencies, domain walls work as a group to increase dielectric permittivity. At THz frequencies, the defective nature of domain walls serves to lower the overall dielectric permittivity, which was also supported by an elastic vibrational model. Although dielectric permittivity is normally frequency independent within RF range, the decrease in dielectric permittivity with increasing frequency is observed in PLS $La_2Ti_2O_7$ single crystal from radio frequency to microwave then to terahertz band, which clearly shows dielectric relaxation of PLS $La_2Ti_2O_7$ at high frequency.

Keywords: ferroelectrics; THz pump; THz probe; ultrafast phase transition; domain wall behavior

References:

[1] Zhang, et al. Journal of the European Ceramic Society, 2021, 41, 73757379.

[2] Zhang, et al. ACS phonics, 2021, 8, 147-151

[3] Zhang, et al. ACS Applied Materials & Interfaces, 2021, 13, 12622-12628.

Functional Inorganics Driven by Immiscibility

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The importance of chemical heterogeneity in functional ceramics is well known and utilised in various applications, for example in core-shell type dielectrics for temperature-stable capacitors, functionally graded ceramic coatings and thin film heterostructures. Here, we exploit the metastable nature of the $BiFeO_3$-$BaTiO_3$ pseudo-binary system to create a new category of polycrystalline microstructure with controlled nanoscale chemical heterogeneity and local electric field distribution achieved by simple heat treatment methods, including quenching and thermal ageing. The characteristic features of the resulting 2-phase nanostructure, including the scale and amplitude of elemental partitioning, disruption of polar symmetry and the local electric field orientation, are investigated using advanced atomic scale scanning transmission electron microscopy (STEM). This approach provides unprecedented control over the functional ferroelectric properties, yielding remarkable transformations from a normal ferroelectric with a well-saturated polarisation-electric field hysteresis loop to either a relaxor ferroelectric exhibiting antiferroelectric-like characteristics or an ultra-hard piezoelectric with enhanced de-poling temperature, increased from 450 to 850 °C, and mechanical quality factor, from 50 to 883. Our findings provide new insights into the disruption of ferroelectric ordering and a bottom-up pathway to synthesize bulk ferroelectric heterostructures with exceptional functionality, for numerous applications using functional oxides.

Keywords: bismuth ferrite, barium titanate, immiscibility, nanoscale phase separation, quenching, thermal ageing

Session M2B: Piezoelectric Materials

Piezoelectric Polymers for Energy, Sensing and Biomedical Applications

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Properties of functional polymers at the nanoscale can be significantly different to their bulk properties. The ability to engineer material properties at the nanoscale gives rise to a wide range of applications in fields such as biomedicine and energy harvesting. Our research involves understanding structure-property and functionality relationships in novel polymer-based piezoelectric nanostructures, with a focus on the role of phase, crystallinity and morphology on their functionality. At the same time, these nanomaterials can also be integrated into sensors and energy harvesters using advanced microscale additive manufacturing techniques to create a range of functional devices, including those aimed at biomedical or clinical applications. For example, a combination of aerosol-jet printing and 3d printing can be used to fabricate "soft" functional interfaces based on piezoelectric polymer nanostructures for sensing and stimulation of cells, and also to enhance and control piezoelectricity in printed structures based on collagen for possible applications in tissue engineering. The ability to control properties at the nanoscale through processing therefore allows for subsequent integration into functional devices through additive manufacturing.

Porous Bacterial Nanocellulose Films as a Matrix for Piezoresponsive Applications

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The Internet of Things (IoT) is a rapidly evolving technological ecosystem that continues to demand greater connectivity among devices. This interconnected network aims to link everything, everywhere, simultaneously. This is possible through key-enabling technologies such sensor- and atuactor- based technologies and energy harvesters.[1]. This is a great opportunity for piezoelectric materials as they allow conversion of mechanical energy into electrical energy and vice versa. The lack of flexibility of nowadays' piezoelectrics is the driving force for the searching for new materials.[2] One of the most promising routes to produce flexible piezoelectrics is through the development of composites using a polymeric matrix with a piezoelectric embedded within it [3]. In our work we have been working with zinc oxide (ZnO) as biocompatible piezoelectric and bacterial nanocellulose (BC) as flexible matrix. We have developed composite films through an in-situ microwave procedure growth of our ZnO nanoparticles within the matrix and have characterized the structure, morphology and piezoresponse of these composites. These structuralfunctional relationship will be fully presented and discussed.

Keywords: zinc oxide, bacterial nanocellulose, piezoelectric, sensors, flexibility

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Multiaxial Ferroelectricity and Piezoelectric Energy Harvesting from Organic Plastic Crystals

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Ferroelectric materials (which also exhibit pyroelectricity, piezoelectricity, and optical second harmonic generation) have enormous applications such as capacitors, energy materials, mechanical sensors, memory devices (ferroelectric random access memories, FeRAMs), radio frequency identification (RFID) cards, optoelectronic materials, surface acoustic devices and microactuators. But, harnessing the exceptional efficiencies offered by singlecrystal-based ferroelectric materials becomes nearly impossible for use in devices, particularly in the flexible variants, owing to their brittleness. While brittle crystals' tendency to crack on mechanical impact greatly limits their durability in the devices, rigidity makes any postcrystallization reconfiguration unthinkable, for instance moulding them into desired three dimensional shapes. In this regard, *Plastic Crystals* (PCs) can be the potential candidates to mitigate some of the above mentioned challenges because of their softness arising from orientational or translational degrees of freedom of the constituent molecules or ions in their solidstate structure.[1-4] Herein, we report a series of organic plastic crystals which show multiaxial ferroelectricity because of their order-disorder solid-to-solid phase transitions from high temperature and high symmetric paraelectric phases to the low temperature and low symmetric ferroelectric phases. Also, we have studied their piezoelectric energy harvesting abilities by demonstrating some real-life applications like LED lighting and capacitor charging and analysed their piezoelectric performances from crystal engineering point of view i.e. by a comparative study of their polarization charge density and quantitative mechanical properties like elastic modulus (E) and hardness (H). Ferroelectric property is important for their piezoelectric and energy harvesting applications because the materials can be poled and moreover, being multiaxial ferroelectrics, the materials can be used in polycrystals and in composite films.[3] Materials that possess multiaxial ferroelectric properties with switchable spontaneous electrical polarization hold great promise in electronic memory and optoelectronic applications. We hope, this study will certainly boost the ongoing research on PCs specially for designing efficient piezoelectric and multiaxial ferroelectric materials and repurposing them for multidirectional applications.

Keywords: multiaxial ferroelectricity, piezoelectric energy harvesting, organic plastic crystals, crystal engineering, mechanical properties

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Session M3A: Photoferroelectrics and Piezocatalysis

Ferroelectric Nanocomposites for Enhanced Solar Energy Conversion

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Ferroelectrics have gained substantial interest for solar energy conversion, both as photovoltaics (PVs) and photocatalysts or photoelectrocatalysts (PEC). Ferroelectrics can separate photoexcited carriers due to their intrinsic asymmetry – known as the bulk photovoltaic effect (BPVE) – which differentiates them from conventional semiconductor PVs, which require a junction to create the asymmetry and separate carriers. In PEC the depolarization field can also aid in separating photoexcited carriers, increasing efficiency and allowing switchable photocurrents to be achieved via poling. However, BPVE efficiencies are intrinsically limited by the wide bandgaps of most ferroelectrics, and efforts to lower the bandgap substantially reduces photovoltage due to the increased photoconductivity. Similarly, PEC efficiencies of ferroelectrics are limited by the poor light absorption and low intrinsic catalytic efficiency. We have developed novel ferroelectric-photovoltaic and ferroelectric-photocatalyst nanocomposite electrodes, whereby nanostructured ferroelectric thin films are combined with narrower bandgap photocatalytic or photovoltaic materials. Using piezoresponse force microscopy (PFM) we have demonstrated that despite the small feature size and increased porosity the $BaTiO_3$ thin films retain their ferroelectric properties and domains can be controllably switched. The nanostructured $BaTiO_3$ films demonstrate intrinsic PV and PEC activity, which can be switched by poling the films (macroscopically), albeit with low overall photocurrents. Deposition of photoabsorbers within the pores leads to substantial increases in the photocurrent and therefore power conversion efficiency of the systems. Importantly, the photocurrent can be modulated by poling the system, demonstrating a controllable enhancement of the efficiency via the polarization of the ferroelectric material. We highlight the importance of the 'parallel' arrangement of ferroelectrics and photoabsorbers in the nanocomposites, which allows the ferroelectric to effectively couple to the light absorbing material to modulate charge carrier separation without hindering charge transport to the electrodes or electrolyte, allowing the benefits of both materials to be effectively combined.

Keywords: ferroelectrics, photovoltaics, photocatalysis, composite

$BaTiO_3$/Pt Hybrid Material for Enhanced Piezocatalytic H_2 Production

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Piezocatalysis has emerged as a promising field of research that offers green and sustainable processes, regardless of the use of light or electricity as an energy source. By using mechanical energy, piezocatalysts can facilitate complex chemical transformations. Among various applications of piezocatalysis, the generation of hydrogen (H_2) through water splitting has gained significant interest. However, it has been observed that many studies do not report addressing crucial factors that have a major impact on the efficiency of the piezocatalytic process, often overlooking important experimental details. In this study, we use ultrasonication as a form of mechanical energy to produce H_2 from sustainable fuel-water mixtures, focusing on both sonochemical and piezoelectric effects. Our research emphasises the need to evaluate the individual contributions of sonochemical and piezocatalytic processes to catalyst performance. Additionally, we investigated the impact of acoustic intensity on these phenomena. To increase the rate of H_2 production, we combined a Pt metal cocatalyst with $BaTiO_3$ using a simple solid-state method. Interestingly, this hybrid material showed a four-fold increase in H_2 production compared to pristine $BaTiO_3$ and the sonochemical reactions that occurred in the absence of a catalyst. Furthermore, $BaTiO_3$/Pt demonstrated consistent and stable piezocatalytic performance over a long period of ultrasonication. In particular, the experimental energy efficiency of this system was found to be remarkable compared to other experiments reported in the literature. The results of our study provide convincing evidence of the synergistic benefits of hybrid materials in the improvement of piezocatalytic processes. By reporting on these findings, we aim to address existing research gaps and contribute to the development of piezocatalysis as an efficient and sustainable process.

Keywords: piezocatalysis, cocatalyst, solid-state synthesis, H_2 production, acoustic intensity

Laser Induced Crystallization of Ferroelectric Glass Ceramic for Water Cleaning Applications

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This research presents the first study on laser-induced crystallization to prepare glass-ceramics for water-cleaning applications. In previous reports, glass crystallization was accomplished through heat treatment at a specific temperature determined by performing differential scanning calorimetry (DSC). The new method proposed in this study offers advantages in terms of speed, control, less damage, less contamination, and miniaturization for the crystallization of glass-ceramics. Glasses were prepared using the conventional melt-quench technique and then crystallized using a laser power source. The resulting glass-ceramic was analyzed using X-ray diffraction (XRD) and Raman spectroscopy to determine its structure and phase, while field-emission scanning electron microscopy (FESEM) was used to examine its morphology. The band gap of the glass ceramic was determined using UV-vis spectroscopy. The photocatalytic degradation of methylene blue dye (MB) was done under visible light irradiation.

Keywords: laser induced crystallization, glass-ceramic, photocatalysis, dye degradation

Strain Mediated Photovoltaic Properties in Ferroelectric Nanocomposites

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Ferroelectric materials possess spontaneous polarization and reversible electric-field-induced switching. The resulting unique mechanical, electrical and optical properties have attracted increasing research interest for their potential applications in non-volatile and high-density memories, light modulation, self-powered sensors, and energy harvesting. Moreover, their intrinsic polarization creates a built-in voltage capable of separating photogenerated excitons producing currents without the need for a heterojunction, a mechanism known as the bulk photovoltaic effect (BPVE). The BPVE can produce a photovoltage above the material's bandgap surpassing the S-Q limitations of classic semiconductor heterojunctions. However, the high photovoltage is limited by conductivity which, combined with the intrinsic wide band gap, results in unremarkable efficiencies below 1%. In this work, we create a two-phase ferroelectric-semiconductor vertically aligned nanocomposite (VAN) to overcome the conductivity shortcomings of the ferroelectric while retaining its photovoltaic properties. The ferroelectric material is grown epitaxially together with an insulating phase using the pulsed laser deposition (PLD) technique. The effects of deposition parameters and strain on the microstructure and electrical properties are evaluated before and after the secondary phase is removed via wet chemical etching.

Keywords: ferroelectric, thin film, bulk photovoltaic effect, PLD, vertically aligned nanocomposite

Role of Structural and Orbital Characteristics on the Ferroelectric Photovoltaic Response

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In recent times, the ferroelectrics are considered as potential materials for energy related applications. In particular, the anomalous photovoltaic (PV) response exhibited by the ferroelectric systems attracted immense research interest. Although, there are mechanism reported to understand the bulk photovoltaic effect, efforts to explore the correlation among the PV properties, structural and orbital characteristics are vital to design the ferroelectric system for their PV applications. In this work, we have established a strong correlation among the structural, orbital and photovoltaic characteristics of the lead-free ferroelectric $Ba_{0.875}(Bi_{0.5}Li_{0.5})_{0.125}TiO_3$ (BBLT) oxide, subjected to electric poling, through experimental and theoretical studies. We report 2-fold enhancement in orthorhombic phase fraction along with anomalous PV response with 12 V as open-circuit voltage upon poling in comparison to the unpoled sample. Further, the poling induced structural distortion is analyzed through the (ex-situ and in-situ) Raman and Rayleigh analysis. To substantiate the experimental insights, the DFT calculations carried out on the BBLT system revealed significant changes in the orbital characteristics of low-symmetric orthorhombic phase compared to the robust electronic structure of the tetragonal phase. In addition, we demonstrated that field induced additional z-axis-oriented delocalized orbitals at the band edge in orthorhombic phase could favor large shift current and hence high PV response. The present studies provide the design parameters to engineer the ferroelectric system for better photovoltaic characteristics suitable for device applications.

Keywords: bulk photovoltaic effect, conduction band edge, orbital characteristics, Raman spectrum, structural distortion

Opto-Electronic Control Domain Manipulation in Ferroelectric Oxides

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Interaction between light and ferroic order parameters in nanostructures leads to new physical functionality. In this respect, the quest for opto-electronic control of energy-efficient ferroelectric materials is gaining importance for fast memory applications. Here, we explore the light-induced polarisation switching behaviour in polycrystalline (100 nm), epitaxial (100 nm), and epitaxial free-standing BaTiO3 (18 nm) films. It is observed that after writing the domains with positive and negative voltage, the materials always return to their original downward polarisation state under illumination for both polycrystalline and epitaxial films. The material also exhibits significant enhancement in the amplitude response, which is confirmed by the imaging and spectroscopy analysis under dark and illumination conditions. Importantly, the free-standing BaTiO3 film illustrates domain-switching immediately after illumination. On the other hand, the epitaxial BaTiO3 film shows a slow domain switching response compared to the free-standing relaxed BaTiO3 thin film. Overall, in this presentation, we will discuss observed photoferroelectrics outcomes of robust electric and optics control polarisation cycling of the device for neuromorphic computing.

Keywords: photoferroelectrics, domain switching, polarisation, PFM, neuromorphic computing.

Session M3B: Energy Harvesting

Processing of Smart Porous Electro-Ceramic Transducers (ProSPECT)

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The continuing need for improved performance and reduced power requirements of electronic components, for example for wireless sensor networks, has prompted renewed interest in the development of advanced piezoelectric and pyroelectric sensors which can also be coupled with harvesting technologies capable of capturing energy from ambient vibrations and heat. This presentation provides an overview of piezoelectric materials for sensing, with the closely related sub-classes of pyroelectrics and ferroelectrics. The particular advantages of exploiting porosity in these fascinating materials are emphasised, including how the pore structure and volume fraction can be tailored to optimise the dielectric and ferroelectric properties of these materials; these include aligned pores formed by freeze casting, see Fig. 1. Examples of modelling and manufacture of porous materials sensors and energy harvesters are discussed, including SONAR applications and hydrostatic behaviour. The potential of novel porous, composites, and sandwich structures are briefly described, and the range of potential benefits of using porosity in ferroelectrics and finally overviewed. This work is supported by UKRI Frontier Research Guarantee on "Processing of Smart Porous Electro-Ceramic Transducers - ProSPECT", project No. EP/X023265/1.

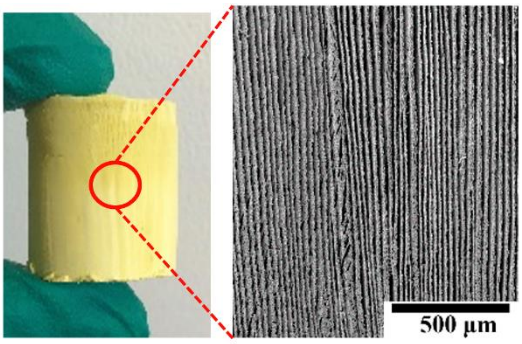

Figure.1 Example of freeze cast porous microstructure

Keywords: piezoelectric, pyroelectric, ferroelectric, sensors, harvesting

Damage Analysis of Functionally Graded Piezo Electric Materials (FGPM)

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During the last decades, research on functionally graded material (FGM) and functionally graded piezoelectric material (FGPM) were significantly increased. Despite the advance in the understanding of the behavior of these materials [1], the prediction of damage and the load that FGM and FGPM structures can sustain is still a great challenge [2]. In this work, we propose, first, to analyze the damage of FGM and FGPM structures using Phase-Field damage model. The impact of polarization on behavior of FGM will be explored (numerally) to improve structure resistance in energy harvesting applications. The second part of this work focuses on a numerical investigation of damage of Ni/BaTiO3 FGM. This investigation will be based on the experimental observation of Ni/BaTiO3 FGM structure [3]. The Comparison of damage behavior between a theoretical FGPM (continuous evolution of properties through the thickness) and layered FGPM will be investigated.

Keywords: FGM, FGPM, layered FGPM, phase-field damage

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Development of Piezoelectric Films Based on PVDF and PVDF/$BaTiO_3$ with Enhanced Performance for Energy Harvesting Applications

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Piezoelectric materials have attracted researchers' attention due to their ability to directly convert applied strain energy into usable electric energy by means of piezoelectric effect. Although piezo energy harvesting has been investigated since the late 1990s [1], it remains an emerging technology to harvest energy from vibration to power sensors. Despite most of the high-performance piezoelectric materials depend on lead (PZT) [2], currently, much interest is focused on the development of lead-free piezoelectric materials due to its high toxicity. In this work, poly (vinylidene fluoride) (PVDF) and PVDF/ barium titanate-based films are developed by following extrusion and compression moulding. Subsequently, to increase the β-phase content [3] of the PVDF matrix and therefore, its ferroelectric behaviour, the obtained PVDF and PVDF/$BaTiO_3$ films are uniaxially drawn in a mechanical testing machine and quenched in water to avoid the relaxation of the polymer chains. Finally, these films are subjected to a polarization process in oil bath (under temperature and high electrical fields) to make them piezoelectric. The poled films are characterized by FTIR analyses showing an enhancement of crystalline β-phase while improved piezoelectric values such as d_{33} piezoelectric coefficient and output voltage response (under tensile tests) are observed. The presented work is based on the research carried out in InComEss project [4] funded from the European Union's Horizon 2020 research and innovation program under grant agreement No 862597.

Keywords: piezoelectric, PVDF, $BaTiO_3$, composites, energy harvesting

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Relevant Parameters to Increase the Harvested Energy of a ZnO Nanowires-Based Nanogenerator

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Harvesting mechanical energy from the environment to power an electrical device and making it autonomous is a real challenge. At GREMAN laboratory, the nanogenerators use a direct piezoelectric effect to convert mechanical energy into electrical one by using ZnO nanowires in a 1-3 piezo-composite structure. These nanogenerators work in a capacitive mode thanks to a dielectric polymer layer placed on the composite structure. Due to the different kinds of used materials inside the nanogenerator, different phenomena are involved in this application. The screening effect of the free electrons coming from the n-type semiconducting ZnO nanowires is one of the most important but polarization effects in the ZnO nanowires or in the polymer capacitive layer are also very important to take into account. This work provides some trends to follow to increase the yield of such a device by using a coupled piezoelectric and semiconducting model developed in Finite Element Method simulations with *COMSOL Multiphysics*®. Relevant intrinsic parameters such as diameter and surface traps density of the ZnO nanowires, dielectric permittivity and thickness of the polymer capacitive layer or extrinsic parameter such as resistance load are studied. The aim is to show how they modify more or less the harvested energy for a given mechanical excitation. By knowing which parameter changings have more impact than the others, nanogenerator design or materials choices can be adapted to increase the harvested energy.

Keywords: energy harvesting, 1-3 piezo-composite, semiconducting nanowire, finite element method.

A Comprehensive Energy Flow Model for Piezoelectric Energy Harvesters: Opening the Black Box

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Piezoelectric materials have significant potential as mechanical energy harvesters and, as the core component of the harvester, holds the key to the power output. While the energy harvesting figure of merit (FoM_{ij}) is frequently used to evaluate the potential performance of an energy harvesting material [1], differences between the power predicted by the FoM_{ij} and the measured output are often observed, but have yet to be analyzed in detail [1,2]. To address this challenge, this paper establishes a new comprehensive energy flow model which assesses the energy extraction, conversion and transfer of a piezoelectric harvester. The energy flow model is experimentally verified for a variety of excitation conditions, with a range of piezoelectric materials fabricated to yield contrasting mechanical, dielectric and piezoelectric properties. Excellent agreement was observed between the measured data and the energy flow model and, compared with the classical FoM_{ij} index, the energy flow model significantly reduced the maximum error in predicted power by ~70%. This work provides a holistic approach to fill the knowledge gap in predicting the power output of piezoelectric energy harvesters and can direct future research in understanding the effect of material modification on overall harvesting performance.

