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Jožef Stefan Institute
Ljubljana, Slovenia

FerroSchool 2024

November 18th – 21st, 2024

Jožef Stefan Institut, Ljubljana, Slovenia

Programme
and
Book of abstracts

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BOOK OF ABSTRACTS

FerroSchool 2024

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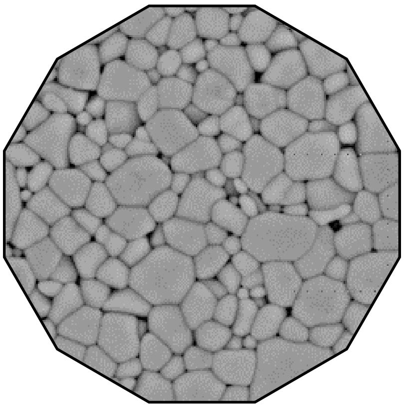

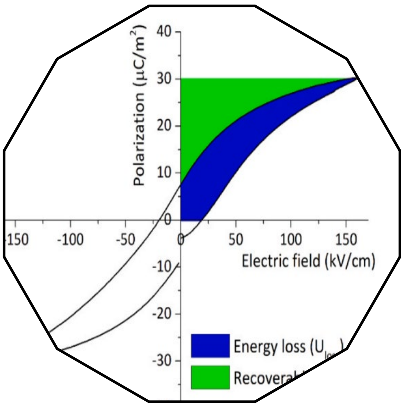

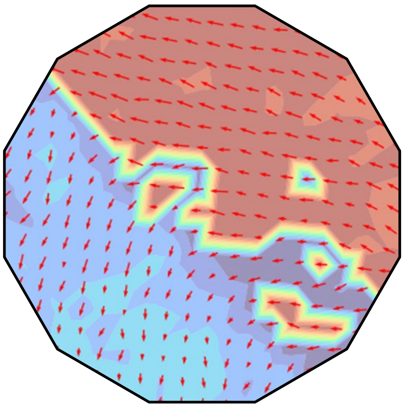

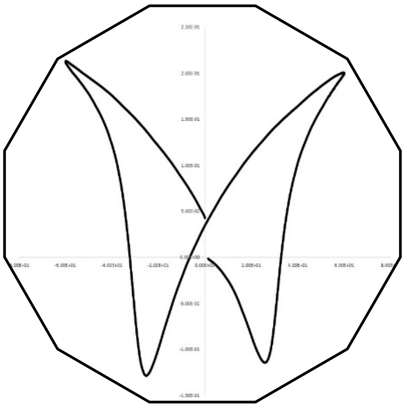

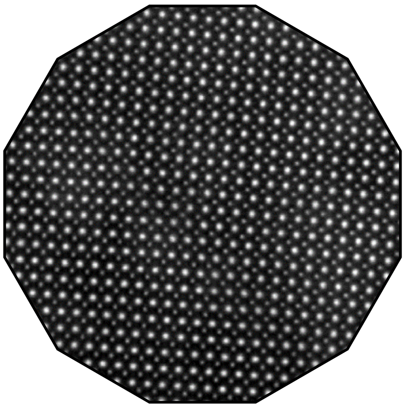

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WELCOME ADDRESS

The FerroSchool 2024 continues a successful tradition of the annual international FerroSchools, supported by IEEE Ultrasonics, Ferroelectrics, and Frequency Control Society (UFFC-S). The school is organized by researchers from Electronic Ceramics Department of Jožef Stefan Institute, and will be held on November 18th – 21st, 2024, at Jožef Stefan Institute, Ljubljana, Slovenia.