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Towards Spatially Resolved Measurements of Thermal Transport in Ferroelectrics Using Scanning Thermal Microscopy

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Scanning Thermal Microscopy (SThM) is a valuable tool for mapping thermal properties of materials and temperature distributions in *in-operando* devices with nanoscale spatial resolution. I will discuss how SThM can be used to visualise and study the role of domain wall microstructure on heat flow in ferroelectric materials. Interest in using ferroic domain boundaries to enable active control of heat flow has been steadily growing over the last decade and it is well established that they inhibit thermal transport through phonon scattering. However, the more recent discovery that some types of domain wall exhibit enhanced electrical conductivity suggests there might be untapped potential for them to instead act as thermal conduits. To date, direct, local measurements of either of these domain wall thermal behaviours (i.e. as phonon scatterers or as thermal conduits) have yet to be reported. In this talk, I will describe our efforts to locally map spatial variations in thermal conductivity associated with such microstructural inhomogeneity. Our approach involves periodic heating of a thin gold bar deposited on the sample surface (Figure 1(a)) and spatially mapping the resulting temperature oscillations by using the scanning probe as a mobile temperature sensor (Figure 1(b)). We demonstrate proof of principle imaging by mapping thermal contrast across the metal/dielectric layers of a multilayer ceramic capacitor (MLCC) and then use this approach to investigate the thermal transport properties of conducting domain walls in $LiNbO_3$.

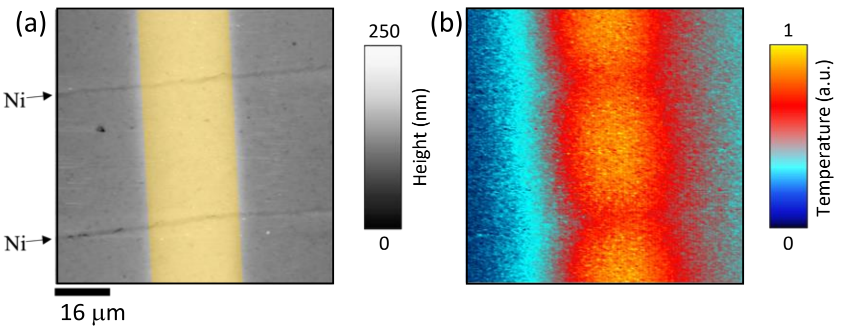

Figure 1: (a) Topography and (b) temperature map measured on heated surface of a cross-sectioned MLCC. Yellow shaded region in (a) represents gold heater

Keywords: scanning thermal microscopy, ferroelectrics, domain walls, thermal transport, lithium niobate, multilayer ceramic capacitors

Understanding Micro Electrical Contact Measurements - an Experimental and Modelling Study

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The research of piezoelectric and ferroelectric materials plays a huge role in the development of a variety of devices. Understanding and reporting back their electrical properties is crucial so accurate comparisons can be made. Typically, to obtain properties such as energy density and breakdown strength, we study the electrical response of these materials at high fields. To achieve the electric field strengths necessary, micro local contacts are used. We have previous shown that in using effect micro contacts the electric field experienced in the sample is not trivial due to spreading of the current and field from one contact to the other. Here using a combination of multi-physics finite element modelling and experimental characterization we show that in using a top micro electrode and a full bottom electrode, the electric field generated is non unform leading to field strengths in the material over four times higher than that generated through a conventional full electrode configuration. This effect is dependent upon factors such as thickness of the sample, contact radius, position, and orientation and can introduce significant errors in the extract measured values of permittivity, strain, and energy storage. Our results demonstrate the importance of understanding how micro contact configurations can influence the electric field and therefore impact values for important parameters of capacitors in literature that could be misleading if the spreading effect is not considered.

Keywords: micro-contacts, local property measurements, finite element modelling, electrical characterization

Versatile Electromechanical Characterization of PVDF in Changing Environmental Conditions

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Piezoelectric polymers are gaining interest due to their unique properties, e.g. high piezoelectric voltage constant, g_{33}, related to high electromechanical sensitivity, when compared to their ceramic counterparts. Due to their favourable thermo- and electromechanical properties, piezoelectric polymers are of great commercial interest for many applications such as ductile sensors in healthcare applications - including wearable smart patches, smart textiles, haptic (touch sensitive) screens and conformable strain gauges for configurable and morphing structures. In the biomedical and consumer markets in particular, sensing applications require highly reliable and homogeneous materials, necessitating the need for accurate and traceable material property data. A suitable measure of material homogeneity can be seen in the distribution of the material's piezoelectric constant d_{31} (or d_{32}) that is, measured within the plane of the polymer film. In the development of novel chemistries and new production processes, detailed evaluation of the electromechanical performance of piezo materials is critical. One of the most prominent piezoelectric polymers is polyvinylidene fluoride (PVDF), used in sonar hydrophones, touch sensitive detectors, and various thermal imaging systems. In this study, a precise characterization of PVDF samples is carried out using a new measurement instrument – the ESPY31 - yielding accurate piezoelectric d_{31}/d_{32} data. Example data sets are shown, calibration and accuracy of measurement data is reviewed, and reliability of the test system evaluated. Mechanical load is applied to the PVDF sample and the current as an indicator of charge is recorded. In addition, temperature and humidity dependent measurements are conducted.

Keywords: PVDF, piezoelectric polymer, electromechanical properties, temperature dependency, humidity dependency

The Role of A-Site Vacancies in the Formation of Temperature Stable Dielectrics in the $NaNbO_3$ - $La_{1/3}NbO_3$ Solid Solution

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This study investigates the $La_xNa_{1-3x}NbO_3$ perovskite solid solution formed between nominally A-site occupied $NaNbO_3$ and highly A-site deficient $La_{1/3}NbO_3$ end members. Specifically, this work aims to create A-site vacancies, introduced within the solid solution as charge compensating defects consequent of the trivalent La^{3+} substitution for Na^+ in the ABO_3 perovskite structure and to correlate their influence on the dielectric properties. Conventional dielectric spectroscopy (DS) analysis reveals a noticeable suppression of the permittivity variation of the system, alongside an associated antiferroelectric-relaxor type transition, as the A-site vacancy concentration increases. Structural investigations involving Rietveld analysis of laboratory X-ray diffraction data reveals a series of phase transitions across the solid solution, with notable diffuse scattering offering insight into the disruption of long-range ordering associated with the $NaNbO_3$ end member – something that may be responsible for the observed flattening in the dielectric response with temperature. Impedance Spectroscopy (IS) measurements suggest good dielectric behaviour (electronically insulating behaviour) can be retained for low doping concentrations of La ($0 \leq x < 0.15$), complementary to low dielectric loss data from DS measurements. Concentrations above this threshold are proposed to induce Na^+ conduction with a maximum conductivity of ~6.3×10^{-5} Scm^{-1} at 300°C for a composition for $La_{0.25}Na_{0.25}NbO_3$. This ionic conductivity correlates well with the high dielectric loss observed for these materials by DS measurements.

Keywords: a site vacancy, dielectric, temperature stable dielectric, Na^+ conduction.

In Situ Characterisation of Ephemeral p-n Junctions Inside Ferroelectric Domain Walls

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Ferroelectric materials are renowned for their distinctive microstructure, characterized by a patchwork of domains where local electrical dipoles align, separated by domain walls that act as interfaces between these domains. What's particularly noteworthy is that while most ferroelectrics possess inherent electrical insulation properties, domain walls can exhibit conductivity [1]. It is now recognised that when a modest positive bias is applied to thin film heterostructures of lithium niobate (LNO), the domain walls exhibit a remarkable behaviour, tilting away from the polar axis and forming what are known as charged head-to-head (n-type) domain walls, which exhibit strong conductivity [2-4]. In this study, we perform *in situ* crosssectional transmission electron microscopy (TEM) imaging of bias-induced domain wall dynamics, allowing us to "live" image the domain wall tilting under applied electric fields. This investigation has yielded a remarkable finding: certain sections of conducting domain walls transition from n-type to p-type as the direction of the applied bias changes. It seems that we are creating a new kind of dynamically formed domain wall p-n junction. Although p-n junctions are commonly found in improper ferroelectric systems like boracites and rare-earth manganites, what we have observed in focused ion beam (FIB) slices of LNO represents a unique phenomenon. The in-wall p-n junctions only exist within a finite bias range, and hence are truly ephemeral in nature. Through monitoring the current-voltage response, we observe striking diode-like characteristics. Moreover, thanks to the dynamic nature of these *in situ* TEM studies, we evaluate the mechanisms involved in the formation of these transient p-n junctions.

Keywords: domain wall nanoelectronics, p-n junctions, in situ TEM

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Session M4B: Lead-free Materials

Bismuth Ferrite Solid Solutions: New Pathways to Microstructural and Functional Property Engineering

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Perovskite-structured solid solutions of bismuth ferrite with barium titanate (BF-BT) have shown great potential for diverse applications, such as energy storage capacitors, piezoelectric transducers and electrocaloric devices. The processing procedures employed to synthesize BF-BT ceramics by solid state reaction exert a strong influence on their structure and properties, often resulting in core-shell type microstructural features. The evolution of microstructure in donor-doped BF-BT ceramics will be illustrated by micro-chemical studies of the heterogeneity in calcined powders and sintered ceramics, using SEM, TEM and nano-SIMS. Among their many intriguing characteristics, BF-BT ceramics exhibit remarkable improvements in ferroelectric ordering and functional properties in response to thermal treatment by quenching from high temperatures (>800 °C). Despite numerous investigations during the past 10 years, the origin of these transformations has not yet been identified conclusively, with several different mechnisms being proposed; these include thermodynamic instability of $BiFeO_3$, domain stabilization by dipolar defect associates, influence of oxygen vacancies on structural distortion, variations in lattice strain and cation-anion bond lengths, and immiscibility between the BF and BT components. In recent experimental studies, we have focused on the modification of quenched BF-BT ceramics by long-term annealing at intermediate temperatures (~500 to 700 °C), which is shown to provide a well-controlled approach to induce the suppression of ferroelectric properties. Through extensive investigations using high resolution TEM-based techniques, we have identified a novel nanoscale phase separation mechanism that is characterized by periodic variations in the concentrations of the constituent elements. As well as providing the answer to the origin of the quenching effects in BF-BT ceramics, this finding can lead to unprecedented control of functional behaviour in a wide range of related oxide solid solutions.

Revisiting the Equilibrium Symmetries at the "MPB" of the BNBT Solid Solution System and Their Influence on the Multifunctional Properties

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The lead-free solid solution system, studied as alternative to lead titanate zirconate as piezoelectric ceramic, of $(Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO_3$ (BNBT100x) is well-known by its structural complexity near the MPB [1]. Authors have studied the processing-structure relationships of submicron structured ceramics obtained by air sintering and hot-pressing from auto-combustion sol-gel nano-powders [2,3]. In contrasts with the commonly accepted globally cubic perovskite structure for unpoled ceramic BNBT6, which evolves under the applied field to a tetragonal and rhombohedral phase coexistence, we have proposed a three phases model [4,5]. The unpoled ceramic has a majority globally cubic perovskite coexisting with a rhomboedrally (R3c) distorted one and a nanosized phase at the surface, that can be observed in ceramic flat specimens and is not present in powder samples [5]. This structure evolves to a textured majority (R3c) rhomboedral perovskite under the applied field. Here we present the study of ceramics obtained by mixed oxides, whose microstructure stays in the range of few microns. Their properties at the electromechanical resonances of thin disks are characterized by the iterative method of analysis of impedance curves [6] and their crystal structure by X-ray diffraction analysis together with Rietveld refinement. The subtle, processing-related differences among the studied ceramics are presented and the general validity of the structural three phases model is tested.

Keywords: bismuth sodium barium titanate, electric field induced phase transition, xrd, dielectric permittivity, piezoelectricity

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High-Performance BCZT Piezoelectric Ceramics Achieved by Ultra-Low Temperature Processing

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The growing market demand for the replacement of lead-based materials within different types of devices (such as motors, sonars, transducers) has made the development of lead-free ceramic materials a hot research topic [1]. Within this context, the environmentally friendly Barium Calcium Zirconate Titanate (BCZT) has been reevaluated as a possible candidate to replace lead-based ceramics, due to the high quasi-static piezoelectric coefficient reported for a particular composition (620 pC/N) [2]. On the other hand, this system presents some disadvantages, such as the high temperatures of synthesis and sintering required for the processing. In this perspective, the processing schedule constitutes a key point for obtaining high-sensitivity piezoelectric ceramics with a pure single-phase [3]. For the above-mentioned reasons, this study aims to evaluate the influence of the processing parameters (milling vessel and media, synthesis, and sintering temperatures) on the properties of the $(Ba_{0.92}Ca_{0.08}Zr_{0.05}Ti_{0.95})\ O_3$ ceramic. Thermal analysis (TGA/DSC), X-ray diffraction (XRD) augmented with the Rietveld method, scanning electron microscopy (SEM) and dielectric and electromechanical properties measurements were used to thoroughly analyze the influence of each step of the processing route on the final product. Starting from new representative examples of thermal and mechanical combined approaches, it is shown that optimal electromechanical properties (K_p= 35%, Q_m=155, d_{33}= 455 pC/N) can be achieved while the synthesis (700 °C/2h) and sintering temperatures (900 °C/ 4h and 1280 °C /6h) were significantly reduced [4]. The potential of investigated routes for the fabrication of high performance lead-free BCZT piezoceramics, and some of the related challenges, are also briefly discussed.

Keywords: barium calcium zirconate titanate; attrition ball- milling; ceramics; piezoelectrics

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Evolution of Structural, Ferroelectric and Piezoelectric Properties of Spark Plasma Sintered Lead-Free KNN-Li/Ta Ceramics

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European legislation has imposed restrictions of hazardous substances, especially for Lead-based materials due to environmental and toxicity reasons. Since these materials are widely used in piezoelectric based technologies, such as actuators or transducers, it enforces to find different substitutes. Among the potential candidates, the Niobate Sodium Potassium ($K_{0.5}Na_{0.5}NbO_3$, KNN) is promising. By adjusting its different substituents and phases, it can reach properties equivalent to Lead-based piezoelectric materials [1]. Spark Plasma Sintering (SPS) process offers the opportunity to limit alkaline volatilization that could appear during conventional sintering [2], to control the microstructure and to produce high densified ceramic up to 99 %. Previous work on Spark Plasma Sintered and Tantalum substituted KNN (KNN-Ta) have shown an enhancement of its piezoelectric properties (k_p=59%, d_{33}=160 pC/N) in comparison of conventional sintered ceramics (k_p=42%, d_{33}=140 pC/N) [3]. Literature puts forward that achieving the proper Lithium (Li) and Tantalum (Ta) substitution in conventional sintered KNN, can greatly enhance this coefficient up to $d_{33} \approx 250$ pC/N [4] through monitoring Orthorhombic-Tetragonal phases. Here, we propose to combine Li, Ta substitutions in KNN and SPS process which have not yet been deeply studied [5]. SEM analyses confirm the microstructural control of the ceramics obtained by the SPS. Moreover, the substitution rate confirms a structural change of the material that has been evaluated by XRD and Rietveld analysis. Together with this structural change, the material undergoes an evolution of its ferroelectric and piezoelectric properties. XPS analyses have been performed in order to assess its remaining oxygen vacancies. The overall characterizations have been carried out in order to understand and achieve optimal control of the piezoelectric properties through co-substitution and SPS process for piezoelectric ceramics available for end users.

Keywords: spark plasma sintering, piezoelectric properties, lead-free ceramics, lithium, tantalum, potassium sodium niobate.

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Insights into the Early Size Effects of Lead-Free High-Sensitivity Piezoelectric $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$ Across the Micron Range

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Ferroelectric, high-sensitivity piezoelectric $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ stands out among lead-free perovskite oxides for its very large piezoelectric charge coefficients and strain under electric field, comparable to best commercial soft PZT piezoceramics. However, transfer to industry is being hindered by processing issues, and the preparation of high-quality, reliable ceramic materials with tailored microstructure remains as a challenge. Indeed, best performances have been reported for very coarse grained materials, and attempts to refine microstructure below the 10-µm grain size consistently resulted in significant loss of functionality. This is very different to the cases of $Pb(Zr,Ti)O_3$ and other lead-containing perovskite systems with enhanced response at a morphotropic phase boundary like $BiScO_3$-$PbTiO_3$ or $Pb(Mg1_{/3}Nb2_{/3})O_3$-$PbTiO_3$ that maintain high piezoelectric coefficients well into the submicron range. We present here a comprehensive study of the grain size effects on the properties of $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ across the micron scale, down to the verge of the submicron one. This required the processing of a series of high-quality, dense ceramics with progressively refined microstructures by spark plasma sintering of nanocrystalline powders obtained by mechanosynthesis. Results clearly show a distinctive evolution of properties across the micron scale. Very good overall performance is maintained between 10 and 5 µm, while distinctive relaxor features appear below this size. This strongly resembles grain size effects in $Pb(Mg1_{/3}Nb2_{/3})O3$-PbTiO3, known to be driven by the slowing down of the relaxor to ferroelectric transition with size reduction. Kinetics however would slow down across a significantly larger scale for $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$, which suggest the presence of comparatively large random elastic fields in the phase convergence region of the system. Role of possible unrelaxed microcrystalline strain is also considered.

Keywords: ferroelectrics, piezoelectrics, lead-free, grain size effects, relaxors

Session T1: Plenary and Industry

Inside Piezoelectricity:
The Structural Origins of Electromechanical Coupling

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Although there is a continuing need for the discovery of new piezoelectric materials, there is no accepted understanding of how crystal chemistry influences the magnitude of the intrinsic piezoelectric effect. Here we show that the piezoelectric coupling coefficient can be defined purely in terms of the differentials between the observable structural variables of strain and polarization in the direct and converse effects, allowing an understanding of how energy conversion is dependent upon the individual ionic piezo-displacements in the crystal unit cell. It is demonstrated that to maximize the magnitude of the piezoelectric coupling factor and charge coefficient, the induced displacements of the cations should be as large as possible, whilst, perhaps counter-intuitively, that of the anions should be vanishingly small, or vice versa. This conclusion is validated through DFT calculations of strain and polarization in simple perovskites in which the displacements of the oxygen ions are artificially restricted, resulting in enhancement of both the charge and coupling coefficients. Accordingly, it is recognized that the "universal" relationship between d_{33} and k_{33} in perovskite oxides is a consequence of the virtually invariant piezoelectric contribution of the oxygen sublattice. The possibly anomalous behaviours of soft PZTs and relaxor-lead titanate single crystals are examined and discussed in terms of the above insights. These findings provide much-needed, crystal chemistry "design rules" for high performance piezoelectric materials. Whilst they may be of limited use in the familiar world of perovskites, they could be highly influential in the selection of functional groups in the design of new organic piezoelectric materials, for which the design space is much larger than for the perovskite oxides.

Keywords: piezoelectricity, ferroelectricity, theory

Performance of KNN in Resonant Applications

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PI Ceramic has been a major supplier of piezoelectric components since 1992. With in-depth knowledge of piezo technology, we meet customer requirements and develop innovative piezoceramics from the material to the assembly. In addition to hard and soft PZT, PI Ceramic has also successfully developed lead-free alternatives in recent years. Due to the fact that Bismuth-Sodium-Titanate (BNT) and Potassium-Sodium-Niobate (KNN) do not have as high piezoelectric properties as their PZT equivalents, semi-static applications are not well served with lead-free materials at the moment. However, we see interesting properties within some specific applications working in resonance. In this talk insights will be given into the performance of KNN in resonant applications.

Keywords: piezo component, piezo material, piezo ceramic, lead-free, KNN, potassium-sodium-niobate

Research and Development of Lead Free Ceramics for Acoustic Transducers

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Piezoelectric materials, as a conversion medium between mechanical and electrical energies, are now widely used in many domains such as medical instruments, tele-communication, car industry, music industry, consumer electronics, seismic exploration, energy harvesting and defence industry. Piezoelectric materials used in the defence industry, especially in underwater acoustics, are largely based on lead zirconate titanate ceramic PbZrxTi1−xO3 (PZT) due to their exceptional performance. PZT ceramics are the core of most sonar and are used in most acoustic sensors for underwater military applications: hydrophones, sonobuoys, dipping sonars, variable depth and hull mounted sonars, torpedoes, and mine hunting sonars. The toxic nature of lead is of great concern during lead mining and the manufacture, use, and disposal of lead-based products. However, it was not until 2002 that directives regulating the use of Pb and other toxic elements in commercial products were introduced [1]. At the European level, the directives RoHS [2] and REACH [3] aim to remove lead from all applications for which its contents are over 0.1% by mass. Because of the critical applications in which they are engaged (medical, military, etc.), PZT-type materials received temporary exemptions because lead-free replacements are not yet available but will eventually have to be replaced by materials using less harmful chemicals. Despite academic research being extremely active in this domain, researchers have not yet gathered all the interesting properties of PZT ceramic on a single alternative lead-free piezoelectric material. Reproducibility of the measures conducted in laboratory and scaling up the manufacturing process to industrial scale still raise numerous issues. As a user of large quantities of piezoelectric ceramics for sonars, Thales is also concerned by the environmental problems associated with PZT and with the restrictions imposed by European legislation. Thales Research and Technology France has been working for several years on the development of lead-free ceramics and here we present the results of research into the preparation of BaTiO3-doped ceramics using a green process carried out at laboratory level, as well as its implementation on a pre-industrial scale. The ceramic process has been optimized and allow to scale–up the production until pre-industrial batches ~50 kg of lead-free piezoelectric BT doped material. Dense ceramics were obtained by uniaxial pressing of atomized BT-doped powder and under air conventional sintering at T > 1000 °C, the poled ceramics presents a piezoelectric coefficient d33=240pC/N, coupling factor kt=42% and Tc =110°C.

Keywords: piezoelectric ceramics, PZT ceramics, lead-free ceramics, “green process”, doped BaTiO3 piezoceramics.

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Applicability of Lead Free Piezoelectrics for Ultrasonic Evaluation

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Lead based electroceramics, including PZT, are currently exempt from the EU ROHS legislation, which bans the use of materials in electronics that contain > 0.1wt% of lead. The exemption is under regular review, including in 2022/3. If the exemption were removed, the impact would be significant on European businesses, particularly the manufacturers, and users of PZT. Currently no lead-free materials exist which have identical performance to PZT in terms of both sensitivity/activity and operating temperature; the vast majority of piezoelectric devices would suffer a prohibitive loss of performance when constructed from these materials. The focus of a significant proportion of lead-free research has understandably been on optimising the activity/sensitivity, however, this can come at the expense of other parameters. These other properties can have an equal or greater effect on the performance, depending on the application, such as mechanical quality factor and acoustic impedance. Here we consider the alternative factors that can impact the applicability of lead-free piezoelectric ceramics within a sensor, looking specifically at the performance for ultrasonic evaluation. We compare the properties of selected lead free piezoelectrics to current lead-based materials, noting the specific properties, which could allow for use in certain applications. We model the performance of these materials for ultrasonic evaluation and then demonstrate their performance in an ultrasonic inspection probe and compare it to that of PZT-based sensors.

Keywords: piezoelectric, lead-free, ultrasonic, NDT, sensor

Session T2A: Piezoelectric Materials and Processing

Ferroelectric Ceramic Thick Films: Processing and Applications

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Nowadays, no one can imagine life without electronic devices. Modern electronic devices and all the electronic components integrated in them must be reliable, powerful, cost-effective, and of the desired size and weight. Electronic components are often manufactured using thick film technology, in which particles dispersed in a specific solvent are deposited layer by layer on a substrate, followed by heat treatment at elevated temperature, ~900 °C. The resulting thick films have a thickness of up to several tens of micrometers. Techniques for processing thick films are screen printing and inkjet printing. The quality of the thick films is influenced by a combination of many parameters, including the properties of the dispersions, the printing conditions and the post-deposition curing, all of which must be optimized and properly adjusted for each individual application. This paper addresses the processing of sodium potassium niobate-based thick films by screen printing and lead zirconate titanate-based thick films by inkjet printing. The preparation of dispersions, especially organic and aqueous-based systems, and their properties required for the chosen deposition technique will be addressed. The influence of processing conditions such as waveform, number of layers, annealing temperature, time and atmosphere on the structure, microstructure and functional properties of the thin films will be summarized. We will show that the obtained thick films have a variety of desirable properties, which are particularly suitable for the realization of ultrasonic transducers and energy harvesters.

Keywords: thick films, screen printing, inkjet printing, lead zirconate titanate, sodium Potassium niobate, ultrasound transducers, piezoelectric energy harvesters.

Textured Lead-Free Porous Piezoelectric Single Crystal-Like Ceramics

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Porous piezoelectric ceramics can possess a unique combination of high piezo-coefficients and low permittivity compared with their dense counterparts. The high piezoelectric activity and low permittivity result in high piezo-sensing and energy-harvesting properties. Texturing these porous piezoelectric ceramics is a novel method to further enhance the piezoelectric properties, approaching that of single crystals. Generally, the tape-casting process is used to fabricate dense textured ceramics, however, it is less suitable for fabricating porous textured piezoelectric ceramics. This work reports on the fabrication of lead-free textured porous piezoelectric ceramics using a directional assembly of piezoelectric templates by freeze-casting. Different types of ceramics templates, such as non-ferroelectric Al_2O_3 and ferroelectric $NaNbO_3$ and $BaTiO_3$ materials are used for the textured growth. Since aligning the ceramics templates using a freeze-casting process is challenging, initial studies were undertaken using Al_2O_3 templates. The application of external fields, such as a magnetic field during the freeze-casting process is also considered to enhance the alignments of the templates. Alignment of the templates during freezing was confirmed using scanning electron microscopy images. Preliminary results of textured ceramics will be presented, and the challenges faced during the fabrication process will be discussed. This work is supported by UKRI New Horizons on Porous Piezoelectric Single Crystal Sensors (POPSICALS); Project No. EP/X018679/1).

Keywords: lead-free, porous, texturing, single crystal, piezoelectric

Enhanced Properties of Relaxor-Pt Single Crystals Poled Under an Alternating Current Electrical Field

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Relaxor-PT singe crystals have been applied in advanced piezoelectric devices because of their high piezoelectric and electromechanical coupling properties that are attributed to their unique domain structures. Recently, alternating current poling (ACP), as a new domain engineering method, was used successfully to further enhance the dielectric and piezoelectric properties of relaxor-PT single crystals. In this talk, an overview of ACP will be given first by reviewing the published findings on ACP of relaxor-PT single crystals with different compositions, vibration modes and dimensions. Domain structures of ACP single crystals and their relationship with the dielectric and piezoelectric properties will also be discussed. Moreover, the stability of ACP single crystals under external thermal, electrical and stress stimulations is studied to explore the implementation of ACP in relaxor-PT single crystals. At the end of this talk, challenges and future perspectives will be discussed as well as the potential applications of ACP single crystals.

Session T2B: Thin Films

Ferroelectric Properties of Halide Perovskite Molecular Semiconductor Thin Films

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Molecular semiconductor ferroelectrics have a bandgap below (3 eV) and are suitable for various applications as sensors, actuators, memory devices, and in photo-ferroelectrics such as optical switches and ferroelectric photovoltaics. There is an increasing rising demand for the miniaturisation of microelectronics, compact energy sources and energy storage devices due to emerging technologies such as the Internet of Things (IoT) and Wearables. As a result of these technological developments, ferroelectric thin films are receiving unprecedented research attention.[1] Halide perovskite semiconductors with tunable structural, dimensional and compositional properties are the most active materials, which have gained tremendous attention in the past decade for various optoelectronic devices.[3] In the present research, a family of dimensional engineered halide perovskite thin films which are solution processed under ambient air conditions, and at low temperatures (100 °C), are investigated for their ferroelectric/piezoelectric and pyroelectric properties. The importance of interface engineering to maximise the polarization (0.5 μC/cm^2 vs 5 μC/cm^2) and piezoelectric d_{33} coefficient ~ 2 pC/N were identified and correlated with the corresponding microstructural and optoelectronic properties. The present study provides new insight into maximising the energy harvesting properties of halide perovskite-based molecular ferroelectrics.

Keywords: dimensional engineering, d33 coefficient, polarisation, flexible devices

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Solution Deposition of Magnetoelectric (1-x)$BiFeO_3$-x$PbTiO_3$ Ferroelectric Films on Ni-substrates

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Simple and cost-effective procedures for the direct integration of ferroelectric perovskite oxides with Ni substrates is demanded to fabricate multifunctional metallic MEMS, such as dual-source energy harvesters. This is a handicap in the case of lead-containing morphotropic phase boundary (MPB) perovskite films for high piezoelectric response, because these perovskites and nickel are thermodynamically incompatible, and either formation of NiO_x or reduction of perovskite elements takes place depending on the processing conditions, giving rise detrimental film-nickel interfaces. The solid solutions of the $BiFeO_3$ with other ABO_3 perovskites, such as $PbTiO_3$ show an improved structural stability compared with pure $BiFeO_3$ and an enhancement of the ferroelectricity/piezoelectricity in the proximity of the MPB, where the rombohedral and tetragonal phases, associated to $BiFeO_3$ and $PbTiO_3$, respectively, coexist. The previous study of the crystal structure and ferroelectric properties of films of this solid solution on Pt-coated Si substrates has allowed us to determine that the MPB in these films is close to the 0.65$BiFeO_3$-0.35$PbTiO_3$ composition.[1] Therefore, we have devised in this work the deposition of MPB $BiFeO_3$-$PbTiO_3$ thin films on ferromagnetic Ni metal and the study of the functional properties of these materials. Ni substrates with different thickness (from 1.7 mm thick to Ni foils) have been tested for the solution deposition of the MPB $BiFeO_3$-$PbTiO_3$ films. Among other strategies, we demonstrate the low-temperature solution processing to be an effective means of kinetically limiting nickel oxidation. The resulting $BiFeO_3$-$PbTiO_3$ films on Ni show appropriate ferroelectric properties and a distinctive magnetoelectric response. In addition, this perovskite system, not explored before on Ni, has much larger switchable polarization than the widely studied Pb(Zr,Ti)O_3, showing, in addition, an excellent down-scaling behavior of ferroelectric properties until the verge of the nanoscale. The magnetoelectric response of these MPB $BiFeO_3$-$PbTiO_3$ films on Ni is discussed in comparison with results reported in the literature for other piezoelectric lead-based perovskite films on Ni.

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Tailoring Grain and Domain Morphology in Ferroelectric Aurivillius Phase Thin Films via Controlled Supersaturation Conditions

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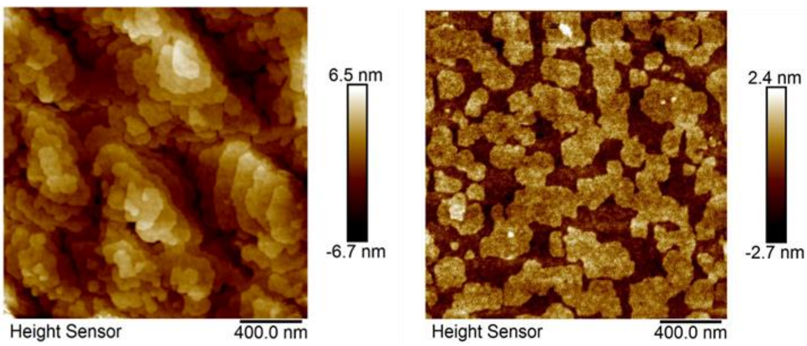
Ferroelectric thin films hold enormous potential for a wide range of device applications, such as synaptic devices based on Ferroelectric Tunnel Junctions (FTJs), non-volatile memory and data storage. However, achieving the desired thin film morphology and domain structure specific to each application requires the development of customized growth methods. In this study, we have developed two parallel synthesis processes using Direct Liquid Injection Chemical Vapor Deposition (DLI-CVD) to synthesize Aurvillius phase $Bi_4Ti_3O_{12}$ thin films tailored for distinct device applications. DLI-CVD enables the frontier development of ultra-thin films with precise control over thickness, employing industrially-relevant synthetic processes. By manipulating the supersaturation levels, we successfully synthesized films with two distinct morphologies of phase pure $Bi_4Ti_3O_{12}$. In the case of high supersaturation conditions, where all precursors are simultaneously injected into the reactor, the resulting topography exhibited characteristics of Frank-van der Merwe growth. Conversely, under low supersaturation conditions, where precursors are sequentially injected, we observed the formation of growth spirals along the crystallographic orientation of the substrate. Varying growth parameters, including oxygen partial pressure, during nucleation was shown to control the growth spirals as evidenced by Atomic Force Microscopy (AFM). Additionally, we report the impact of other factors including cooling pressure, temperature, and bismuth excess using X-Ray Diffraction and AFM. Using AFM-based nano-milling in conjunction with Piezoresponse Force Microscopy, we contrast the ferroelectric response of the thin films as a function of milled depth. Furthermore, we investigate incorporation of magnetic cations (iron and manganese) to the Aurvillius phase structure using low supersaturation DLI-CVD to explore multiferroic properties. These findings provide valuable insights into the growth of Aurivllius phase thin films and offer opportunities to tailor the ferroelectric and multiferroic properties of Aurvillius phase thin films for diverse device applications.



(a.) (b.)

Figure. 1. (a) AFM image of Aurivillius phase $Bi_4Ti_3O_{12}$ synthesized on $SrTiO_3$, demonstrating formation of growth spirals with step heights approximately 1.7 nm (half unit cell) thick. (b) Disappearance of spiral growths with increasing oxygen partial pressure

Keywords: aurivillius phase, ferroelectric thin films, atomic force microscopy

Flexible Piezoelectric Nanogenerators Based on Halide Perovskite Thin Films

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The piezoelectric energy harvesting research was dominated for a long time by oxide perovskite ceramics due to their high piezoelectric coefficient. However, the present market requires the devices to be adaptable to custom design for their easy integration with the emerging microelectronics industry. The fragile nature of conventional oxide ceramics poses a real barrier for them to be used in these applications [1]. Among the promising alternatives, the halide perovskites with the structure of ABX_3 got a better response due to its near room temperature preparation, easy tunability of properties, structural softness, and lightweight over the conventional oxide perovskites; particularly the 2D halide perovskites with better stability is a suitable replacement for the conventional ceramics for energy conversion devices. Here we developed a Ruddlesden-Popper 2D halide perovskite based thin-film ferroelectric and characterized its structural and functional properties suitable for piezoelectric energy conversion and sensor applications. The film processing conditions were varied to optimize the ferroelectric response through the detailed characterization such as X-ray diffraction, dielectric spectroscopy, P-E loop and d_{33} measurements [2]. The developed flexible energy harvesters will be employed to drive the low-power electronic components in Internet of Things (IoT) and Wearables, thereby making these technologies less reliant on primary batteries and more sustainable and environment friendly [3].

Keywords: nanogenerator, halide perovskites, ABX_3, thin films, piezoelectricity, sensors

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Session T3: Plenary

Piezoelectric Materials as Active Biomedical Implants – a "Two-Body Problem"

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Piezoelectric materials are widely used as sensors and actuators, for energy harvesting and vibration control in many industrial and every-day devices. They have established themselves as well in the medical device market as core components in e.g. ultrasound applications and for surgical tools. For *in-vivo* applications, this versatile class of materials could similarly enable localized pressure sensing, energy harvesting from muscle motion or stimulation of tissue re-generation after surgery. However, piezoelectric materials have not made the jump into clinical usage so far. The main challenge here is that materials used *in-vivo* have to be biocompatible. This is a concept that goes way beyond simple chemical toxicity but covers all aspects that influence the safe performance of a material at the implant site under the complex conditions that the body imposes. The investigation and adaption of piezoelectric materials for *in*-vivo applications is a rapidly growing research field that brings together scientists from a wide range of disciplines. Here, we will take an in-depth look into the state of the art of the applicability of piezoelectric materials for *in-vivo* biomedical applications. This will be done both from the view of the body as well as from the view of the implant material – as both influence each other. We will investigate the boundary conditions that the body imposes on implant materials in different applications and how these might impact the functionality and stability of piezoelectric implants. And *vice versa* we will explore the influence of material properties, such as surface topography, chemical composition and mechanical properties, on the living system. In that spirit, we will discuss future application areas for this versatile class of materials in the biomedical realm.

Session T3A: Piezoelectric Composites

Elaboration and Evaluation of Ni/$BaTiO_3$ Functionally Piezoelectric Graded Material Properties

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In recent years, new composite materials called Functionally Graded Materials (FGM) have emerged, initially developed to resolve thermal problems. Their feature is that their properties vary continuously in one or more directions. They consist of a combination of two materials, often ceramics and metals, with different structural and functional properties, ideally transitioning continuously between them. More recently, this concept has been extended to piezoelectric materials, known as Functionally Graded Piezoelectric Materials (FGPM). Their aim is to enhance energy recovery capabilities or active vibration control by replacing traditional structures with piezoelectric patches with a single FGPM structural material. The disadvantages associated with conventional smart structures, such as potential delamination and debonding of patches, are reduced or even eliminated. The numerical simulations show their effectiveness in active vibration control and energy harvesting. However, very few articles deal with the elaboration of FGPM. This work deals with the elaboration and characterization of FGPM made from Nickel and BaTiO3 powders. Cylindrical samples of monolayers and FGM (5 layers) with a diameter of approximately 10 millimeters and a thickness of 5 mm have been manufactured using the Spark Plasma Sintering (SPS) technique. An interesting approach involves using an ultrasonic device to measure the speed of longitudinal and transverse acoustic waves transmitted through the sample, enabling the determination of elastic properties such as Poisson's ratio and Young's modulus. The density, Young modulus, Poisson ratio and hardness have been characterized for various compositions. A power law-based homogenization approach depending on volumetric fraction has been proposed. The polarization and the characterization of piezoelectric properties is in progress.

Keywords: FGM/FGPM materials, spark plasma sintering (SPS), mechanical characterization, power Law

PVDF-BST-Based Magneto-Electric Flexible Composites

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Flexible composites are gaining considerable attention for their distinct electrical properties and versatility. In this study, a flexible composite was prepared through a solution method, using Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) as a matrix in which varied proportions of $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) and $SrFe_{12}O_{19}$ powders were integrated. BST displays ferroelectric properties at room temperature (RT). In pursuit of magnetoelectric coupling at RT, $SrFe_{12}O_{19}$ powders were incorporated into the composite alongside BST, in equivalent proportions. An initial solution was prepared by dissolving the matrix in dimethylformamide (DMF), with subsequent incorporation of the particles within the polymer matrix. The optimal homogeneity was ensured through the addition of a surfactant during the fabrication process. The prepared solution was cast onto a flat Petri glass surface, then subjected to a drying process at 140°C for 20 min, to form flexible thick films. The prepared flexible thick films were further subjected to a comprehensive analysis to investigate their structural, microstructural, electrical, and magnetic properties, to elucidate the precise formation, arrangement, and interaction of the particles within the PVDF-HFP matrix. Broadband impedance spectroscopy analyses shown improved interfacial polarization and an increased number of internal microcapacitors as a relaxation source. Lastly, the magnetic properties were assessed in relation to the desired magnetoelectric coupling. Through our detailed exploration of the particle/polymer materials, we aim to shed light on the effects of particles size, shape, distributions, interfaces, and local crystalline structure/defects on the effective responses of the macroscopic properties in magnetoelectric PVDF-HFP-based composites.

Keywords: flexible composites, magnetoelectric coupling, ferroelectric, thick films

Curie Temperature Manipulation to Improve Dielectric and Piezoelectric Properties of $BaZr_{0.15}Ti_{0.85}O_3$ Ceramics

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Ferroelectric materials show anomalies of electrical, mechanical, optical, and caloric properties in the vicinity of the ferroelectric-paraelectric phase transition (Curie temperature- T_C). Unfortunately, for pure ferroelectrics, this transition is very sharp and at high temperatures, which makes them difficult to use for microelectronics applications. The common approach to lowering the T_C is doping at the A or B site of the perovskite cell. Another approach is to create a reduced atmosphere by forming oxygen vacancies. While the shift in the T_C due to the addition of different doping elements has been reported by many authors, the change in the T_C due to oxygen vacancies and the induced strain was rarely reported [1]. In the present paper, we induced a shift of T_C of $BaZr_{0.15}Ti_{0.85}O_3$ ceramics by adding different amounts of multi-walled carbon nanotubes (CNT). Ceramics were obtained by sintering at 1500 ^oC the mixed powders using a thermal treatment like other porous ceramics prepared previously [2]. X-ray diffraction data showed the phase purity and complete combustion of CNT. Dielectric properties were investigated at room temperature for frequencies between (10^0-10^6) Hz and a decrease of permittivity from 2500 to 1500 at f=1 kHz, for a small addition of CNT was recorded, while for the highest CNT content permittivity increase to 5000. The temperature dependence permittivity shows a shift of T_C from 63 ^oC to room temperature with increasing CNT addition and low dielectric losses for all ceramics and temperatures. Ferroelectric properties show a complex behavior with a decrease of P_s with CNT addition and a modification in the hysteresis loop.

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Session T3B: Thick Films

Screen-Printed Lead-Free, Low-Cost Piezoelectric Composites for Posture Monitoring

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In response to the growing number of posture-related health issues and the increasing need for eco-friendly and affordable materials, this study investigates the formulation and application of barium titanate ($BaTiO_3$) based screen-printable inks for low-cost and lead-free flexible sensors. Comprehensive experiments were conducted to evaluate the rheological, structural, and morphological characteristics of the printed composites, as well as their sensing performance. Screen-printable inks were formulated and characterized in terms of their shear frequency-dependence, stress frequency-dependence, and three-part recovery tests to study the effect of the plasticizer and $BaTiO_3$ microparticles on the rheological response of the composites. The structural and morphological characteristics were examined through Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The functional sensing behavior was investigated through impedance spectroscopy, piezoelectric, and ferroelectric experiments. The study extends to the development and testing of an Arduino-based system, integrating these $BaTiO_3$ printed piezoelectric sensors for practical posture monitoring. The research findings showcase the potential of such affordable, eco-friendly systems in advancing posture monitoring capabilities. This work thus lays the groundwork for future innovations in the rapidly evolving field of smart wearable technology, offering valuable insights for subsequent research endeavors.

Keywords: BaTiO3, screen printing, lead-free sensors, posture monitoring, arduino, wearables

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Impact of a Substrate Layer on Piezoelectric Coefficients

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In the process of disposing piezoelectric transducers on specific shapes and forms, the use of a substrate above and under the piezo might be necessary. Therefore, depending on the substrate properties (material, thickness), the piezoelectric coefficients might change leading to a loss in the electromechanical coupling. The purpose of the works conducted in the LGEF at INSA – Lyon was to study the impact of this substrate layer depending on its thickness. A model of the impact of a substrate layer on the piezoelectrical coefficients has been derived from [1] and successfully compared to experimental data. This model gives the variation of certain piezoelectric coefficients such as k_{31} *or* d_{31} for various brass volumes relative to the ceramic volume. For example, k_{31} decreases with a thicker brass substrate layer. The piezo electric transducers used are NAVY II PZT that are 580 microns thick and the substrate was a brass layer with a thickness going from 50 microns to 400 microns. After applying a silver covering on both electrodes and polarizing the ceramic, the piezoelectric coefficient k_{31} is measured by applying an electric sweep with a network analyser and compared with various thicknesses of brass during this study. The model fits very well the results for a brass substrate, giving good expectations on the use of this model to evaluate the impact of a substrate layer (from various materials) on electromechanical coupling of piezoceramics.