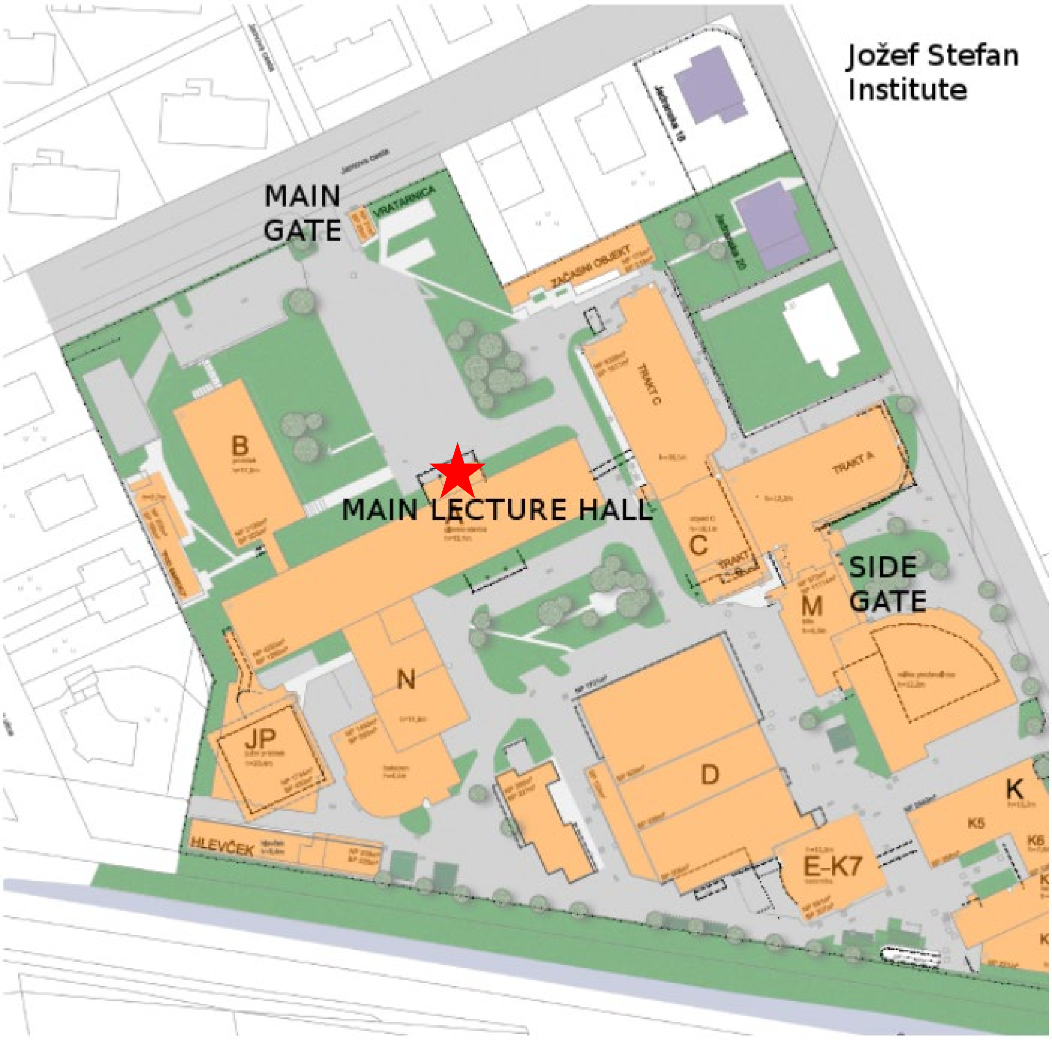
FerroSchool 2024 aims at bringing together students, postdocs and scientists at any career stage interested in ferroelectric materials. The emphasis is on educating young ferroelectricians that will continue the research and innovation development in this technologically important field. A general overview of fundamentals, materials design and processing, measurement techniques and applications of ferroelectric materials will be given through lectures by internationally-recognized academics and researchers. Scientific exchange and networking opportunities will be offered through a range of social activities including poster presentations facilitating participants to communicate on their own work with experts in the field.

Mojca Otoničar
Ferroschool chair

How to reach the venue:

- **Walking**: The city center (Congress Square) is about 20–30 minutes away
- **City bus**: Bus number 1 stops near the institute's side entrance (Jadranska stop). Check the bus route map. You can pay with your credit card onboard; the fare is 1.30 EUR
- **Taxi**: Download the "Metro" taxi app from the Apple Store or Google Play Store

Map of Jožef Stefan Institute



PROGRAMME

	DAY 1, 18.11.2024	DAY 2, 19.11.2024	DAY 3, 20.11.2024	DAY 4, 21.11.2024
8.00	*Registration*			
8.45	*Opening remarks*			
9.00	**Novak** Physics of ferroelectrics	**Elissalde** Conventional and unconventional sintering techniques of ferroelectric materials	**Buixaderas** Raman scattering and broadband dielectric spectroscopy: A useful combo for ferroelectrics	**Džeroski** Machine learning for material science
10.30	*Coffee break*			
11.00	**Iñiguez** Computational approaches dedicated to ferroelectric materials: first principles	**Glinšek** Solution-based processing of thin-film oxides for piezoelectric applications	**Garcia** Scanning probe microscopy for functional oxide thin films	**Stoica** Designing underwater devices with ferroelectric materials
12.30	*Lunch*			
14.00	**Iñiguez** Computational approaches dedicated to ferroelectric materials: second principles	**Rojac** Electrical and electromechanical responses in ferroelectrics	**Benčan** Local structure of ferroelectrics by electron microscopy techniques	**Webber** Mechanics of ferroelectrics
15.30	*Coffee break*			
16.00	**Gorfman** Introduction to crystallography of perovskites	**Glaum** Mechanisms of aging and fatigue in ferroelectrics	LAB VISITS	**Dkhil** Towards neuromorphic computing using ferroelectric and related materials
17.30	POSTER SESSION			
18.30	Welcome reception			
19.00			School dinner	Goodbye party