Keywords: piezoceramics bending, curved structures, vibration damping, multi-frequency damper

Acknowledgments: We would like to thank the DGA for the financial support.

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Fabrication and Application of Piezoceramic Thick Film Sensors for Process Monitoring of Cutting Tools

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Piezoceramic thick films offer the possibility of integrated solutions for sensors, actuators, ultrasonic transducers, and generators. Depending on application field piezoceramic material (soft, hard) and substrate base needs to be adjusted. Especially substrate material has a decisive influence on the piezoelectric coefficient of the piezoceramic thick film because of thermal constraints and possible chemical reactions. For sensors in machine tools, only special steel grades are of significance. We therefore investigated influence of material selection and layer sequence on piezoceramic properties to build thick film sensors for real-time process monitoring and controlling in cutting tools. Detailed information of cutting force is required for improving the performance of milling or turning processes. They are of key relevance for optimizing tool life and reducing workpiece waste by predicting tool wear and possible breakage. This allows for optimizing resource use and output quality of the workpiece. We recently developed novel systems for measuring the cutting force in direct vicinity of the cutting tool in milling and turning machines. The unique design and features of the new sensors enable accurate and continuous force measurement as well as the indication of wear. The results of the experimental investigations are presented and compared to results of a conventional dynamometer.

Keywords: sensor, piezoceramic thick film, process control, process monitoring, cutting tool

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Session T4A: Processing of Piezoceramics

$BaTiO_3$ Ceramics by Cool-SPS at 600°c: Towards More Sustainable Lead-Free Ceramics?

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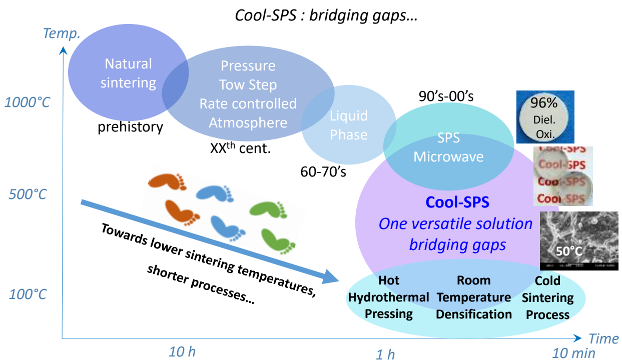
Success in sintering lead-free, ternary perovskites by Cool-SPS while preserving their physical properties paves the way towards more sustainable materials and processes. Lowering the environmental footprint associated to ceramics requires to reduce the sintering time and temperature needed for efficient sintering. In addition, it is desirable to limit the use of harmful chemical elements such as lead in functional materials. Trying to address the first challenge, many new sintering methods [1,2] are being developed to sinter ceramics at low temperature such as Room Temperature Fabrication, Cold Sintering Process or Reactive Hydrothermal Liquid-Phase Densification. Low temperature sintering can now claim many successes and appears as a convincing route towards more sustainable shaping processes. Among the diversified approaches to low temperature sintering, Cool-SPS can be used to obtain highly densified ceramics of thermodynamically fragile materials at low temperature and high pressure [3-7], with an adapted sintering strategy taking advantage of its many degrees of freedom [8-10]. In the present communication, we report the Cool-SPS processing of lead-free functional perovskites, trying to shape more sustainable materials with more sustainable processing routes. Several simple, ternary perovskites from this large family were rapidly and successfully densified by Cool-SPS, with final relative densities ranging from 80% to 95%. Experimental parameters, monitored *in situ* during the sintering, were studied in order to investigate and optimize the sintering path. The evolution of these parameters highlights events like chemical reaction and densification, providing hints to improve the relative density of the final ceramic. In addition, the microstructures and dielectric properties of the final materials were investigated, in order to confirm the preservation of functional properties and their eventual evolution through Cool-SPS processing. In the end, we will demonstrate that Cool-SPS allows for the elaboration of dense ceramics of lead-free functional perovskites, that it bridges gap in the range of sintering conditions, between solvent-assisted methods and temperature-activated sintering (Fig.1), indeed paving the way towards more sustainable materials and processes.

Figure.1 Complementarity of sintering strategies



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Keywords: cool-SPS, perovskite, $BaTiO_3$, dielectric, functional, sustainable

Behind the Enhanced Electrical Performance of Flash Sintered Potassium Sodium Niobate Ceramics

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In view of sensor, actuator, and energy harvesting applications, lead-free $K_{0.5}Na_{0.5}NbO_3$ (KNN) ceramics present such benefits as high ferroelectric transition temperature and elevated piezoelectric coefficient, if their content of secondary phases is diminished. Alternative sintering techniques, including electric field- and current-assisted Flash sintering, are promising for low thermal budget production of single-phase KNN ceramics, which electrical properties however have not been widely disclosed so far. Here, KNN ceramics Flash sintered at 900 ºC for 60 s only is successfully demonstrated to be of high performance. These ceramics with Pt electrodes cured at 900 ºC possess room-temperature remnant polarization P_r = 21 μC/cm^2 and longitudinal piezoelectric coefficient d_{33} = 117 pC/N, slightly superior to that for KNN ceramics conventionally sintered at 1125 ºC for 3 h with identical electrodes [1]. At the same time, the electrical performance of as-sintered ceramics obtained using Flash and conventional processes with sputtered Au electrodes has opposite relation. Thus, comparative and systematic ferroelectric, dielectric permittivity, impedance spectroscopy, and DC conductivity analysis shows that heat treatment, synergistically needed for the Pt electrode curing and ceramic defect relaxation, is not less important than the low thermal budget Flash sintering process for potential applications of Flash KNN ceramics in innovative low-carbon technologies.

Keywords: ferroelectrics; lead-free piezoelectrics; KNN; heat treatment

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New Dielectric Ceramics with Ultralow Sintering Temperatures and Dielectric Loss for Passive Integration

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With the development of electronic and information system towards miniaturization and high density integration, especially the speedy applications of system in package and internet of things, it is required that the electronic materials and components should have the matching properties such as high performance, multifunctional, high frequency enabling and low energy consumption. The highlights of our research on the novel LTCC (Low Temperature Co-fired Ceramic) dielectric ceramics with ultra-low dielectric loss and high thermal conductivity for 3D passive integration and advanced electronic packaging will be presented, while the remaining challenges and the promising opportunities of the development will be mentioned as well.

Keywords: LTCC, passive integration, dielectric properties, sintering, electroceramics.

Session T4B: Piezoelectric Materials

Piezoelectric Biomolecules for Lead Free, Reliable, Eco-Friendly Electronics

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Billions of piezoelectric sensors are produced every year, improving the efficiency of many current and emerging technologies. By interconverting electrical and mechanical energy they enable medical device, infrastructure, automotive and aerospace industries, but with a huge environmental cost. Amino acids are the most basic biological components, and they are cheap and simple to crystallize, with significant piezoelectricity in single crystal and polycrystal forms. However, this response is highly anisotropic, and precise, orientated control over crystallisation is required to maximize the piezoelectric output of a crystalline amino acid device for development into a cohesive ceramic-type element. Our research is taking on the challenge of developing biomolecular crystals as organic, low-cost, high-performance sensors, to out-perform and phaseout inorganic device components with dramatically reduced environmental impact. In this talk I will discuss our methodologies for the design, growth, and engineering of these novel piezoelectric materials under three pillars: An ambitious computational workflow to enable the design of super piezoelectric crystalline assemblies by combining high-throughput quantum mechanical calculations with machine learning algorithms; A new method of growing polycrystalline biomolecules, allowing for easy, efficient creation of macroscopic piezoelectric structures; Establishing effective electromechanical testing procedures to characterise fully insulated and contacted biomolecular device components. Even 'weak' organic piezoelectric with modest piezoelectric constants can yield significant voltages in response to strain because the piezoelectric voltages produced under an applied force are inversely proportional to the material's dielectric constant.

Keywords: piezoelectrics, bioelectrets, crystals, density functional theory, energy harvesting

Piezoresponsive biocomposites

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The development of piezoresponsive biocomposites and the understanding of the relationship between composition; structural and morphological features; and the functional properties has been the focus of our research at CICECO – Aveiro Institute of Materials of the University of Aveiro. In this presentation it will be described the challenges that we have been facing on the development of biocompatible piezoresponsive materials based on polysaccharides and piezoelectric ceramic nanoparticles for sensors, actuators and energy harvesters.

Keywords: Piezoelectricity, electrostritive, flexible devices, electromechanical response, polysaccharides

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). Also, this work was funded by national funds, through FCT, IP, in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, changed by Law 57/2017. FCT is acknowledged by the PhD fellowships ref. UI/BD/151142/2021 and SFRH/BD/150787/2020.

Micro and Macro Electromechanical Characterization of Chitosan Films

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The investigation of electromechanical properties in chitosan-based composites represents a rapidly growing and exciting area of research with significant potential applications in electronics, sensing, and biomedicine [1]. However, elucidating the source of their electromechanical performance has proven to be challenging, given variations in fabrication conditions and measurement methodologies. In this study, a systematic characterization of chitosan pristine films was conducted. Structural characterization was achieved through X-Ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) methods. Mechanical properties of the films were evaluated using tension until rupture tests following ASTM D 882 and 883 practices. The electromechanical performance was investigated using piezoelectric force microscopy (PFM) technique, including the analysis of the second harmonic signal [3] and piezoelectric sensitivity measurements. The findings revealed that the primary contributors to the electromechanical performance were the electrostrictive and electrostatic effects, prompting further inquiry into non-piezoelectric components in dielectrics [2]. Additionally, the study focused on the electrostrictive component of chitosan-based bionanocomposites, specifically comparing the effects of chitin nanostructures and barium titanate nanoparticles on the electromechanical performance of the chitosanbased films fabricated via the solvent casting method. This investigation aims to enhance the understanding of bionanocomposites derived from polysaccharides, particularly in the context of their potential use for future flexible electronic applications.

Keywords: chitosan film, electromechanical characterization, piezoresponse force microscopy

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). Also, this work was funded by national funds, through FCT, IP, in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, changed by Law 57/2017. FCT is acknowledged by the PhD fellowship ref. UI/BD/151142/2021. COST Action CA18132 is acknowledge for STSM funding.

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3D-printed Polymer Composite Devices Based on a Ferroelectric Chiral Ammonium Salt for High Performance Piezoelectric Energy Harvesting

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The advent of three-dimensional printing has unlocked fresh possibilities for creating intricate structures, which play a crucial role in the advancement of flexible and wearable electronic devices. There is a growing demand for high-performance devices that utilize organic ferro- and piezoelectric compounds, as they offer significant advantages over conventional piezoceramics. These compounds address key limitations such as toxicity and difficulties in processing at high temperatures. Herein, we present a 3D-printed composite of a chiral ferroelectric organic salt {$[Me_3CCH(Me)NH_3][BF_4]$} (1) with biodegradable polycaprolactone (PCL) polymer that acts as an efficient piezoelectric nanogenerator (PENG). The ferroelectric property of 1 arises from its polar tetragonal space group $P4_2$, which has been confirmed by *P-E* loop measurements. Piezoresponse force microscopy (PFM) revealed a characteristic 'butterfly' and hysteresis loops. The amplitude vs. drive voltage measurements of PFM indicated a relatively high magnitude of the converse piezoelectric coefficient for 1. PCL polymer composites of 1 with varying weight percentages (wt%) were prepared and subjected to piezoelectric energy harvesting tests, which shows a maximum open-circuit voltage of 36.2 V and a power density of 48.1 μW cm^{-2}. The practical utility of this device was further tested by preparing a gyroid-shaped 3D-printed structure, which again showed an excellent output voltage of 41 V and a power density of 56.8 μW cm^{-2}. These findings demonstrate benefits of using organic piezoelectric compounds for building biodegradable PENG devices using advanced manufacturing technologies.

Keywords: three-dimensional printing, ferroelectric, piezoelectric

Session W1A: Capacitor Materials

Strategies for Optimising Energy Storage Properties in Electroceramics

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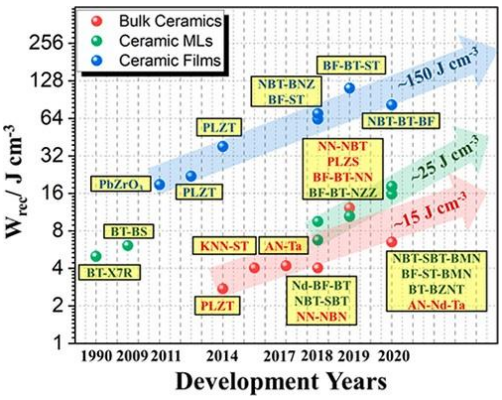
Materials exhibiting high energy/power density are currently needed to meet the growing demand of portable electronics, electric vehicles and largescale energy storage devices. The highest energy densities are achieved for fuel cells, batteries, and supercapacitors, but conventional dielectric capacitors are receiving increased attention for pulsed power and power electronic applications due to their high power-density, high-voltage and fast charge-discharge speed. The key to high energy density in dielectric capacitors is a large maximum but small remanent (zero in the case of linear dielectrics) polarisation and a high electric breakdown strength. Polymer dielectric capacitors offer high power/energy density for applications at room temperature, but above 100 °C they are unreliable and suffer from dielectric breakdown. For high-temperature applications, therefore, dielectric ceramics are the only feasible alternative. Lead-based ceramics such as La-doped lead zirconate titanate exhibit good energy storage properties, but their toxicity raises concern over their use in consumer applications, where capacitors are exclusively lead free. Lead free compositions with superior power density are thus required. In this talk, key factors to improve energy storage properties such as the control of local structure, phase assemblage, dielectric layer thickness, microstructure, conductivity, and electrical homogeneity through the choice of base systems, dopants, and alloying additions will be discussed to guide future research in high power/energy density capacitors.

Figure. 1 Development of Electroceramics (bulk ceramics, ceramic multilayers and films) for high energy density capacitors



Keywords: electroceramics, energy density, optimization strategies, dielectric, electrostatic

Antiferroelectric-like Tetragonal Tungsten Bronzes for Capacitor Applications

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Multilayer ceramic capacitors are used in abundance globally due to their prevalence in electronic devices and are typically based on the ferroelectric perovskite, barium titanate ($BaTiO_3$). However, due to its significant collapse in relative permittivity above T_C and at high fields, $BaTiO_3$ has limitations for applications under extreme conditions. Meeting the demand for high-specification capacitors is becoming an increasing technological challenge. Antiferroelectrics provide a promising solution due to their enhanced polarizability at high field and temperature-stable permittivity. Tetragonal tungsten bronzes (TTBs) are a class of materials with the general formula $A1_2A2_4B1_2B2_8O_{30}$. They are structurally related to the commonly studied ABO_3 perovskites but with additional chemical and structural flexibility. Although ferroelectric TTBs have been widely studied, compositions which exhibit antiferroelectric-like behavior have only recently been reported.[1-4] Understanding the origins of the desired antiferroelectric-like behavior is key for future development. The complex chemistry and structural complexity of these materials, however, requires a suite of techniques including electron, neutron and synchrotron diffraction combined with dielectric, ferroelectric and second harmonic generation measurements in order to untangle the composition-structure-property interrelationships. Here we will discuss some of our recent work in this area.

Keywords: ferroelectric, antiferroelectric, tetragonal tungsten bronze, multilayer ceramic capacitors

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Bismuth Potassium Titanate - Bismuth Ferrite Based High Energy Density Ceramic Capacitors

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$K_{0.5}Bi_{0.5}TiO_3$ (KBT) is a perovskite structured ceramic which has a broad ferroelectric phase transition (TC) at ~300°C. Unlike many of its ferroelectric perovskite counterparts such as $BaTiO_3$, $PbTiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$ and despite being lead-free, KBT is not extensively used within solid solutions to form functional ceramics; exceptions include Bell and co-workers who developed high temperature piezoelectric ceramics using KBT as a base. There are even fewer reports of KBT being used for dielectrics for the fabrication of capacitors, despite its high Tc in comparison to $BaTiO_3$; the mainstay of the ceramic capacitor industry. Much of the reluctance to develop functional ceramics based on KBT stems from difficulty in processing with typically only a short temperature interval available between an adequate sintering temperature and melting. In this contribution, we present the unique crystal chemistry of KBT and illustrate how the suitable dopants not only engender functional properties but also permit greater control over sintering. Examples include $(0.6\text{-}x)K_{0.5}Bi_{0.5}TiO_3$-$0.4BiFeO_3xRe(Mg_{2/3}Nb_{1/3})O_3$ (KBT-BF-xReMN, Re = rare earth) with $0.08 \leq x \leq 0.10$ giving comparatively high energy density, Wrec ≥ 3 J/cm3 and efficiency, η~75% at an intermediate Emax ~250kV/cm and high electrostrain, high temperature materials based on $0.91K_{1/2}Bi_{1/2}TiO_3$-$0.09(0.82BiFeO_3$-$0.15NdFeO_3$- $0.03Nd_{2/3}TiO_3)$.

Keywords: ceramics, ferroelectrics, perovskite, capacitors

Dielectric Behavior of High Entropy Ferroelectrics

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High entropy materials represent interesting properties, such as a preference to form single phase materials, lattice distortions, small grain sized microstructure and unexpected properties that go beyond the rule of mixtures of their constituent components. Recently three groups of high entropy ceramics, including perovskite structured ABO_3 ferroelectrics, Aurivillius phase ferroelectrics and perovskite layer structured (PLS) ferroelectrics, were successfully prepared and characterized [1-3]. ABO_3 ferroelectric $(Pb_{0.25}Ba_{0.25}Sr_{0.25}Ca_{0.25})TiO_3$, including 4 elements at A-site, contains minor secondary phase and perovskite structured ferroelectric phase which includes nano domains. When the elements at A-site were increased from 4 to 6 in the structure, single phase ferroelectric $(Pb_{1/6}Ba_{1/6}Sr_{1/6}Ca_{1/6}Na_{1/6}Bi_{1/6})TiO_3$ was prepared, which can be attributed to high entropy effect. Two-layer structured Aurivillius phase high entropy ceramics, $(Ca_{0.25}Sr_{0.25}Ba_{0.25}Pb_{0.25})Bi_2Nb_2O_9$ and $(Ca_{0.2}Sr_{0.2}Ba_{0.2}Pb_{0.2}Nd_{0.1}Na_{0.1})Bi_2Nb_2O_9$ were prepared and both ceramics are single phase with space group $A2_1am$ at room temperature. Multi-domain configurations, including long range ordered ferroelectric domains and nano domains, were observed in the ceramics. Their improved piezoelectric constant was attributed to their low coercive fields, which were related to the multi domain configurations. Additionally, single phase four-layer structured Aurivillius phase $ABi_4Ti_4O_{15}$ ceramics with 3, 4, 5 and 6 elements at A-site were separately prepared using solid state reaction. Their dielectric breakdown strength (BDS) increased with entropy increase and the ceramics with 6 elements at Asite showed the highest DBS due to maximized local stress field. Relaxor ferroelectric behaviour was observed in PLS $(Ca_{0.5}Sr_{0.5}Ba_{0.5}Pb_{0.5})Nb_2O_7$ high entropy ceramic which is singlephase structure with space group Cmcm. The relaxor ferroelectric behaviour is characterized by a broad and frequency-dependent permittivity maximum and a current peak around zero electric field in I-E loops. Its value of the relative permittivity $\varepsilon' = 130$ at 1 kHz and room temperature is much larger than that for conventional PLS ceramics $Sr_2Nb_2O_7$ ($\varepsilon' = 42$) and $Ca_2Nb_2O_7$ ($\varepsilon' = 38$). This can be attributed to the presence of polar nano regions and the lattice distortion effect in high entropy materials.

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Session W1B: Lead-free Materials - Applications

Enhanced Piezoelectric Properties and Ageing Behavior in Highly Aligned Porous Bismuth Ferrite-Barium Titanate Ceramics

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Piezoelectric sensors and actuators are used in space, robotics, medical, military, automotive, and other applications under extreme conditions. Piezoelectric sensors must survive harsh conditions and have steady piezoelectric properties in order to have excellent sensitivity, stability, and robustness. Lead-free bismuth ferrite-barium titanate (BF-BT) piezoceramics that possess high Curie temperatures over 400 °C and piezoelectric charge coefficient (d_{33}) over 200 pC/N are a potential replacement material for the hazardous lead-based lead zirconate titanate (PZT) for high temperature applications [1]. In this work, we freeze-casted $0.70BiFeO_3$+ $0.30BaTiO_3$ + 1mol% MnO_2 (BFBT30) materials to create an aligned porous microstructure using freeze cast techniques for high temperature piezoelectric sensing applications. We observed that the introduction of highly aligned porosity, 40% ≤ vp ≤ 60%, improved the poling efficiency and significantly reduced the ageing effects relative to the dense BFBT30. The dense and porous BFBT30 ceramics had similar longitudinal piezoelectric coefficients d_{33} immediately after poling, yet the dense samples were observed to age faster than porous ceramics. After 24 hours, for example, the porous samples had significantly higher d_{33} values ranging from 112 to 124 pC/N, compared to 85 pC/N for the dense samples. Moreover, Porous samples exhibited three and five times higher longitudinal piezoelectric voltage coefficient $\boldsymbol{g_{33}}$, and energy harvesting figure of merit $\boldsymbol{d_{33}g_{33}}$ than dense samples due to the increase in d_{33} and decrease in relative permittivity with porosity, making them more promising for high-temperature sensing and energy harvesting applications.

Keywords: lead free piezoceramics, aligned porous microstructure, sensing and harvesting, high Curie temperature

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Design, Testing, and Comparative Analysis of Lead-Free KNN-NTK and PZT Piezoceramics in a Time-of-Flight Flowmeter Application

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The RoHS regulation may soon prohibit the use of lead in piezoelectric ceramics for industrial monitoring and control instruments. Consequently, alternative solutions, such as lead-free KNN piezoceramics, need to be explored for applications such as time-of-flight flowmeter transducers. A direct comparison of material parameters indicates that PZT materials are still superior to their lead-free alternatives. However, there is limited research evaluating KNN piezoelectric ceramics and comparing them to PZT in industrial settings. A water flowmeter transducer was designed for experimentation, investigating capacitance, sensitivity, bandwidth, and impedance differences. The findings show that KNN-NTK piezoelectric ceramics have lower overall transmitted energy than PZT when simply replacing the active element. The sensitivity of lead-free transducers was found to be 38% lower than lead-containing transducers. Consequently, an empirical approach was taken to improve the sensitivity of lead-free flowmeter transducers by increasing the area of the active element – adjusting the diameter of KNN-NTK ceramics discs from 7mm to 9mm. Results show that, with certain adaptations in the dimensions and design of the transducer, KNN-NTK can reach and even exceed the performance of PZT for a flowmeter application. In conclusion, KNN-type lead-free piezoceramics can serve as a substitute for PZT in sensing transducers, albeit with some performance losses. However, design modifications could be made to maintain performance in time-of-flight flowmeter applications with a compromise in robustness, dimensions, and other transducer properties. These findings contribute to the preparation of the expiration of the RoHS exemption for PZT and open up new research avenues for optimizing lead-free piezoelectric ceramics in an industrial context.

Keywords: lead-free piezoceramics, KNN, RoHS, PZT, time-of-flight flowmeter, acoustic impedance

Development of Pb-Free Ceramics for Various Piezo Applications

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The invention of new devices for home appliances, vehicles, and smart equipment has been made possible by the availability of elegant materials. The toxicity of the components used in the products coupled with commercial gains became secondary in the drive of such development. The development of Pb-based piezoelectric materials, with their inherent adverse impacts on individuals and the environment, is one such notable example. Commercially available piezoelectric materials like PZT cover a wide range of applications, including actuators, sensors, and transducer devices, in the functionality of combining mechanical and electrical energy. A viable solution is to create new Pb-free materials to replace the hazardous components of the current gadgets. Our strategy is to create new, environmentally friendly piezoceramics that have characteristics that are extremely comparable to PZT's and can take the place of specific piezoelectric goods. We think that by defining perks (important material properties) for a certain application, this can be accomplished. This, in our opinion, will enable us to preserve the quality of the piezo material when it is included into the industrial device directly. Currently, we have developed $Na_{0.4}K_{0.1}Bi_{0.5}TiO_3$ ferroelectric ceramics. The discovered Pb-free ceramic with their competitive qualities have the potential to replace the Pb-based ceramics currently used in commercial devices. We have successfully demonstrated such one-to-one replacement in spark igniter and piezo buzzer devices. Additional products will also be built, creating additional opportunities for tactical and civil applications.

Keywords: ceramic, ferroelectric, environment-friendly, non-resonant, spark igniter, piezo buzzer

Qualification of Modified $(Ba,Sr)(Sn,Ti)O_3$ for Electrocaloric Components Fabrication

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Over the past decade solid-state cooling based on caloric principles like the electrocaloric (EC) effect has been investigated as an alternative to vapor compression-based technologies. Promising EC materials for prospective applications should possess large entropy change, low dielectric loss and high dielectric strength to allow for large EC temperature change in the intended working range. We recently showed that lead-free ferroelectric materials based on modified $(Ba,Sr)(Sn,Ti)O_3$ (BSSnT) achieve large and broad EC temperature change around room temperature. The fabrication of BSSnT multilayer ceramic (MLC) components for high EC effects remains challenging because of the high sintering temperature of the material and abnormal grain growth. In the present work, we investigate the influence of sintering additives on the sintering behavior and the resulting microstructure of BSSnT bulk ceramics prepared through solid-state synthesis. Adding CuO significantly decreases the sintering temperature whereas the addition of MgO and $CaCO_3$ lead to a significant decrease of grain size. The dielectric, ferroelectric, and electrocaloric properties of BSSnT bulk ceramics with sintering additives will be presented and discussed in detail. The optimization of the sintering process of MLC components based on BSSnT with MgO addition to achieve higher breakdown fields and thus larger EC effects is subject of our ongoing research.

Keywords: lead-free, electrocaloric, sintering additives

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Session W2: Plenary

Unlocking the Piezoelectric Response of Ceramic Thick Films

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Many vibrational energy harvesting systems are based on ceramic piezoelectric films deposited on an elastic substrate, which converts mechanical vibrations to electrical energy. Such technologies are critical for unattended wireless systems as a means of remotely generating the energy required for operation. Of the available deposition technologies, powder aerosol deposition is particularly attractive for the development of ceramic films as it can rapidly produce thick films at room temperature through particle fracture and impact consolidation, allowing for the development of porous films, composite structures, and combinations of various material classes, such as glasses, ceramics, metals, and polymers. In particular, the deposition rate is excellent, producing film thicknesses in excess of 100 µm within minutes. Despite these advantages, there remain several critical issues that limit the piezoelectric properties of the deposited films and their eventual implementation into energy harvesting systems, including large internal stresses, enhanced conductivity in insulating materials, and a nanograined microstructure. Interestingly, the deposited films are in a non-equilibrium state due to grain boundary defects that can be relaxed through thermal treatment and adjusted through atmospheric control. This presentation will discuss the current understanding of the mechanisms responsible for the film deposition and adhesion in powder aerosol deposition of oxide ceramic films, as well as how to improve them through control of defects. Here, the mechanical response of ferroelectrics is critical, where various methods to characterize the deposition stress and the local residual stress states will be shown. In addition, a method to produce free-standing films will be presented that allows for the direct observation of as-processed films in the non-equilibrium state, resulting in a number of interesting observations.

Session P1: Advanced Characterisation

Spatially Resolved High Voltage Kelvin Probe Force Microscopy: a Novel Avenue for Examining Electrical Phenomena at Nanoscale

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KPFM in its present form frustratingly precludes imaging samples or scenarios where large surface potential exists (due to surface charges) or large surface gradients are created. Even though the technique works very well in the low bias regime, surface voltages higher than 10V can not be reliably measured due to the requirement for larger applied biases in the nap-pass. If the potential regime measurable via KPFM could be expanded beyond the ±10 V by augmenting the configuration to apply and measure larger voltages, the adapted high voltage KPFM (HV-KPFM) system would then enable precise and reliable measurements and mapping of surface potentials and potential gradients in the high voltage regime (>10V). This in turn could open up pathways towards a range of novel experiments where the detection limit of regular KPFM limits access to the physical phenomena. In this work, we have extended the voltage regime for Kelvin probe force microscopy thus realising High Voltage Kelvin probe force microscopy (HV-KPFM). We demonstrate that the developed technique can measure surface potential with accuracy. Equally, potential gradients in interelectrode gaps have been mapped reliably in the high voltage regime. We demonstrate the neutralisation of the surface charges and utilise HV-KPM mapping to visualise the neutralisation process in the HV regime. Finally, we have employed HV-KPFM for direct spatial mapping of potential barriers across grain boundaries in positive temperature coefficient of resistivity (PTCR) ceramics where the boundaries play a crucial role in determining the PTCR behaviour. The results clearly demonstrate that HV-KPFM realised on a commercially configured atomic force microscope can be used as an effective tool to fill in existing gaps in surface potential and potential gradient measurements while also opening pathways for novel studies in materials physics (pyroelectrics being an excellent example).

Keywords: Kelvin probe microscopy, pyroelectrics, functional mapping, high voltage, electrical phenomena, ferroelectrics

Investigating Electrothermal Properties of Domain Walls Using Scanning Thermal Microscopy

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Domain walls in ferroelectrics can be considered an exciting new type of functional interface with properties that can differ significantly from bulk. A decade of research has focused on exploiting the electrical property variation seen within domain walls with a view to creating voltage configurable devices, such as transistor and memristors, where device functionality is derived entirely from the walls. Similarly, reconfigurable thermal devices based on voltage control of the number of phonon-scattering domain walls interrupting heat flow pathways have also been demonstrated using ferroelectric thin films. Overall, however, much less is known about the fundamental thermal properties of domain walls and their influence in these proposed electronic and thermal devices. We have been using Scanning Thermal Microscopy (SThM) to investigate the response of domain walls in $LiNbO_3$ devices from a thermal point of view. Electrically conducting domain walls in $LiNbO_3$ are up to 13 orders of magnitude more conducting than the surrounding bulk and can be straightforwardly created by poling with a biased atomic force microscopy (AFM) probe. We investigate their thermal properties using the SThM mode, in which the AFM probe is repurposed as a temperature sensor capable of imaging temperature distributions with nanoscale spatial resolution and temperature resolution of order of 10mK in ambient conditions.

Keywords: scanning thermal microscopy, ferroelectrics, domain walls

Development of a Microbridge Device for Thermal Conductivity Measurements for Ferroelectrics

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In recent years, domain walls in ferroelectrics and multiferroic systems have attracted a great deal of attention. It has been demonstrated that nanoelectric devices could be made from ferroelectrics by exploiting the electrical or thermal properties of the domain walls inherent to these materials [1,2]. For example, the phonon-scattering rates can be manipulated by changing the density of domain walls, enabling voltage control of thermal conduction [2]. However, measurements to date of thermal conductivity modulation in thin film ferroelectric devices has typically involved sophisticated optical techniques that require complex back extraction of thermal conductivity values. We have developed a microbridge device which can perform sensitive direct thermal conductivity measurements on small ferroelectric samples, requiring only a current source and lock-in amplifier to perform the measurements. The microbridge, which consists of the ferroelectric sample of interest suspended across two resistive micropatterned heater elements, can be fabricated using a focused ion beam microscope. One of the resistive elements serves as a dual heaterthermometer and the other serves as a passive thermometer. Therefore, the temperature gradient, and hence the thermal conductivity of the sample can be determined as a function of voltage modulated sample microstructure. The measurements can be performed from room temperature down to 5 K within a closed-cycle cryostat. A sensitivity of below 5 mK in temperature measurements at room temperature was achieved, suggesting that temperature gradients as small as ~1 mK/μm could be measured in our ferroelectric samples.

Keywords: microbridge, ferroelectrics, domain wall nanoelectronics, thermal conductivity

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Multiple Innovations in Characterizing Piezoelectric Materials

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Characterisation of piezoelectric materials is a key part. The IEEE standard is the only approach that can produce a full elastopiezodielectric matrix. However, it requires multiple samples. This often involves difficulties preparing the samples for all the isolated modes, resulting in incomplete properties and expensive procedures. An alternative approach is to use a single sample (SS), performing a combination of resonant ultrasound spectroscopy (RUS) plus electrical impedance spectroscopy (EIS), and using optimisation. SS characterisation needs high thickness of piezoelectric materials as well as equipment and measurement skills associated with RUS. Providing higher thickness of piezoelectric material is challenging and RUS measurement may be lacking in materials labs and technician skills.The present work simplifies the SS by introducing two different approaches including miniature size to avid bulky thicknesses, and single measurement to not need RUS. The only experimental measurement needed is EIS. A series of dynamic finite element analyses and optimization is performed using commercially available software, i.e. OnScale and Matlab. The material input parameters are changed to minimise the differences between numerical and experimental measurements. The first verification is investigated on PZT4 and PZT8. Then the method is done on an experimental measurement of a PZ54 piezoelectric material. While the results show reasonable convergency, a third approach is also introduced to use complex numbers in the piezoelectric constitutive equations for each of the properties to consider a comprehensive loss. Because the IEEE standard assumes piezoelectric material is lossless, and the SS uses only two electrical and damping parameters for the loss parameters. For this aim, a complex piezoelectric materials library is being developed on an opensource software, MoFEM. This will not only improve the accuracy of characterization, but also using an open-source software package, results in easy access and no cost on licenses.

Keywords: advanced characterization, piezoelectric, miniature, single sample measurement, optimisation

Non-Contact Characterisation of Piezoelectric Materials

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Piezoelectric materials play a key role in various technological applications owing to their unique elastic-piezoelectric-dielectric (EPD) properties, often represented in matrix form. Traditional methods for obtaining these properties, as defined by IEEE standards, rely on Electrical Impedance Spectrometry (EIS) of various samples, some with high aspect ratios, to permit the analysis of individual electroacoustic modes. Combining all outcomes allows the extraction of the EPD matrix. Nevertheless, the requirement of multiple samples yields high cost due to manufacture and discrepancies between different samples. This, in combination with sample contact requirements, are impractical in many cases where materials are needed to be tested under elevated temperature and pressure conditions. With continuous demand for new piezoelectric materials, an alternative approach has been studied utilising only single samples, usually a cube of side several mm. This method combines EIS, Resonant Ultrasound Spectroscopy (RUS) and an optimisation algorithm to extract independent properties within the EPD matrix. Although this eliminates the need for multiple samples, it still necessitates physical contact with the sample, while RUS brings additional measurement inaccuracies due to difficulties in thick sample preparation and poling. This study discusses the potential of a non-contact, approach for characterising piezoelectric materials. The proposed methodology utilises a high-power laser to generate ultrasound waves within a compact, single, 1 mm^3 cube sample. The resulting vibrations at various points on the sample's surface are detected using a laser Doppler vibrometer (LDV) with post processing of the measurements through an optimisation package required to extract specific piezoelectric properties. The present study is at early stage, with equipment assembled and preliminary results obtained through finite element analysis. Future work is required to determine the feasibility of extracting the full EPD matrix for different types of piezoelectric materials. This research represents a further step towards advancing the characterization of piezoelectric materials under simulated operating conditions, paving the way for more efficient and accurate assessments in a wide range of applications.

Keywords: advanced characterisation, piezoelectric materials, applications, operating conditions

Session P2: Capacitor Materials

Investigation of Structural, Microstructural and Dielectric Properties of Nd-substituted Bismuth Ferrite Ceramics

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Given the global challenges posed by energy scarcity and climate change, there has been a surge in the development of alternative and sustainable energy technologies including solar, wind, geothermal, ocean energies etc. These technologies aim to replace fossil fuels with cleaner and renewable sources. As a result, there is a growing demand for efficient devices to store, and discharge energies effectively. The commercially available devices for energy storage are mainly: batteries and capacitors. Batteries are preferred for long-term and stable energy storage due to their higher energy density. However, their drawback lies in the lower power density, making them unsuitable for high-power applications including Pulse Power Devices (PPD), Directed Energy Weapons (DEW), Super-high Power Electronics, Active Armor, etc. As a result, there has been increasing interest in researching ferroelectric materials with improved electrical energy-storage capabilities. In this work, lead-free Nd^{3+} doped bismuth ferrite ($Bi_{1-x}Nd_xFeO_3$, x = 0, 0.1, 0.15, 0.20) (BNFO) was prepared by conventional solid state synthesis route using appropriate raw materials and sintered at 900°C, as estimated by the thermogravimetric analysis (TGA) of the calcined powders. The primary objective of this work was to study the influence of Nd^{3+} doping on the structural, microstructural and temperature and frequency dependent dielectric properties of bismuth ferrite (BFO). The X-ray diffraction pattern exhibited a shift in the structural phase of the Nd^{3+} doped BFO samples from *R3c* to *Pnma*, accompanied by a reduction in impure phases. Furthermore, the FESEM micrographs demonstrated a decrease in grain size as the dopant concentration increased. A significantly higher dielectric constant was achieved for BNFO compared to pure BFO. Temperature dependent dielectric study showed the phase transition of BNFO is of antiferroelectric type and well above the room temperature. The details of the experimental results and analysis will be presented in this paper.

Keywords: dielectric properties, energy storage, antiferroelectrics, bismuth ferrite, lead-free ferroelectrics

High Resolution Spatial Mapping of the Electrocaloric Effect in a Multilayer Ceramic Capacitor Using Scanning Thermal Microscopy

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The electrocaloric effect is a well-known phenomenon where adiabatic application of an external electric field to a material results in a reversible temperature change. Interest in using these materials for environmentally friendly solid-state refrigeration applications has been rejuvenated by the discovery of giant electrocaloric effects in thin films. While the electrocaloric effect can be well described macroscopically through a thermodynamic approach and is understood to arise from changes in dipolar configurational entropy, the effect at the microscopic scale is not as well characterised. To date, infrared cameras represent the best spatial resolution available for in-situ imaging of temperature fields associated with electrocaloric effects, but features are limited in detail to the level of a few microns. Scanning Thermal Microscopy is emerging as a powerful Atomic Force Microscope based platform for mapping dynamic temperature distributions on the nanoscale. To date, however, spatial imaging of temperature changes in electrocaloric materials using this technique has been very limited. We build on the work of previous studies to show that Scanning Thermal Microscopy can be used to spatially map electrocaloric temperature changes on microscopic length scales, here demonstrated in a commercially obtained multilayer ceramic capacitor. In our approach, the electrocaloric response is measured at discrete locations with point-to-point separation as small as 150nm, allowing for reconstruction of spatial maps of heating and cooling as well as their temporal evolution. This technique offers a means to investigate electrocaloric responses at sub-micron length scales, which cannot easily be accessed by the more commonly used infra-red thermal imaging approaches. We intend to use this technique to elucidate the behaviour of other electrocaloric materials and to examine the influence of microstructural inhomogeneity on electrocaloric response.

Keywords: electrocaloric, scanning thermal microscopy, ferroelectric

Lead-Free $BiFeO_3$ – $CaTiO_3$ Ferroelectric Ceramics for High-Temperature Energy Storage Applications

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As the global population increases, energy consumption is also increasing day by day. As of now we mostly rely on non-renewable resources which are the primary reason for global warming and pollution. As an alternative, the usage of stored energy gained interest in recent years due to numerous applications in various sectors including aviation, medical, weapons, pulsed power sources, electrical and electronic devices, sensors, transducers, and electric vehicles. Electrostatic energy storage capacitors are the optimal choices due to their high-power density and high-temperature sustainability capabilities. In the present investigation, we have explored the structural, microstructural, electrical, dielectric, and ferroelectric properties of lead-free (1-x) $BiFeO_3$-$x$$CaTiO_3$ (x = 0, 0.6, 07, 0.8 and 1.0) ferroelectric ceramics. Rietveld refinement technique revealed the phase transformations ($BiFeO_3$ - rhombohedral to orthorhombic), phase fractions (%), unit cell volume changes, and distortions in partially substituted (1-x) $BiFeO_3$-$x$$CaTiO_3$ ceramics. Four orders of reduction in leakage current density (J) were observed from x = 0 (pure $BiFeO_3$) to x = 0.8. The leakage current was reduced by inhibiting Fe^{+3} to Fe^{+2} transition which is critically analysed from X-Ray photoelectron spectroscopy. Fe^{+3} to Fe^{+2} transition was suppressed from 34% for x = 0.6 to 17% for x = 0.8. Electrically inhomogeneous microstructures revealed the possibility of multiple dielectric anomalies from temperature-dependent dielectric properties. The improved relaxor ferroelectric behaviour (γ = 1.60 for x = 0.6 to γ = 1.80 for x = 0.8) is confirmed by degree of diffusivity (γ) using Curie-Weiss law. A high-energy density of 2.5 J cm^{-3} was obtained for x = 0.7 with sample thickness of 0.3 mm. Stable Polarization-Electric field (P-E) curves were obtained up to 190 ºC indicating that the lead-free BFO-CTO relaxor ferroelectric ceramics can be used for high-temperature energy storage applications.

Keywords: leakage current, dielectric constant, relaxor-ferroelectrics, recoverable energy density, polar-nano regions

Lead-Free $BiFeO_3$ and $AgNbO_3$-Based Ceramics for Dielectric Energy Storage Capacitors

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The worldwide surge in demand for portable electronics and electric vehicles has necessitated advancements in energy storage technologies that can deliver enhanced power and energy densities. Dielectric capacitors, as crucial energy storage devices, have garnered significant interest due to their exceptional power density and rapid charge-discharge capabilities. However, a substantial scientific and technological challenge has been the pursuit of less toxic, lead-free materials. Lead-free ceramics, specifically relaxor ferroelectrics and antiferroelectrics, present promising alternatives because of their minimal remanent polarizations and high dielectric breakdown strengths. We have proposed innovative dopant methodologies in $BiFeO_3$-$SrTiO_3$ (BF-ST) relaxor ferroelectrics in our recent work. First, Nb-doping is used to augment resistivity by mitigating hole conduction and fostering electrical homogeneity. Secondly, we introduce alloying with a third endmember, $BiMg_{2/3}Nb_{1/3}O_3$ (BMN), to decrease polar coupling without diminishing the average ionic polarizability. Employing these approaches, we have achieved an unprecedentedly high energy density for BF-ST in multilayer ceramics. Furthermore, we have substantiated the underlying mechanisms that bolster the optimization of energy storage density in $AgNbO_3$based antiferroelectric ceramics. We accomplished this through an amalgamation of theoretical computations, in-situ synchrotron x-ray diffraction, and transmission electron microscopy data. This research provided the first observation of a field-induced ferrielectric phase and the inaugural proposition of four principles for designing high-energy-density antiferroelectric ceramics. Both these studies offer explicit engineering guidelines for creating lead-free ceramics intended for high-energy-density capacitors.

Keywords: energy storage capacitors, relaxor ferroelectrics, antiferroelectrics, in-situ synchrotron X-ray diffraction

Session P3: Fundamentals of Ferroelectrics

Revisiting the "Giant" electric field induced strain in Sr-doped K0.5Na0.5NbO3

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$K_{0.5}Na_{0.5}NbO_3$-based ceramics are among the most studied Pb-free piezoceramics, as potential contenders to replace piezoelectric actuators based on hazardous $Pb(Zr,Ti)O_3$ ceramics. For these applications, the magnitude and the temperature stability of the electric field induced strain is of paramount importance. A significantly large number of research efforts ranging from chemical doping of $K_{0.5}Na_{0.5}NbO_3$ ceramics to microstructural texturing have been reported over the last two decades as different approaches to tailor their piezoelectric performance. Recently it was reported that Sr-doped $K_{0.5}Na_{0.5}NbO_3$ ceramics can exhibit a socalled giant electric field induced strain exceeding 1% [1]. This surprisingly large response is revisited in this work, using specimens prepared following the experimental procedures reported. In addition, to gather further insights from a doping concept based on A-site replacement, other divalent species, such as Ca and Ba were employed in the fabrication of $K_{0.5}Na_{0.5}NbO_3$-based ceramics [2]. In this study, we compare the electric field induced polarisation and strain of those ceramics and establish their basic crystal chemistry.