INVITED SPEAKERS

Nikola Novak	*Jožef Stefan Institute, Slovenia*	Physics of ferroelectrics
Jorge Íñiguez-González	*Luxembourg institute of science and technology, Luxembourg*	Computational approaches dedicated to ferroelectric materials: first principles & second principles
Semën Gorfman	*Tel Aviv University, Israel*	Introduction to crystallography of perovskites
Catherine Elissalde	*CNRS, University of Bordeaux, France*	Conventional and unconventional sintering techniques of ferroelectric materials
Sebastjan Glinšek	*Luxembourg institute of science and technology, Luxembourg*	Solution-based processing of thin-film oxides for piezoelectric applications
Tadej Rojac	*Jožef Stefan Institute, Slovenia*	Electrical and electromechanical responses in ferroelectrics
Julia Glaum	*Norwegian university of science and technology, Norway*	Mechanisms of aging and fatigue in ferroelectrics
Elena Buixaderas	*Czech academy of sciences, Czechia*	Raman scattering and broadband dielectric spectroscopy: A useful combo for ferroelectrics
Vincent Garcia	*CNRS, Thales, France*	Scanning probe microscopy for functional oxide thin films
Andreja Benčan	*Jožef Stefan Institute, Slovenia*	Local structure of ferroelectrics by electron microscopy techniques
Sašo Džeroski	*Jožef Stefan Institute, Slovenia*	Machine learning for material science
Laura Stoica	*Thales, UK*	Designing underwater devices with ferroelectric materials
Kyle Webber	*Friedrich-Alexander University of Erlangen-Nürnberg, Germany*	Mechanics of ferroelectrics
Brahim Dkhil	*University Paris-Saclay, France*	Towards neuromorphic computing using ferroelectric and related materials

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Optimization of antiferroelectric and relaxor properties in $NaNbO_3$-based solid solutions for enhanced energy storage performance

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The potential of lead-free relaxor antiferroelectric materials for electrical energy-storage applications is gaining massive attention because of their high energy density capabilities. These are brought by reversible switching from antiferroelectric (AFE) to ferroelectric (FE) phase, while relaxor-like characteristics reduce the losses and contribute to increased conversion efficiency. Although sodium niobate ($NaNbO_3$) is a well-known antiferroelectric perovskite, it is difficult to stabilize its antiferroelectric phase, while introducing relaxor behaviour presents an additional challenge. It was previously shown that introducing dopants on the A and/or B-site of the ABO_3 perovskite, for example, adding a small amount of $SrSnO_3$ into the matrix of $NaNbO_3$, contributes to stabilization of the AFE phase.

In this research work, our main goal was to stabilize the AFE phase in $NaNbO_3$ by doping with Sr and Sn, and to further study the effects of dopants on the structure and energy storage properties of the material. The bulk ceramics were processed via the solid-state synthesis and sintering and characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). XRD and SEM confirmed the partially successful incorporation of dopants, with some SnO_2 remains at the grain boundaries. Mn-doping increased the incorporation level of Sn into the matrix and caused reduced dielectric losses (electrical conductivity) and increased the energy storage efficiency. Temperature-dependent phase transitions were studied using differential scanning calorimetry (DSC) and dielectric permittivity measurements. The phase transitional behavior of $NaNbO_3$ is greatly affected by the addition of $SrSnO_3$, showing a noticeable downward shift in the polymorphic phase-transition temperatures. The polarization – electric field hysteresis loops measured on the pure and doped materials proved the effectively stabilized AFE phase in $SrSnO_3$-modified $NaNbO_3$ with reversible field-induced phase transitions to FE in agreement with literature. Furthermore, additional 1wt% Mn-doping allows significantly modified energy storage properties.

In the future, we will look into a wider variety of dopants to maximize dielectric performance, increase efficiency by reducing the switching hysteresis, and phase stabilization in lead-free sodium niobate systems for high-efficiency energy storage device.