Keywords: piezoelectric, Pb-free, KNN, strain, polarisation

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Are There Antiskyrmions in Barium Titanate?

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The prediction and experimental confirmation of magnetic skyrmions - the objects with nontrivial swirling spins patterns - revolutionized the physics of nanoscale magnetism and opened new horizons for spintronics. In spite of the inherently shorter and faster correlations of the electric polarization, the recent developments in electric skyrmionics follow these innovations. This work reveals that classical ferroelectric perovskite - BaTiO3 - can host 2-3 nm wide polar columns spontaneously surrounded by a unique noncollinear polarization pattern that has never been described before. We analyze how this pattern is formed and stabilized. Based on its negative integer topological charge, we name this soliton as "ferroelectric antiskyrmion". For preliminary computer experiments, see [arXiv:2303.07389].

Keywords: ferroelectrics, topological defects, domain walls, modelling

Behaviour of Ferroelastic and Ferroelectric Domains in $AgNbO_3$ Under Temperature and Stress Influence

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By deploying different modes of atomic force microscopy, both ferroelectric and ferroelastic domains with distinct morphology and orientations are observed in the well-known antiferroelectric $AgNbO_3$, consistent with the theoretical studies. With temperature, ferroelectric domains disappear across its M_1 -M_2 phase boundary when it becomes antiferroelectric. In contrast, ferroelastic domains remain stable at 100 °C, consistent with the fact that the ferroelasticity persists till high-temperature antiferroelectric phase regions. In addition, it is found that the number of ferroelectric domains inside the sample is related to the level of Ag deficiency. With applying compressive stress, the ferroelectric surface domains would gradually respond to the stress, which either grow, shrink or change shape. In comparison, the ferroelastic surface domains seem to show better mechanical resistance and did not respond as much as the ferroelectric domains.

Keywords: antiferroelectric, ferroelastic domains, stress effects, defects, piezoresponse force microscopy

Session P4: Lead-free – Materials and Applications

Stability of Electromechanical Properties in Co Modified Aurivillius $CaBi_4Ti_4O_{15}$ at Elevated Temperature

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Bismuth layer-structured ferroelectric (BLSF) are of great interest, belonging to the Aurivillius-type ceramics, primarily due to their high T_c. These materials are utilized in sensors, actuators, transducers, micro-electro-mechanical systems (MEMS) that operate at elevated temperature including ferroelectric Random Access Memory (FeRAM) applications. In this work, we focused on Calcium Bismuth Titanate ($CaBi_4Ti_4O_{15}$, CBT) and prepared it by using conventional solid-state route and modified with x = 2,4 and 6 mol % of Co_3O_4. Incorporation of Co did not bring about significant structural changes, as revealed by X-Ray Diffraction data, however, scanning electron microscope (SEM) micrographs displayed highly anisotropic grains with highest aspect ratio (w/l) of 0.1911 for x = 4 mol%. Temperature-dependent dielectric study showed that the Curie Temperature of the CBT ceramic was not compromised, rather improved from 771.3°C to 788.2°C with the increase in Co concentration to 6 mol%. The composition of CBT modified with 4 mol% Co showed the lowest dielectric loss of 0.0967 at 1 MHz, and lowest conductivity value of $1.7310 X 10^{-5}$ $(\Omega\ cm)^{-1}$ at high temperature of 725°C. The piezoelectric charge coefficient (d_{33}) measured at room temperature is also found to increase from 4.2 pC/N to 6.8 pC/N with the Co concentration due to B-site substitution of the Ti^{4+} ions. The electromechanical coupling (k_p) and mechanical quality factor (Q_m) were measured at elevated temperatures showed distinctive properties upto the temperature of 450°C stating that ceramics can be used for high temperature piezoelectric application. The highest k_p was offered by the composition of CBT modified by 4 mol% Co, which varied from 4.806% that measured at room temperature to 4.793% at 450°C, while Q_m decreased from 702 to 390. These results showed CBT modified with 4 mol% Co offered high T_c, low dielectric loss, optimal piezoelectric coefficient, stable electromechanical properties combined with the highest mechanical quality factor, making it the best composition for the electromechanical application at room temperature and elevated temperatures.

Keywords: BLSFs; $CaBi_4Ti_4O_{15}$; electromechanical properties; MEMS applications; high T_c material

The Effect of A-site Vacancies on the Thermodynamic Stability of $Sr_{2.2}Na_{0.6+x}Nb_{5-x}Ti_xO_{15}$ Ceramics

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Strontium sodium niobate (SNN) has a tetragonal tungsten bronze (TTB) crystal structure and performs relaxor-like weak frequency dispersion [1]. Also, SNN is attracting attention for applications such as temperature-stable dielectrics, electro-optic and energy storage material as a Pb-free piezoelectric material for actuator applications [2]. However, according to work carried out by Di-Sheng et al. [3], SNN is not thermodynamically stable, preferring to decompose into its constituent niobates and therefore limits the applicability of these materials. To understand this behaviour, polycrystalline ceramics of $Sr_{2.2}Na_{0.6+x}Nb_{5-x}Ti_xO_{15}$ (x = 0.00, 0.05, 0.10, 0.20) with A-site occupancies ranging from 93% (x= 0.00) to 100% (x = 0.20) were fabricated using traditional solid-state synthesis. X-ray diffraction, scanning electron microscopy, and dielectric and impedance spectroscopy were used before and after annealing to investigate the role of A-site vacancy concentration on the thermodynamic instability of these materials. The initial results suggest that a greater vacancy concentration results in increasing thermodynamic instability.

Keywords: strontium sodium niobate, tetragonal tungsten bronze, thermodynamic instability

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Ferroelectric Hardening in $BiFeO_3$-$BaTiO_3$ Ceramics

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Ferroelectric materials can be tailored to satisfy various requirements for different types of applications, such as sensors and actuators, particularly those that need to operate in the high temperature range (200-600 °C), beyond the capability of commercial lead zirconate titanate (PZT) ceramics. The $BiFeO_3$-$BaTiO_3$ (BF-BT) pseudo-binary solid solution has been recognized as one of the most attractive systems due to its high Curie temperature and thermally-stable piezoelectric properties. Many studies have been published during the last decade to evaluate the effects of compositional modifications and heat treatment procedures on the structure and properties of such BF-BT ceramics. Conventional 'hard' PZT ceramics are prepared through the use of acceptor dopants, which introduce dipolar defect associates with oxygen vacancies that act to reduce domain wall mobility. The resulting materials generally exhibit an enhanced coercive field, improved stability under high electrical drive levels and much lower dielectric losses. A comparable approach to hardening of BF-BT ceramics by acceptor dopants has not yet been demonstrated and would inevitably be impaired due to the increasing losses due to conduction at high temperatures. In the present work, the potential for hardening of ferroelectric properties in BF-BT by the alternative mechanism of phase separation is explored. Light donor doping of 0.7BF-0.3BT ceramics was achieved by adjusting the Fe/Ti ratio, in order to suppress the mechanisms associated with ionic and p-type electronic conductivity. Both as-sintered and quenched (from 1000 °C) samples were subjected to long-term annealing for a period up to 200 h at temperatures from 500 to 600 °C, in order to establish the possible effects of phase separation, induced by thermodynamic immiscibility, on crystal structure, microstructure and functional properties. Analysis of ferroelectric hardening effects will focus on the ferroelectric hysteresis characteristics, piezoelectric coefficients and quality factor.

Keywords: ferroelectric hardening, ageing, quenching, phase separation, bismuth ferrite-barium titanate

Electroelastic Database of Doped Barium Titanate Ceramic for Transducer Applications

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Barium titanate ($BaTiO_3$) is a well-known ferroelectric material which was intensively studied in the early 50's. Indeed, $BaTiO_3$ has been rapidly substituted by lead zirconate titanate (PZT) materials, which exhibit higher piezoelectric properties. However, PZT materials contain lead and their increasing success is associated to health and environmental problems. Therefore, tremendous efforts have been devoted to the development of competitive lead-free counterparts and $BaTiO_3$ compositions comeback on center stage as promising candidates. From a batch of 10 kg of synthetized co-doped barium titanate powder, several ceramics with specific shapes were characterized to the delivery of a complete accurate set of elastic, dielectric, and piezoelectric constants. These databases are relatively rare in literature but are essential for numerical simulations of new devices integrating these piezoelectric materials. For the establishment of this set of material constants, resonance-antiresonance method was first used. In this case, measured and calculated values were mixed. This can lead to violations in the interrelations between particular groups of electromechanical parameters and non-consistent database is provided. In this study, a method based on a genetic algorithm was used to optimize the consistency of the full set of material constants through the minimization of a defined criterion [1]. In order to verify the robustness of this characterization method, it was first successfully applied to a well-known material (soft PZT: Pz27) whose complete database is provided by the manufacturer [2]. Secondly, full consistent database of BTCaCoNb was delivered with a dielectric constant at constant strain of 1375, a piezoelectric coefficient (d_{33}) of 208 pC/N and a thickness coupling factor (k_t) of 42%.

Keywords: lead-free, piezoelectricity, database, transducer

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Thermal Stability of Electromechanical Properties in Optimally Poled 0.5(Ba0.7Ca0.3)TiO30.5Ba(Zr0.2Ti0.8)O3 Ceramics

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Morphotropic phase boundary (MPB) composition, $0.5(Ba_{0.7}Ca_{0.3})TiO_3$-$0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ ceramics was prepared using conventional solid state reaction followed by sintering. Rietveld refinement of X-ray diffraction (XRD) data confirmed the coexistence of rhombohedral and tetragonal phases. A uniform and dense microstructure with average grain size 6.8 µm was seen in scanning electron microscope (SEM) micrographs. The sintered density obtained for the sample sintered at of the sample was measured using Archimedes principle and linear shrinkage method considering isotropic shrinkage and found ~97% in both cases. Temperature dependent dielectric measurement shows Curie temperature ~ 80°C. An optimal poled sample (field = 5.2 kV/mm, temperature = 60 °C, time = 30 min) showed d_{33} = 411 pC/N, g_{33} = 351 Vm/N. Temperature dependent resonance-anti resonance study further revealed the stability of electromechanical properties way up to 75°C.

Keywords: morphotropic phase boundary (MPB); BCT-BZT; electromechanical properties, microstructure; dielectric properties

Lead-free Piezoceramic Materials for Transducer Applications

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Lead zirconate titanate (PZT) is the most common piezoelectric material used in transducer applications. Its superior piezoelectric properties can be attributed to the presence of a morphotropic phase boundary at the Zr:Ti ratio of 52:48 as it allows for multiple polarization directions, enhancing its piezoelectric and ferroelectric properties. However, future EU legislation will limit the lead-content of devices by weight to 0.1%, pushing for research into lead-free piezoelectric materials. For this project, bismuth ferrite-barium titanate (BF-BT) compounds are doped with Mn and Sm and are prepared and investigated for their piezoelectric properties. BF-BT was chosen for its strong piezoelectric properties, also attributed to the presence of a morphotropic phase boundary. A variety of processing variables are used to investigate their effect on the piezoelectricity and structure of the different compositions which will help to optimize the materials' piezoelectricity. The compositions will then be tested for their performance in Sonar transducers, and the results are compared to those consisting of PZT transducers. For Sm-doped BF-BT, the formula used was $0.67Bi_{1.03}FeO_3$-$0.33[Ba_{1-x}Sm_xTiO_3]$, where x=0.00-0.03. The best results achieved were a d_{33} of 85 pC/N and T_c of 436^{o}C, at x = 0.01. For Mn-doping, the formula used was $0.67Bi(Fe_{1-x}Mn_x)O_3$-$0.33BaTiO_3$, where x=0.01-0.02. The best results achieved were d_{33} of 176 pC/N and T_c of 450^{o}C, also at x=0.01. For Mn-doped BF-BT, the process of air-quenching (fast cooling from 1000^{o}C to room temperature) has reduced defects in its crystal structure and has improved its piezoelectric performance in comparison to slow-cooling from the sintering temperature. Future research will involve co-doping BF-BT with Sm and Mn at the same time, and water quenching the material.

Keywords: piezoelectric, ferroelectric, lead-free, BF-BT, transducer

Piezoelectrics for High Temperature Transducers

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Increasing demands on performance are driving the development of new piezoceramic materials with enhanced stability under extreme environmental conditions, including higher levels of mechanical stress, electric field and temperature. In the present work, we focus on the structure-property relationships in $BiFeO_3$-$BaTiO_3$ (BF-BT) solid solutions, with particular attention to the improvement in ferroelectric Curie point relative to that of conventional lead-based materials. BF-BT ceramics were prepared by solid state reaction including the processes of ball milling, calcining the mixed powder, die pressing, sintering and further heat treatment. The piezoelectric properties of BF-BT piezoceramics can also be enhanced using a post-sintering heat treatment involving rapid cooling by quenching in air. Results are presented to demonstrate the impact of high temperature annealing and quenching processes on the crystal structure and functional properties of BF-BT ceramics, including the increase of Curie temperature and depolarization temperature, enhancement of polarization values, and superior stability of the piezoelectric properties. These improvements can be attributed to the change in crystal structure and microstructure. Increasing quenching temperature resulting in gradual evolution of the domain configuration from labyrinthine to more ordered lamellar type patterns, corresponding to the higher rhombohedral distortion and indicated by the more obvious peak splitting in the {111} XRD peak profiles. The quenched specimens display temperature-stable piezoelectric coupling, k_p, values greater than 0.45, while the Curie temperature and depolarization temperatures are up to 450℃ and 400℃ respectively, confirming their potential for applications in high temperature piezoelectric transducers.

Keywords: piezoelectrics, ferroelectric properties, lead-free materials, quenching effects, bismuth ferrite-barium titanate.

Session P5: Photoferroelectrics and Piezocatalysts

Accurate Band Alignments for Complex Heterojunctions from First Principles: The Case of α-Fe_2O_3/$BaTiO_3$ Interface

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In recent years, combined experimental and theoretical efforts have been devoted to understanding the factors that control the band alignment in the interface of semiconductor heterojunctions where the transport properties are controlled by the electronic band profiles at the interfaces: the valence and conduction band offsets. Their estimation can be easily achieved via Density Functional Theory (DFT) calculations. Nevertheless, due to the self-interaction error in most exchange-correlation DFT functionals, none of those approximations properly describe band gaps of semiconductors and insulators, which leads to a wrong prediction of band offsets. In this regard, hybrid functionals can be more suited than semi-local methods to perform band-gap calculations; but its application on complex heterojunctions can be challenging due to the size of the intended models. Here, we evaluate a simple scheme for calculating the band alignments with a high computational efficiency. Within this scheme, the potential-alignment values are calculated with the PBE functional, and then combined with bulk band structure calculations computed with the HSE06 hybrid functional. This scheme allowed us to model a more complex epitaxially-compatible interface: the α-Fe_2O_3/$BaTiO_3$ system. This is a prototypical interface, identified by the Electronic Lattice Strain procedure, as being suitable to couple together a semiconductor light absorber (Fe_2O_3) and a ferroelectric that can produce a bulk photovoltaic effect ($BaTiO_3$) in a nanocomposite thin film device for an improved solar energy harvesting. In such a coupled system, the limitations of light absorption in ferroelectrics and photovoltage in semiconductors could be overcome by using the ferroelectric to influence the coupled semiconductor. Apart of improving the description of the band alignments of the interface with the aforementioned scheme, we were able to account the polarization of the $BaTiO_3$ system within the PBE functional with a Hubbard-type correction to the Ti 3*d* orbitals, where U_{eff} = 2.6 eV.

Keywords: heterojunctions, interfaces, bulk photovoltaic effect, $BaTiO_3$, α-Fe_2O_3, band-offset calculations, HSE calculations

Quantification of Phase and Amplitude Response by Piezoresponse Force Microscopy

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The manifestation of polarization versus electric field hysteresis loop is a distinctive feature of ferroelectricity, which can even arise from experimental artefacts. Therefore, the misinterpretation of loops arises from the surface artefacts as evidence for ferroelectric behavior can mislead the obtained outcomes. The identification of accurate ferroelectric response becomes more complicated when the measurement is performed at the nanoscale by piezoresponse force microscopy (PFM), a powerful technique to characterize and manipulate the ferroelectric domain. Although the switching spectroscopy-PFM (SS-PFM) technique received significant attention in quantifying the electromechanical (EM) response, the accurate PFM image processing, and its consequence on the quantification of EM response do not process much attention so far. In this presentation, we will describe how to obtain artefact-free PFM phase and amplitude images from ferroelectric materials. The difference between the images containing intrinsic and non-intrinsic responses will be identified by post-imaging analysis. Furthermore, the EM response will be obtained by the SS-PFM technique under different read voltages (e.g., -1 to +1 V). The selection of genuine EM response out of the SS-PFM technique will be identified after obtaining the average surface potential of the sample by the Kelvin probe force microscopy (KPFM). The phase curve with bias field obtained from the EM measurement will eventually aid in determining the imprint field of the system. Additionally, 2D switching and imprint voltage maps in each domain of a $BaTiO_3$ single crystal are obtained using the datacube-PFM technique, which allows for the determination of the artefact-free spatial variation of PFM phase-amplitude response pixel-by-pixel.

Keywords: ferroelectrics, domain switching, polarisation, PFM, imprint, thin films

Effect of Corona Poling on Piezocatalytic Degradation Using Ferroelectric Nanoparticles

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Piezo-catalysis induced by piezoelectric polarization has been proven to be a powerful technology for potential applications in alternative clean energy sources and environmental remediation. This process directly converts mechanical energy into chemical energy to enhance piezocatalytic efficiency for wastewater treatment, H_2 evolution, and CO_2 reduction. Although still relatively new, the use of ferroelectric materials for piezocatalysis has an effect on the breakdown of organic pollutants and polarization-modulated water splitting. This study focuses on the formation of a heterostructure using ferroelectric ceramics ($BaTiO_3$ and $KNaNbO_3$) as a catalyst and noble metals (Pt, Pd and Rh) as a cocatalyst. We synthesized these materials by solid state reaction followed by high temperature calcination. We investigate the effect of corona poling on ferroelectric ceramics for the degradation of dye/organic pollutants. These ferroelectric powders are characterized by an X-ray diffractometer, scanning electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. UV-Vis and Liquid Chromatography Mass Spectroscopy (LC-MS) are used to analyze the rate of degradation and intermediate products of the catalytic reaction. Our study also suggests that corona poling, which increases ferroelectric polarization, can efficiently promote piezocatalytic activity. We believe that the present work provides a clear understanding of the role of ferroelectric polarization in piezocatalysis.

Keywords: piezocatalysis, ferroelectric polarization, water-waste, dye/pharmaceutical, H_2 evolution, CO_2 reduction.

Examination of Piezoelectric Properties of Polymeric Graphitic Carbon Nitride (g-C_3N_4) and Potential for Pollutant Degradation and Hydrogen Peroxide Generation

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As a graphite-like structured semiconductor with an interlayered morphology, graphitic carbon nitride (g-C_3N_4) is a photocatalytic material widely used for environmental remediation, pollutant degradation and wider applications. With the band gap of 2.6 eV, [1] it has been used as a photocatalyst to produce hydrogen and hydrogen peroxide. Recent research has examined the piezoelectric properties of graphitic carbon nitride for potential energy harvesting applications and g-C_3N_4 based nanogenerators [2], where graphitic carbon nitride has also attracted increasing attention for its piezoelectric catalytic characteristics. In this work the piezoelectric effect of g-C_3N_4 has been examined and combined with controlled aquatic cavitation to generate hydrogen peroxide (H_2O_2). Piezo-catalysis and the piezoelectrochemical process (PZEC) provides a potential route for environmental catalysis by exploiting the mechanical deformation of a piezoelectric material to induce charge transfer. The piezo-catalytic method for producing hydrogen peroxide from sustainable materials [3] therefore provides a promising new approach in the direction of sustainable energy.

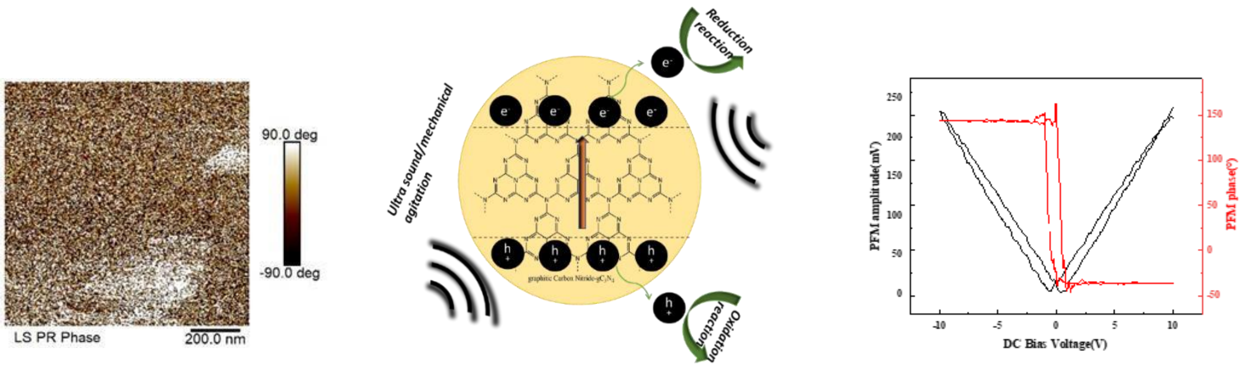

Figure 1. Graphitic carbon nitride (g-C_3N_4) and potential for piezo-catalysis

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Planetary Ball Milling Induced Piezocatalysis for Dye Degradation Using $BaTiO_3$ Ceramics

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Piezocatalysis process is one of the emerging areas utilized in environmental remediation. The process generally makes use of an ultrasonicator for separating the charges, however, piezocatalysis through an ultrasonicator is just limited to laboratory-scale remediation and there are various other limitations associated with its usage. Ball milling (BM) is normally utilized for mixing, grounding, and synthesis of precursors. However, BM in the present study is utilized as a piezocatalysis system where a rotating planetary disk and collisions of milling balls generate enough force such that abundant reactive species are produced, responsible for the degradation of organic dyes. For this, Methylene Blue (MB) dye was used as a pollutant in water with ~5mg/L concentration and $BaTiO_3$ powder as a piezocatalyst. At 200 rpm, the MB dye degradation was ~36, ~61, and ~54% observed with 5, 10, and 15 Zr balls using 0.15 grams of BaTiO3 ceramic powder. The potentiality of BM as a piezocatalysis system was further analyzed at various parameters (e.g. speed of BM and quantities of milling ball), the volume of MB dye, and the dose of $BaTiO_3$ ceramic powder.

Keywords: ball milling (BM); piezocatalysis; $BaTiO_3$; methylene blue (MB) dye

Session P6: Piezoelectric Composites

Ice Templated Lead-Free Porous Ferroelectric Ceramics and Composites for Hydrostatic Applications

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This research presents a transducer, Ice-templated Lead-free Porous Ferro-Ceramic for Hydrostatic Applications, optimized for SONAR applications. Improvements follow the three axes: (i) non-toxic lead-free material, (ii) high hydrostatic performance (hydrostatic voltage coefficient, g_h > 1000%), and (iii) mechanical strength sufficient for the application. Ferroelectric ceramic materials are widely used for both active and passive SONAR. Currently, hydrostatic sensors ('hydrophones') are often based on a piezoelectric acoustic transducer manufactured from dense lead zirconate titanate (PZT) or lead titanate (PT) ceramic. A high-performance porous transducer is presented here that uses an ice templating method to form a highly aligned and interconnected network of thin layers, thereby producing a 3-2 porous ceramic/air composite. In this investigation, the toxic lead-based material is replaced by a doped barium titanate-based material, namely $Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.3}O_3$ (BCZT). Produced by solid-state synthesis and ball milling, this lead-free ferroelectric ceramic exhibits good piezoelectric properties, comparable to lead zirconate titanate; (PZT d_{33} ~ 600 pC/N; porous BCZT d_{33} ~ 500 pC/N). The advantage of the aligned porous ferroelectric materials is the large reduction in the permittivity (ε_r reduced by 50%) and the low piezoelectric charge constant coefficient for lateral stress d_{31}, which is reduced by 95%. As a result of this unique combination, the porous transducer exhibits excellent hydrostatic proprieties, including high hydrostatic parameters (d_h,g_h), with the hydrostatic voltage coefficient, g_h more than 1000% higher than the dense alternatives and more than 100000% for the hydrostatic energy harvesting figure of merit, d_h*g_h. Results are presented using both experimental characterization and simulation using a mathematical model based on piezo-composite connectivity behavior.

Keywords: ferro-ceramic, ice-templated, hydrostatic, SONAR

Swimming Microrobot Based on Piezoelectric Materials

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Piezoelectric actuators, operating in the thickness-vibration-mode, have attracted attention for underwater swimming microrobots. However, developing a high thrust and high velocity piezoelectric swimming micro-robot remains a challenge. Herein, we have developed an acoustic swimming microrobot based on piezoelectric materials. Firstly, the structure of the robot and the housing based on 3D printing will be briefly introduced, which is combined with nanocellulose for water purification. The process and hydrophobic and oleophilic properties of the cellulose were investigated in detail. To analyze the microrobot motion in water based on thickness-vibration-mode, the acoustic impedance and the acoustic radiation force with applied voltage and frequency were theoretically evaluated. Subsequently, we experimentally explored the frequency-dependent impedance and resonance properties, and measured the velocity of microrobots based on high acoustic impedance dense piezoelectric ceramics and porous piezoelectric ceramics with low acoustic impedance. Finally, to further illustrate the practical applicability, we demonstrated that the microrobot not only swims at high speed but can be combined with cellulose for water purification. This work provides new insights on the influence of the porous piezoelectric materials for swimming robots.

Keywords: piezoelectric ceramics, microrobot, cellulose, water purification

Development and Characterization of High-Performance PVDF-Based Piezoelectric Films

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Nowadays, there is a strong interest around the world in the production and implementation of piezoelectric materials, since it represents the best approach for many practical and innovative energy harvesting and sensing applications [1]. Herein, the development of flexible lead-free piezoelectric strips based on poly (vinylidene fluoride) (PVDF) is targeted due to the excellent mechanical properties of PVDF along with its active ferroelectric and piezoelectric properties achieved after its stretching and a polarization process. Beside this, PVDF is a sustainable material which could substitute PZT ceramics (lead [2] zirconate) commonly employed in the fabrication of piezoelectric materials. In this work, PVDF films are developed by compression molding which are subjected to a stretching and polarization process to become piezoelectric. The crystallinity of these films is characterized by DSC and XRD analyses while the β-phase enhancement is addressed by FTIR [3]. The mechanical properties (young's modulus and tensile strength) are studied by following the Normative UNE-EN ISO 527-3:2019. The piezoelectric characterization of the poled films (d33 piezoelectric coefficient and electrical voltage response under tensile tests) are also studied to ensure their reproducibility while finding the optimal production/polarization parameters (poling voltage, time, and temperature) to achieve effective piezoelectric PVDF films for their future implementation into a piezoelectric generator for Energy Harvesting purposes.

Keywords: piezoelectric, lead-free, PVDF, energy harvesting

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The Effects of Cooling Rate on The Microstructure-Piezoelectric Performance of Porous Freeze-Cast Ferroelectrics

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The piezoelectric charge coefficient d_{ij} and the permittivity ε_{ij}^T of a ferroelectric material are important properties which determine the figures of merit for both sensing ($g_{ij} = d_{ij}/\varepsilon_{ij}^T$) and energy harvesting ($FOM_{ij} = d_{ij}^2/\ \varepsilon_{ij}^T$). Using the freeze-casting process, whereby aqueous ferroelectric ceramic particle suspensions are directionally frozen before freeze-drying and sintering to obtain highly aligned porous structures, such figures of merit have been shown to be improved [1] compared to their monolithic dense counterparts. Whilst the effects of porosity have been well studied, little is understood on how various microstructural parameters such as wall defects and wall thickness affect the functional properties. In this study, the effects of cooling rate on the microstructure, and the dielectric and the piezoelectric properties of freeze-cast lead zirconate titanate (PZT) was investigated. It was observed that the average piezoelectric charge coefficient d_{33} increases linearly with the freeze-casting cooling rate: a cooling rate of 1.5˚C/min yielded a mean d_{33} of 225 pC/N, whereas the highest cooling rate used of 4˚C/min yielded a mean d_{33} of 330 pC/N, meaning a 47% increase in d_{33} when a faster cooling rate was adopted. Furthermore, analysis of the microstructures indicated that with faster cooling rates, freeze-cast structures were allowed to form homogeneously with high degrees of alignment which produced more reliable piezoelectric properties, with a significant decrease in the standard deviation in the d_{33} between batches of samples observed. Reductions in the bulk permittivity ε_{33}^T were also observed for a range of samples tested due to its association to porosity compared to the dense samples, however, there is no significant changes of the ε_{33}^T with respect to cooling rate. This study emphasizes the importance of carefully controlling the microstructure of porous ferroelectrics; and opens up new approaches to produce enhanced and more reliable properties in these materials.

Keywords: freeze-cast, cooling rate, porous, ferroelectric, microstructures, functional properties

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Session P7: Energy Harvesting

Piezoelectric Energy Harvesting from Pressure Ripples in Hydraulic Systems

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Hydraulic fluid power systems are essential components in many industries such as transportation and manufacturing. Embracing smart hydraulic systems through digital innovation presents a significant opportunity to improve system efficiency and reliability through predictive maintenance. This can be facilitated through distributed sensor networks, however, wiring a large number of sensors to mains electricity can be costly and logistically challenging, as can regular battery replacement. The potential to harvest mechanical energy from hydraulic systems to power sensor networks and reduce the need for battery replacement is particularly attractive since they inherently have a high energy intensity associated with the high mean pressure and flow, alongside the generation of high-pressure ripples arising from the use of flow control strategies. In this study, we investigate the use of piezoelectric stacks as high-power energy harvesters. A switching valve is integrated within a closed hydraulic system to generate pressure ripples and piezoelectric stacks with varying geometries are integrated in line with the switching valve to assess the energy harvesting performance under a range of conditions. The piezoelectric stack is exposed to hydraulic pressure ripples in the fluid system through a fluid-to-mechanical interface which isolates the stack from the fluid and allows pressure ripples to be strongly coupled to the piezoelectric stacks with a mechanical advantage. The output power of piezoelectric stacks fabricated from hard and soft lead zirconate titanate is measured and used to evaluate a stress-dependent energy harvesting figure of merit, $FoM_{ripple} = d_{33}^2\sigma_{max}/(e_0 e_{33}^T)$, where d_{33} is the longitudinal piezoelectric charge coefficient, σ_{max} is the depolarization stress, and e_{33}^T is the relative permittivity of the piezoelectric ceramic, and e_0 is the permittivity of free space.

Keywords: piezoelectric, energy harvesting, hydraulic, pressure ripples

High Performance Near-Room-Temperature Pyroelectric Energy Harvesting Characteristics of Ferroelectric−Semiconductor Composites

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The pyroelectric energy conversion of low-grade heat energy to electrical energy is important source for several energy application potential. The generation of current in ferroelectric materials which is subclass of pyroelectric material can cause the change in spontaneous polarization with variation in temperature. As environment is concerned lead-free ferroelectric materials with the phase transition near to room temperature are more preferable due to large change in dipole during transition. The large pyroelectric response near to room temperature will make them suitable for room temperature pyroelectric energy harvesting applications. In this work, the composite of ferroelectric $Ba_{0.85}(Bi_{0.5}Li_{0.5})_{0.15}TiO_3$ and semiconducting ZnO are chosen for pyroelectric energy harvesting application for their phase transition near to room temperature and high thermal conductivity. The 10% BBLT-ZnO composite shows a maximum pyroelectric co-efficient and figure of merit for pyroelectric energy harvesting parameter F_E value of 3.032 kJ/m^{3}K^2 at T_C = 45 °C which is 3-fold enhancement compared to the parent BBLT sample. In addition to this, BBLT:0.1 ZnO exhibits a better and comparable figure of merit parameter for pyroelectric sensor applications than other reported ferroelectric material in literature.

Keywords: lead-free ferroelectrics, depolarization, pyroelectric, energy harvesting, Rayleigh analysis, composite

Improved Piezoelectric Performance in PVDF Bimorphs of Opposite Polarization Orientations

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Polyvinylidene Fluoride (β-phase PVDF) is a semi-crystalline thermoplastic polymer that exhibits piezoelectric properties in thickness mode (d_{33} ~ 30 pm/V) and transverse mode (d_{31} ~ 20 pm/V). This can be used in energy harvesting or sensing applications. In this study, we characterized the piezoelectric behavior of a PVDF bimorph structure under the assumption that thin opposite polarization orientation bimorphs would show better piezoelectric performance than identical orientation bimorphs or single layers in a vibrating cantilever device. This follows the opposite compression and tension experienced in top and bottom layer during bending. In order to test this hypothesis, we used COMSOL software for finite element analysis of a single layer and PVDF bimorphs. Following the analysis, we fabricated simple and low-cost structures containing two commercial 100 um thick PVDF layers joint by epoxy glue or 50 um thick double-sided Polyethylene terephthalate tape in opposite and identical orientations, analyzed their piezoelectric behavior and compared them to a single layer specimen, using a piezometer and an in-house built electromechanical setup. The comparison showed expected and different values of d_{33} for each variant, and the electromechanical analysis results were in agreement to the simulations results. Different explanations for the results will be discussed, i.e., electrical and mechanical properties of the epoxy glue and the double-sided tape, processing complexity, and the total hardness and flexibility of the specimen. The results suggest that PVDF opposite orientation bimorphs cantilever devices offer superior performance to their single layer and identical orientation counterparts. This could be useful for low-cost energy harvesting (*e.g.* wind/waves) and sensing.

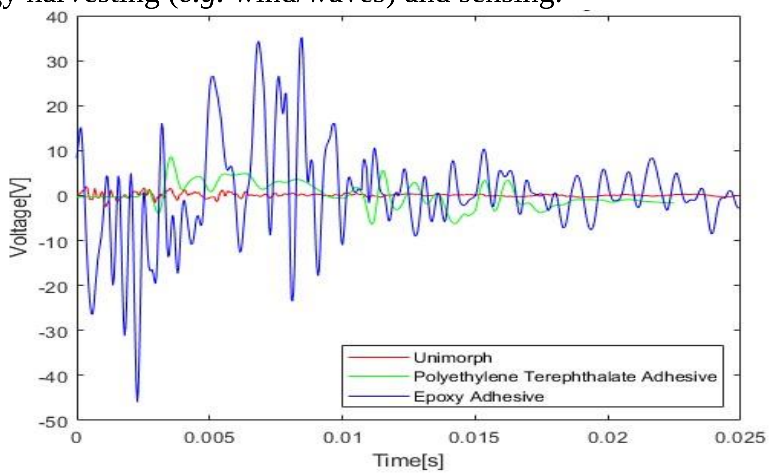

Figure .1 Voltage output comparison between different structures

Keywords: PVDF, piezoelectric, bimorph, epoxy glue, double-sided tape

Piezoelectric Energy Harvesting By Employing Biocompatible Ferroelectric Molecular Cu(II) Complexes

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To meet the increasing energy demand of the world and tackle the rapid exhaustion of non-renewable energy sources, research is presently focused on piezoelectric energy harvesters as sustainable alternatives. Researchers have employed pure inorganic materials like bulk oxides (perovskites and ceramics), polymers, organic molecules, even peptides and organic-inorganic hybrid structures for this purpose. Among these, the oxide systems show excellent piezo and ferroelectric as well as energy harvesting properties but they suffer from huge disadvantages like costly high temperature synthesis methods, almost zero mechanical flexibility, tunability of properties in the long-range and of course bioincompatibility due to the presence of toxic heavy metals. In case of polymers or peptides, stabilizing the polar ferroelectric state which is required for the application purpose (for example β-state of PVDF) is an extremely daunting task. Alternatively, hybrid organic-inorganic perovskite systems offer low temperature and easy processing method, as well as great output performances but these systems also suffer from a number of problems, including the stability of reactive metal halide bonds under aerobic conditions and moisture and the presence of toxic heavy metal ions like lead (Pb). By careful molecular engineering and controlled design strategy, we have overcome almost all of the above-mentioned caveats by employing bio-compatible discrete molecular complexes, which is an active area of research in the current scenario. These Cu(II) metal based complexes not only provide high values of piezoelectric co-efficients (d_{33}= 10-30 pm/V), comparable to the popular bulk materials like $LiNBO_3$, ZnO and polymers like PVDF, PVDF-TrFE etc., but also has appreciable spontaneous polarization values as well, leading to appreciable energy harvesting capabilities in both single-crystal and composite forms. They are light weight, mechanically flexible and easily polarizable in presence of an electric field, making them perfectly suitable to use in various energy harvesting nanogenerators.

Keywords: piezoelectric, ferroelectric, energy harvesting, molecular complex, biocompatible

$BaHf_xTi_{1-x}O_3$ Thin Films: From Sol-Gel Synthesis to Piezoelectric Energy Harvester

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A typical piezoelectric energy harvester is a bimorph cantilever with two layers of piezoelectric material on both sides of a flexible substrate. Piezoelectric layers of lead-based materials, typically lead zirconate titanate, have been mainly used thanks to their outstanding piezoelectric properties. However due to lead toxicity and environmental problems there is a need to replace them with environment-benign materials. Here, main efforts were focused on the preparation of hafnium doped barium titanate ($BaHf_xTi_{1-x}O_3$; BHT) sol-gel materials. The original process developed makes it possible to obtain a high concentrated sol without strong organic complexing agents. Sol ageing and concentration can be controlled to obtain a time stable sol for a few months at room temperature, with desired viscosity and colloid sizes. Densified bulk materials obtained from this optimized sol show good electromechanical properties assuming also good properties in the 31-mode used in the cantilever operating mode: a thickness coupling factor k_t around 50% and a converse piezoelectric coefficient d_{33}^* around 350 pm/V. According to the electromechanical properties, the theoretical behavior in a bimorph configuration has been simulated by finite element method and compared to experimental results obtained by vibrational characterization in terms of resonance and output power values.

Keywords: piezoelectricity, sol-gel synthesis, barium titanate, energy harvesting, finite element method, functional characterization.

Session P8: Processing of Piezoceramics

Modulating Grain Size and its Impact on the Properties of $Ba_{1-x}Sr_xTiO_3$ Ceramics

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Dense, fine-grained $Ba_{1-x}Sr_xTiO_3$ (x=0.2, 0.4) ceramics have been fabricated using nano-powders synthesized via the acetate variant of the sol-gel route, followed by consolidation through Spark Plasma Sintering (SPS). By fine-tuning the SPS parameters, we successfully achieved a reduction in grain sizes (GS) from submicronic to nanometric scale. Structural and microstructural attributes, as well as low and high-field electrical properties, were exhaustively investigated. The interpretation of functional properties considered the interplay between the GS reduction, the influence of the grain structure characterized by a tetragonal core and low-permittivity boundaries, and the diffuse nature of the ferroelectric-to-paraelectric phase transformation, during which a combination of tetragonal and cubic modifications coexist. In the case of $Ba_{1-x}Sr_xTiO_3$, when x=0.2, the Curie temperature (Tc) was found to be 335K, displaying ferroelectric properties at room temperature (RT). When x=0.4, the Curie temperature dropped to 280K, transitioning to a paraelectric state at RT. Notably, the Curie temperature was not influenced by the GS. Although the decreasing of GS reduces the ferroelectric character of the ceramics, it seems to favors the persistence of the high-temperature polar order. Raman spectroscopy highlighted the presence of polar nanoclusters above T_C, with a short-range polar order influenced by the GS reduction. Our study elucidates a direct relationship between GS and the dielectric and ferroelectric properties of the sintered ceramics, emphasizing the pivotal role of GS in optimizing ceramic material properties for a wide array of applications.

Keywords: electroceramics, size effects, phase coexistence, functional properties, ferroelectricity

Properties of PZT and KNN Electroceramics Sintered by SPS Without Post-Annealing

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$Pb(Zr,Ti)O_3$ and $(K,Na)NbO_3$ are perovskite ABO_3 piezoelectric oxides that share the propensity for volatility of the A-site cations which adversely affects the electrical performances. KNN is one of the lead free challenging piezoelectric material but PZT, despite its lead content, is still studied because of its unrivalled properties. Conventional production of piezoceramics include an energy consuming sintering step, typically above 1000°C for several hours. This step rises several issues related to the chemistry and the microstructure. Our goal is to reduce the PZT and KNN sintering temperature, with no post-thermal treatment while achieving properties comparable to those obtained with conventional high-temperature sintering. Spark Plasma Sintering (SPS) whose efficiency rely on the combination of pressure and pulsed current was already used to sinter PZT and KNN ceramics but with sintering temperatures usually higher than 900°C; also a post-annealing treatment under air (700 – 1000 °C) was mandatory to eliminate oxygen vacancies and recover insulating properties. In this work, the effect of sintering conditions, as well as the role of a protective layer between the mold and the powder, have been studied. Commercial powders are used, a micrometer sized PZT powder and a nanosized KNN powder. With the use of a protective layer, made of carbonate powder, and directly placed on the piezoelectric bed PZT powder, the best properties were obtained for the PZT ceramic at 875°C for 5 min. The relative density was 98% and the permittivity and electromechanical coupling factor k_{eff} were respectively 1500 and 40%. For KNN powder, thanks to the reactive nanopowder, with a temperature as low as 700°C and no protective layer, a relative density of 96% was achieved. Here the post-annealing was not compulsory and the KNN ceramics exhibit a permittivity of 660 with a low dissipation factor (0.02). Piezoelectric characterizations are under progress for KNN.

Keywords: KNN, PZT, protective layer, SPS, post-annealing, dielectric and piezoelectric properties

Tunable BNT Particles Morphology Through Topochemical Microcrystal Conversion Synthesis

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Piezoelectric ceramics are part of multiple important industries with applications ranging from sensors to energy harvesters. Among all piezoelectric compositions, lead-free $Bi_{0.5}Na_{0.5}TiO_3$ ceramics are a promising emerging candidate for their low toxicity and good piezoelectric properties. Because piezoelectric ceramics translate mechanical stimuli into electrical ones and vice-versa, improving their mechanicals properties without losing their piezoelectric properties would lead to improved performances, from higher reliability to better energy harvesting capabilities. Bioinspired nacre-like architecture uses a brick-and-mortar microstructure that can potentially improves toughness and strength of ceramics without relying on the ceramic composition. What's more, nacre-like structures, with their long-range alignment of bricks could also provide a way to control the crystal orientation and thus increase piezoelectric properties. In our project, the nacre-like structure will be introduced into lead-free piezoelectric ceramics and using $Bi_{0.5}Na_{0.5}TiO_3$-based bricks. The novel bioinspired ceramic might exhibit increased mechanical property (higher toughness and better strength) and piezoelectric performance (piezoelectricity, ferroelectricity, and energy storage performance) by controlling and texturing their microstructure at multiple length scales. The first step to fabricate these bioinspired ceramics is to develop and understand the synthesis of brick-shaped micron size $Bi_{0.5}Na_{0.5}TiO_3$ using molten salt conversion synthesis. We will thus explore the effect of the amount of different reagent and salt on the size and morphology of $Bi_{0.5}Na_{0.5}TiO_3$ bricks fabricated by topochemical microcrystal conversion from $Bi_4T_3O_{12}$ platelets precursors. The revolved grain nucleation and growth mechanisms are studied, and a novel related systematically powder control strategies are proposed. Based on this, one modified and robust synthesis solution is proposed to obtain $Bi_{0.5}Na_{0.5}TiO_3$ with tunable shape, size, and stable morphology distribution.