Enhancement of Piezoelectric Properties in Barium Titanate Ceramics through <111> Texturing and AC Poling Above Curie Temperature

Adisu Tsige Shibiru[1], Ichiro Fujii[1], Piyush Sapkota[1], Shintaro Ueno[1], Hyunwook Nam[2], Satoshi Wada[1*]

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The environmental and health risks imposed by lead based piezoelectric highlighted the urgent need for developing safer, lead-free alternatives. However, finding alternative lead-free material with comparable properties was challenging. Barium titanate (BT) appears as a model lead-free ferroelectric material to employ different enhancement techniques. Among these techniques, off-polar poling appears as one of the mechanisms for property enhancement. A study showed applying electric field for tetragonal structure along [111] can create three degenerate polarization directions to form engineered domain configuration state.[1] Another study by Wada et al on 110 textured ceramics has showed the highest piezoelectric coefficient (d_{33}) 788 pC/N for BT <110> textured ceramics, one of the main reasons being formation of engineered domain configuration state and higher domain wall density.[2] Moreover, a study by Shibiru et al. on alternating current (AC) poling of randomly oriented BT ceramics poled above the Curie temperature has showed formation of smaller domains relative to conventional direct current (DC) poling with enhanced $d33$ of 528 pC/N [3].To conduct the proposed idea <111> texture BT ceramics was fabricated using 90 % of BT powder with 100nm particle size as a matrix and <111> BT templates of 10 % synthesized from double molten salt method was used. To achieve the orientation tape casing was employed followed by stacking, pressing, and sintering to achieve dense ceramics. Then DC and AC + DC poling was conducted above TC. After sintering a density of 95 % achieved calculated using Archimedes' method. And the Lotgering factor calculated from XRD showed $F111$ = 85 % texturing. Furthermore, piezoelectric properties improvement was observed after AC poling relative to the DC poling, which is understood due to engineering domain state and AC field induced phase transitions allowing smaller domain formation with increased domain wall density. In addition to these, defect relaxing behavior of AC poling contributed for the piezoelectric property improvement. Detail explanation procedures and discussions will be addressed during the presentation.

References:

[1] Shujun Zhang et al. *Progress in Materials Science* 68 (2015) pp. 1–66.
[2] Satoshi Wada, *Ferroelectrics*, 389:3–9, 2009
[3] Adisu Tsige Shibiru et al. *Japanese Journal of Applied Physics*, 63, Number 8 (2024), pp. 08SP10.

La-doped hafnia thick films prepared by aerosol deposition

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The observations of ferroelectricity in hafnia (HfO_2) thin films by Böschke et al. [1] in 2011 have received considerable attention in the scientific community. Further studies have demonstrated a stabilized ferroelectric phase in bulk single crystal and thin films of doped hafnia [2]. However, there is still no detailed study on hafnia thick films prepared by powder-based technologies. Aerosol deposition is a powder-based thick-film deposition method for the preparation of dense thick films at room temperature [3]. Because of the significant strain, the small grain size, and the defects resulting from the powder breakage upon substrate collision, the aerosol deposition method presents a potential solution for the preparation of hafnia thick films exhibiting a stable ferroelectric phase.

In this work, we have prepared the lanthanum-doped hafnia ($Hf_{1-x}La_xO_2$, x = 0, 0.05, 0.1, 0.15) thick films by an aerosol deposition method. The dense and uniform films were successfully prepared on stainless steel substrates. The replacement of Hf^{4+} by La^{3+} in HfO_2 leads to a gradual phase transition from monoclinic to tetragonal/orthorhombic phase coexistence due to larger ionic radii of La^{3+} than Hf^{4+}. The Rietveld refinement of films underpins the dominance of the tetragonal/orthorhombic phase over the monoclinic phase with increasing La concentration. Lanthanum doping into hafnia matrix improves the dielectric behavior. The dielectric breakdown strength of the films with lanthanum is superior to that of pure hafnia. The successful aerosol deposition of hafnia-based thick films opens up the possibility of integrating hafnia-based layers into thick film technology for various applications.

References:

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[2] X. Xu et al. (2021) *Nat. Mater.* 20, 826-832.
[3] D. Hanft et al. (2015) *J. Ceram. Sci. Tech.* 06(03), 147-182.

Piezoelectric $BiFeO_3$ thin films from metalorganic precursor solutions

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Piezoelectric ceramics are functional metal oxides, which respond to an external electric field or external stress. Driven by external electric field the piezoelectric sample elongate or contract enabling the use as actuator.