Keywords: Nacre-like structure, $Bi_{0.5}Na_{0.5}TiO_3$, lead-free piezoelectric ceramics, multifunctional composites, topochemical microcrystal conversion, controllable powder synthesis

Finite Element Modelling and Characterization of Cold Sintering Process for Electroceramic Materials

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The cold sintering process (CSP) is a new technique used to manufacture electroceramic materials that can significantly reduce the processing temperature. The densification process is driven through a combination of high pressures (>200 MPa) and the presence of a transient flux to enable mass transfer, all at moderate temperatures below 250°C. In the present work, CSP is used for the manufacturing of barium titanate ($BaTiO_3$) electroceramics using $Ba(OH)_2{\cdot}8H_2O$ as a flux. Pellets were cold sintered under a uniaxial pressure of 350 MPa and at temperatures ranging from 150°C to 230°C for 2 hours, with a heating rate of 5°C/min for the cold sintering process. The relative density and dielectric properties were measured as a function of different sintering temperatures, namely at 150°C, 180°C, 200°C, and 230°C. Furthermore, scanning electron microscopy was used to observe the microstructure of $BaTiO_3$ under different processing conditions. A finite element model (FEM) is developed by adapting conventional sintering models for the evaluation of the cold sintering process to provide an insight into how the process can be optimized. The model considers coupled mechanical, heat transfer, and densification models to evaluate the stress, temperature, and density distribution in the pellet during the cold sintering process, and is compared to experimental observations from the cold sintered $BaTiO_3$ under different conditions.

Keywords: cold sintering, barium titanate, finite element modelling

Session P9: Thick Films

Development and Implementation of Multifunctional Materials for Printed Electronics in Harsh Environments

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Piezoelectric sensors are gradually revealing their potential in several applications, including medical and aerospace sectors. The screen printing process is perfectly suited to printed electronics and the printing of this type of sensor. The advantage of these sensors is that they can be used to do structural health monitoring. The current technological bottleneck concerns the lack of maturity of the various related technological building blocks but is also attributable to the context in which printed structures are used, which is becoming increasingly restrictive. Efforts must therefore focus on the resistance of inks to high or low temperatures, or to high mechanical and electrical stresses, as well as humidity. This work investigated the thermal ageing of various commercial inks. The pristine commercial inks were analyzed thermally, electrically and chemically. Dielectric and electrical characterizations were carried out on the aged samples. Different dielectric and electrical properties, and evolutions after thermal ageing, were highlighted as a function of the silver ink/dielectric ink pair. Therefore, the study of the synergy between all the elements of sensor is essential. These initial results will be used to select high-performance dielectric and conductive inks. The aim will be to functionalize the dielectric ink with electroactive particles. After validation of these three high-performance technological building blocks, it will be possible to produce a high-performance / high-temperature sensor that can be used in a variety of harsh environments.

Keywords: ageing, harsh environment, polymer composite, piezoelectric sensor, high performance, screen printing

Aerosol Aeposition of $Na_{0.5}Bi_{0.5}TiO_3$-$NaNbO_3$ Thick Films

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Aerosol deposition (AD) is a novel method for the manufacture of ceramic coatings at room temperature, from particulate precursors. In this process, densification is achieved by the impact of high velocity particles on a substrate surface, leading to fracture and plastic deformation. The aims of the present study were to develop suitable powder processing procedures for aerosol deposition of polycrystalline $Na_{0.5}Bi_{0.5}TiO_3$-$NaNbO_3$ (NBT-NN) thick films and to evaluate their microstructure-property relationships. NBT-NN ceramic powders were prepared by solid state reaction, followed by sintered at 1190 °C to produce a set of conventionally sintered reference materials. The NBT-NN powders were subsequently processed further to reduce the average particle size by high energy planetary ball milling and granulation by spray drying, in order to improve their suitability for use in the AD process. Deposition experiments were conducted using a new AD facility within the Henry Royce Institute at the University of Manchester, which is based on a modular *Minilab 125* vacuum system manufactured by Moorfield Nanotechnology Ltd. NBT-NN coatings were produced on stainless steel substrates, with a thickness in the range from 5 to 25 µm. The as-deposited films were found to exhibit reductions in the dielectric permittivity and remanent polarisation in comparison with those of the conventionally sintered ceramics; these effects were attributed primarily to their nanocrystalline nature, as revealed by SEM and TEM examination. Annealing of the NBT-NN coatings from 400 to 800 °C was found to be an effective method to influence the crystallisation and their functional properties.

Keywords: aerosol deposition, lead-free ferroelectric, sodium bismuth titanate, ceramic coatings, crystallisation

Piezoceramic Thick Films on Porous Substrates as Ultrasonic Transducers

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Piezoceramic thick films offer the possibility of integrated solutions for sensors, actuators, ultrasonic transducers, and generators. In the case of ultrasonic transducers, the mechanical properties of the substrate being printed on influence the acoustic properties. Usually, ceramic materials with little damping such as alumina or zirconia are used as substrates for thick films. In order to achieve undisturbed acoustic signals, acoustic cross talk through the substrate and back wall echoes need to be suppressed. In ceramic substrate materials, this can be achieved to a large degree by scattering at suitably sized inclusions or pores. We therefore investigated several shaping technologies for manufacturing substrates with pores, among them additive manufacturing, which allows for the incorporation of precisely located pores and thus pore patterns. We present experimental results of acoustic measurements on substrates with different pore size, size distribution, and pore density. Design principles for maximum "damping" of back wall echoes as well as minimum cross talk have been identified as well as suitable shaping technologies. The experimental results are compared to simulation results.

Keywords: ultrasonic transducer, piezoceramic thick film, linear array, ultrasound imaging

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Effect of Post-Annealing on Microstructure and Electrical Properties of Piezoelectric Thick Films Grown by Aerosol Deposition

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In this study, highly dense $BaTiO_3$ (BT) thick films were successfully deposited by Aerosol Deposition (AD) on glass and kovar® substrates at room temperature. A powder pre-treatment step was necessary to achieve sufficient film thickness from commercial BT powder via AD. The deposition process successfully preserved the tetragonal perovskite phase of the BT powder. However, the as-deposited films exhibited a linear dielectric-like behavior, with high resistivity values indicative of the excellent densification of the deposited BaTiO3 films. The absence of ferroelectricity in the as-deposited films can be attributed to the size effect. To recover the desired piezoelectric and ferroelectric properties, post-deposition annealing trials were conducted at different temperatures in air and under an argon flux. The annealing process successfully restored ferroelectricity above 800 °C, where grain growth became possible and residual stress was further released compared to lower temperatures (< 800 °C). The influence of the annealing atmosphere became particularly significant at 900 °C, as the low oxygen atmosphere promoted greater grain growth. However, the presence of residual oxygen vacancies in BT film annealed under argon flux led to reduced fatigue resistance. Thus, a compromise must be made between enhanced ferroelectricity and the dynamic performance of post-annealed BT films.

Keywords: thick films, aerosol deposition, piezoelectricity, microstructure, electrical properties

Session P10: Ultrasonics and Acoustics

Co-design and AI for Innovation in Ultrasonic Transducers for Underwater Sonar

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Modern sonar systems consist of three separate elements: the piezoelectric material, the electronic circuits, and signal processing which typically uses artificial intelligence (AI). These elements are classically constructed and made by different companies and industries, which are then brought together to work as a single system. Getting these components to operate effectively together can cause issues and results in the whole system being less effective. A systematic review of sonar technologies which utilize co-design of at least two of these three elements was conducted. This was accomplished via a literature search of scientific articles and patent designs. The results show there is currently no sonar system that has all elements incorporated from *one* source, however research incorporating sonar and AI more than doubled between 2021-2022. The incorporation of AI into a sonar system with an application specific integrated circuit (ASIC) would be a more efficient design. To conclude a more refined system with all the elements as one device would be more effective and should be studied extensively in the near future.

Keywords: Sonar, ultrasonic, artificial intelligence (AI), co-design, ASICS

A Simple Design Tool for Single-Element Piezoelectric Ultrasonic Transducers

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A tool for simple single-element ultrasonic transducer design has been developed. Simulated results include acoustic radiation as well as electroacoustic performance. First, pulse-echo radiation patterns in axial and lateral directions of a disc-shaped transducer are calculated assuming a quasi-harmonic piston mode operation with or without focusing. Depths of field and lateral resolutions are deduced. For this, the transducer operation frequency and diameter, the sound velocity of the propagation medium as well as the focusing parameters, either by shaping the piezoelectric element or by adding a lens, are the inputs. Secondly, electroacoustic parameters are calculated using the KLM electroacoustic equivalent circuit approach for a piezoelectric transducer structure including a backing, a piezoelectric element operating in thickness mode and a front layer. For this, inputs are the characteristics of transducer elements (sizes and material constants), the electrical impedances of the driving electronics, i.e. generator and receiver, as well as the sound velocity and density of the propagation medium. Transducer complex electrical impedance and admittance are obtained as well as transmit-receive sensitivity and pulse-echo impulse response, from which parameters such as bandwidth and axial resolution are deduced. The tool only requires a spreadsheet application and can be downloaded free of charge, the authors simply ask users to acknowledge it when they communicate results, and in the case of a scientific publication or conference to include this article in the list of references.

Keywords: single-element piezoelectric ultrasonic transducer; axial radiation; electrical impedance; sensitivity; impulse response; axial and lateral resolutions

Magnetoelectric Bulk Acoustic Resonators for the Ultra High Frequency (UHF) Band

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Magnetoelectric composites have gained recent traction in the domain of passive and active RF bulk acoustic resonators. Composed of carefully controlled stacks of piezoelectric and magnetostrictive materials they are utilised as filters and energy harvesters. In this study, comparative finite element modeling of materials with high spin-orbit coupling is carried out including the effects of piezoelectric encapsulants such as PVDF and Aluminum Nitride. The addition of a magnetostrictive material to the piezoelectric layer provides the added advantage of magnetic-field modulated control of electric field. The designed devices hence double as magnetic field sensors during operation. In order to explore the application of these devices as implantables, analysis of the electromechanical coupling factors is carried out under the presence of different encapsulants comprising of piezoelectric and piezoelectric-dielectric material stacks. Furthermore, the shift in the resonance frequency is analysed as well as the reflection parameters which define the figure of merit of the resonators.

Ultrasound Non-Destructive Evaluation/Testing Using Capacitive Micromachined Ultrasound Transducer (CMUT)

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Recently, there has been a growing interest in ultrasound transducers like Capacitive Micromachined Ultrasonic Transducers (CMUT) due to their sensitivity, scalability, and compatibility with CMOS technology. Their lightweight and miniaturization have led to their adoption in various applications, such as imaging. This study focused on using CMUTs for nondestructive evaluation/testing of stainless steel bars. This research investigated the application of pulse-echo and pitch-catch methods for determining the length of a stainless-steel block of size 101.20mm. The complete system for the pulse-echo method uses a function generator (Tektronix AFG Arbitrary Function Generator 31000) for the AC transmission signal, DC power supply (ea-ps 2042-03b), a single CMUT (University of Tours, France), an oscilloscope and the built circuits required. In the pulse-echo method: the single transducer generates ultrasound signals and propagates through the stainless steel with a constant velocity. The complete system for the pitch-catch method uses a function generator (Tektronix AFG Arbitrary Function Generator 31000) for the AC transmission signal, DC power supply (ea-ps 2042-03b), a two separate CMUTs (University of Tours, France), an oscilloscope and the built circuits required. When the signals encounter different mediums (air and steel interface) or cracks, echo signals are reflected to the transducer. The second method was introduced to confirm the results of the first method. The values obtained through each method were then compared to the actual size of the block, as measured with Vernier Caliper. The pulse-echo method yielded a length calculation with an error of 3.7%, while the pitch-catch method resulted in an error of 5.2 %. In the pulse-echo method, the front echo signal detected on the oscilloscope was the transmitter signal at the front interface of the stainless-steel block, and the rear echo signal was the echo signal received from the end of the stainless-steel surface at a time of 34.57 µs. In the pitch-catch method, the transmitted signals displayed on the oscilloscope were 0 in the time domain, representing the signals sent from the transducer transmitter. The second signal represents the received signals in the received transducer. The first received signal by the receiver transducer was at 17.66 µs, where the value was half of the value obtained when the pulse-echo experiment was conducted. These experimental setups demonstrate the potential of CMUT-based ultrasound for reliable length measurements and defect detection in stainless steel. As a result, the groundwork for further advancements in ultrasonic nondestructive evaluation/testing using CMUTs has been laid.

Keywords: pulse-echo, non-destructive testing, pitch-catch, CMUT, ultrasound, transducers, PCB circuit.

Characterization of Buried Interfaces in Optical Thin Films Using Ultrafast Acoustics

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The interface between two solid materials is a specific structure with material properties that differ significantly from adjacent bulk materials. Interfaces may differ in stoichiometry. They may have strain gradients, dislocations, or other defects in the crystal lattice. They may contain additional absorption bands or trapped charge carriers. Therefore, the driving ambition in many research and application topics is to control the thin film interfaces and their morphology. The highly complex task of efficiently characterizing the interface underlies this ambition. The interfaces, only a few nanometers thick, are typically buried hundreds of nanometers below the surface. Therefore, the reliable extraction of information about their properties is not easy, even for selectively efficient methods at the interfaces. These problems have motivated the work presented in this paper. We demonstrate the possibility of studying buried interfaces using ultrafast acoustics. This method uses a short (a few hundred femtoseconds) laser pulse, called a pump pulse, to generate the acoustic shock wave, which propagates through the sample. The shock wave propagation and its interaction with buried interfaces can be monitored optically by a series of probe pulses following the pump pulse. The probe pulses are reflected from the acoustic shock wave and are measured by the detector. The signal obtained from the detector then contains information about the interaction of the shock wave with the interface. In this work, we will use numerical simulations to demonstrate the possibility of distinguishing the characteristic morphology of the interface, e.g., a step-like interface, an interface with a distinct interlayer, or a gradual interface. The results of the numerical simulations are compared with the experimental data obtained from thin films of SiO_2, Si_3N_4 and SiO_xN_y deposited on a Si substrate. The limitations, the resolution, and other qualitative and quantitative features of the method will be discussed.

Keywords: thin film interfaces, ultrafast acoustics, shock wave propagation, optical characterization, numerical simulations, SiO_2, Si_3N_4, SiO_xN_y

Session P11: Ferroelectrics and Other Materials

Demonstration of a Tunable Acoustic Metamaterial, Employing a 3D Printable Magnetic Membrane as the Active Mechanism

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A key limitation in acoustic metamaterial (AMM) research is the difficulty to manufacture prototypes, largely due to complex designs, small scale features, and multi-material requirements. Due to the nature of metamaterials, which derive their unique abilities from their geometry rather than their innate material properties, operational frequency and bandwidth are often fixed post-manufacture. When considering AMMs with adaptable acoustic properties, manufacturing methods are further restricted due to the active materials required. One way to address these issues is to enable more materials, such as magnetic or piezoceramic composites, to be accessible for initial AMM prototyping. Developing additive manufacturing options further would enable many more AMM designs to be realized experimentally, and therefore progress AMM research closer to widespread industrial application. In this paper, a novel active metamaterial design is presented and validated experimentally. The design consists of a resonant system that incorporates a membrane as the active element, which undergoes a change in resonant frequency under an applied magnetic field. This feature enables frequency control without physical contact and potentially over long distances. Additionally, the device operates at low frequencies with super-subwavelength dimensions. Mass-spring-damper modelling was used to construct the mathematical model, with reference to Kirchhoff-love theory for thin plates, Hooke elasticity, and Langevin Magnetism Laws. The experimental methodology is summarized, including the frequency control method and recording techniques for acoustic response. To create a 3D printable device, a custom magnetic photocurable resin was synthesized. The active mechanism consists of a flexible membrane 3D printed out of a smart material termed as a magnetorheological elastomer. This resin consists of a polymer matrix (primarily BEMA 1822) mixed with magnetite nanoparticles (Fe3O4 50-100nm size) and, after printing, this material exhibits superparamagnetic qualities.

Keywords: acoustic metamaterials, tunable materials, 3D-printing, magnetorheological elastomer, super-paramagnetic, subwavelength.

Ultrahigh Relative Clamped Dielectric Permittivity of PMN-PT Ceramics by the Modification of Samarium

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Ultrasonic transducers are now widely used in ophthalmology, cardiology and other clinical medical fields. Piezoelectric material is a unique active component of medical ultrasonic transducers. The development of piezoelectric materials with outstanding piezoelectric properties and large clamped dielectric permittivity is significant for the development of miniature high-performance ultrasonic transducers. Relaxor ferroelectrics (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$-$x PbTiO_3$(PMN-PT) exhibit high dielectric permittivity, piezoelectric coefficients, and pyroelectric coefficients for medical ultrasonic transducers. In this study, Sm-modified PMN-PT piezoelectric ceramic was prepared on the basis of the columbite pre-synthesis method. The piezoelectric, dielectric, and ferroelectric properties of ceramics have been investigated systematically. With the doping of Sm, the piezoelectric and dielectric properties of the ceramics were significantly improved, demonstrating outstanding piezoelectric coefficient d_{33} of 1100 pC/N, relative dielectric permittivity ε_r of 11177, relative clamped dielectric permittivity ε^s of 4396, coercive field E_c of 3.8 kV/cm, and Curie temperature of 85 °C. The high-piezoelectric properties enhance the sensitivity of devices, while the high relative clamped dielectric permittivity facilitates the electrical impedance matching between the transducer and electrical terminals and promotes the energy transfer between the transducer and the electronics. The proposed ceramics show great potential for the applications of miniature and high-performance needle ultrasonic transducers, which would be significant in the field of clinical medical therapy.

Keywords: Sm-PMN-PT, piezoelectric ceramic, piezoelectric properties, relative clamped dielectric permittivity, ultrasonic transducer

Microwave Synthesis of PMN-PT Ceramics

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PMN-PT piezoelectric ceramics with compositional formula (1-x)PMN-xPT (with x = 0.20 and 0.35) were synthesized with solid state reaction method. The powder samples were sintered by using muffle furnace and microwave furnace. The sintered samples were characterized for structural, dielectric, ferroelectric and piezoelectric properties. XRD and SEM measurements were done for structural analysis. Dielectric constant was measured as a function of temperature at different frequencies. For ferroelectric properties, P-E hysteresis loops were recorded at different temperatures. The samples were then poled using high DC field and piezoelectric coefficients 'd_{33}' was measured. PMN-PT ceramics prepared by microwave sintering exhibit improved properties over conventionally sintered PMN-PT ceramics. As a novel technology, rapid microwave sintering was found to be more effective for the processing of lead based ceramics.

Keywords: microwave sintering, PMN-PT, piezoelectrics, ferroelectrics

Modelling of Metamaterial Response in a Gyroid Ferroelectric Actuator

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This poster will present the metamaterial response observed and modelled in a ferroelectric gyroid actuator. Gyroids are triply periodic minimal surfaces employed here to define the two electrodes encompassing the actuator. The metamaterial behavior described is a contraction of the external cubic volume occupied by the gyroid, which is caused by the way the electrostrictive and piezoelectric effect is exploited in this geometry. The application of an electric field to this structure causes a thickness expansion that contracts the external dimensions of the sample. In the non-linear model adopted to explain this behavior, the Gauss's Law equation and the equations of motion are solved assuming constitutive relations of ferroelectricity, anisotropic elasticity and an electromechanical coupling done by electrostriction relations. A semi-macroscopic phenomenological model with five parameters was employed to model the ferroelectric polarization hysteresis and properties of potassium niobate $KNbO_3$ found in literature were adopted for the elastic and electrostrictive coefficients. The governing partial differential equations were solved with the finite element method, implemented on the commercial software COMSOL. The problem was solved in a 2 x 2 x 2 gyroid unit cell domain where the ceramic polarization direction that specifies the anisotropic elasticity tensor was determined using analytical geometrical expressions. Finally, a model displaying the electromechanical response of a cylindrical sample of the same material is presented for comparison and a figure of merit is suggested for this kind of actuators.

Keywords: modeling of ferroelectric ceramics, metamaterial, piezoelectric actuator

Advances in Electroceramics: An Industrial Perspective

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CeramTec are a global manufacturer of advanced ceramic materials with over 100 years of development and production expertise. CeramTec manufactures a wide range of dielectric and piezoelectric components and assemblies across multiple global manufacturing sites. It is nearly 80 years since the discovery of barium titanate and 70 years since the discovery of lead zirconate titanate. These materials continue to be amongst the dominant materials in the functional electroceramics market owed to their distinct properties. We shall discuss how these well-established materials are able to tap into current global megatrends and what are the anticipated key growth drivers across the next decade and beyond. In that context we shall detail the core competencies of CeramTec's dielectric and piezoelectric materials and how we can stay at the forefront of new developments in the electroceramics market by pushing the envelope on materials, dimensions, and shapes. How the process which we undertake with our customers to collaborate on new designs brings components and assemblies to the electroceramics market in both low- and high-volume applications. We will discuss how it is also a requirement of our own corporate governance and customers alike that we are conscious of the developing environmental restrictions and discussions, although at this time our electroceramic materials continue to be designed and developed into many new applications across many different market segments.

Keywords: industrial perspective, piezoceramics, applications