The most prominent piezoelectric ceramic is $Pb[Zr_xTi_{1-x}]O_3$ (PZT), which is used in many devices. However, these days lead-based materials get more and more restricted by law and therefore lead-free materials are under intense research such as $BiFeO_3$ (BFO), $[Bi_{0.5}Na_{0.5}]TiO_3$ (BNT), $BaTiO_3$ (BTO) and $[K_xNa_{1-x}]NbO_3$ (KNN) [1].

Piezoelectric ceramics are suitable for microelectronics when deposited as a functional thin film on a substrate like platinized silicon-wafer. These thin films have thicknesses ranging from nm to µm and the resulting devices are characterized by a lower energy consumption compared to systems with bulk ceramics. The ceramic thin films can be used in sensor and actuator applications such as micropumps, acoustic transducers, micromirrors and pressure sensors.

This poster demonstrates studies on BFO thin films produced via Chemical Solution Deposition (CSD). For the CSD method, metalorganic compounds are dissolved in a suitable solvent and deposited as thin films on a substrate. This method was chosen because of the possibility to vary the ratio of compounds in the solvent and to optimize a mixture, which ends up in a high-performance ceramic thin film.

In the frame of our study, a metal-nitrate-based material system has been selected to prepare a BFO precursor solution [2]. Further, XRD and SEM analysis were chosen to study the resulting phase and microstructure of the thin film. The poster demonstrates the transition from a porous and granular microstructure to a columnar microstructure by adjusting the parameters of the CSD process.

References:
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[2] A. B. Martínez et al. *Journal of the European Ceramic Society* 2021, 41, 13, 6449-6455.

Comparative analysis of antiferroelectric niobates: Ceramic vs Crystal

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The developments in lead-free antiferroelectric materials are crucial for creating environmentally friendly alternatives to traditional lead-based compounds. Among the primary lead-free perovskites, $NaNbO_3$ is receiving significant attention as a potentially effective alternative because of its antiferroelectric qualities and potential applications in energy storage. $NaNbO_3$ is a complex material with a rich phase diagram with multiple temperature-dependent phase transitions. Mechanisms such as polarization distribution, soft mode dynamics, and octahedral tilting are involved in the structural alterations that cause these transitions. Understanding the precise mechanisms underlying these phase transitions is an area of active research, having implications for advanced material design and fundamental science.

We compared the ceramics and crystal of the $NaNbO_3$ using Raman and infrared spectroscopy. The dynamics of phase transitions during cooling from the paraelectric phase or heating are discussed with the similarities and contrasts observed in the spectra. The manifestation of these phases is seen by the different experimental techniques in the spectra measured at various temperatures. Our findings show some variations in behaviour of vibrational modes between the two forms, which can be attributed to features such as grain boundaries, microstructure, and defect states in the ceramics that are absent in the single crystals. Infrared spectroscopy is used to determine the changes in the absorption characteristics of the ceramics due to their polycrystalline nature. Comparing $NaNbO_3$ crystals to ceramics enables differentiation between intrinsic features of pure single crystals and extrinsic influences in polycrystalline ceramics, which affect phase transitions, dielectric performance, and suitability for applications. The combination of compositional manipulation and optimization of synthesis methods anticipates a significant increase of the antiferroelectric behaviour, and therefore the energy storage capacity; but also the possibility to engineer slim antiferroelectric P-E hysteresis loops to reduce the energy loss during the energy recovering process. Our next step will explore the promising future of strategically selected dopants in this system to further enhance these properties.

This work is supported by the Czech and Slovenian Research Agency, project 24-10699K

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[1] D. Yang et al., J Mater Chem A Mater 8, 23724–23737 (2020).
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Modulating Electrical Conductivity in $0.67BiFeO_3$-$0.33BaTiO_3$ Lead-Free Piezoceramics Synthesized Through Mechanochemical Activation

Antonio Iacomini[1], Maja Koblar[1] and Tadej Rojac[1,2]
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Lead-based relaxor ferroelectrics, such as PMN-PT, have been extensively studied since 1959 due to their remarkable electromechanical properties. Despite many years of research, the underlying mechanisms that contribute to the ultrahigh piezoelectric properties of PMN-PT remain a topic of ongoing debate. Recent findings suggest that the intrinsic disorder found in relaxors could enhance the dielectric and piezoelectric responses, stemming from lattice dynamics and domain-wall movement. However, with the growing trend towards lead-free piezoelectric materials, there is a pressing need to replace PMN-PT and other lead-based relaxors. Among the lead-free ferroelectric materials, the $BiFeO_3$-$BaTiO_3$ (BFO-BT) system, particularly with a morphotropic composition of approximately 67% BFO, emerges as a promising candidate due to its favorable piezoelectric properties (exceeding 110 pC/N) and high Curie temperature (over 400°C). Nonetheless, the BFO-BT system faces two primary challenges: i) a heterogeneous composition that includes core-shell structures and secondary phases, and ii) a high leakage current attributed to the evaporation of Bi_2O_3 during sintering and changes in the valence state of iron cations. To address these challenges, defect engineering within the BFO-BT system is crucial, necessitating a methodical investigation of point defects. This study focuses on the synthesis and examination of point defects in both undoped and Mn-doped BFO-BT ceramics produced via mechanochemical activation (MA). The MA technique has proven to be a straightforward and efficient approach to produce high-quality BFO-BT ceramics characterized by high densities and minimal core-shell structures and secondary phases. Furthermore, point defect investigations are conducted by assessing electrical conductivity across a temperature range of 25-700°C and varying O_2 partial pressures (10-6 to 1 atm). This enables the in-situ observation of redox processes, oxygen non-stoichiometry, and defect states, with a particular emphasis on oxygen vacancies and p- and n-type conduction mechanisms.

References:

[1] G. Ferrero et al., J. Eur. Ceram. Soc. 43, 350-361 (2023)

Correlating A and B site Co-Doping effects and the crystallographic structural analysis of Pb and Bi free $Sr_2NaNb_5O_{15}$ (SNN) Tetragonal Tungsten Bronze

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The demand for Class II dielectric base metal multilayer ceramic capacitors that can operate beyond 300°C is growing. Strontium Sodium Niobate ($Sr_2NaNb_5O_{15}$, SNN) doped with Ca, Y and Zr has been proposed as a potential Pb and Bi free Class II capacitor material for use in multilayer ceramic capacitors [1]. High relative permittivity (εr ~1300-1500) over a wide temperature range (-65 ^{O}C-300 ^{O}C) and low dielectric losses are reported for z = 0.05 and 0.025 for Sr2−2zCazYzNaNb5-zZrzO15[1]. The structure property relationships behind this composition's performance remain ambiguous. The crystallographic structural evolution of Sr2NaNb5O15 and doped counterparts across varying temperatures has been under debate. This includes room temperature crystal structures, with aristotype tetragonal P4bm [2] to orthorhombic Im2a [3] frequently reported.

High resolution synchrotron X-Ray diffraction on a series of triple doped powders based on Sr_2–2zCazYzNaNb$_5$-zZrzO$_{15}$ (z = 0.0125, 0.025, 0.037, 0.05 and 0.075) have been studied between 100 K and 600 K with a parent orthorhombic Ama2 space group [4, 5]. We report a link between the c lattice parameter changes and polar mode saturation at both dielectric anomalies (T_1 and T_2) frequently reported for $Sr_2NaNb_5O_{15}$[6], alongside a positive thermal expansion in a and b lattice parameters on heating. The c lattice parameter increased from 100 K to 250 K followed by a negative thermal expansion up to the Curie temperature, T_2 (~530 K) highlighting a ferroelectric polar mode softening nearing T_2 and its saturation at T_2. A plateau of the negative thermal expansion is observed with increased B site Zr^{4+} dopant. A site Ca^{2+} and Y^{3+} doping results in the plane distortion of the octahedral framework, disrupting long-range ferroelectric ordering, lowering T_1 and frequency dispersing εr at T_1. B site Zr^{4+} doping (Zr^{4+} for Nb^{5+}), decreased tetragonality, increasing orthorhombic strain, destabilising the ferroelectric mode along c axis, lowering T_2 and εr at T_2. This work aims to develop an understanding of the relationship between crystal and local structure to the dielectric response of a series of the novel Pb and Bi free Sr_2–2zCazYzNaNb$_5$-zZrzO$_{15}$ tetragonal tungsten bronzes.

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Effect of microstructure on antiferroelectricity in $NaNbO_3$

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Current conventional capacitor devices are made of ferroelectric ceramics with lower energy storage capability compared to the antiferroelectric ceramics. Antiferroelectrics utilize the phase transition under certain applied electrical field which can be observed via double hysteresis loop. Transition from antiferroelectric to ferroelectric phase requires high energy due to polarization of domains parallel to the applied field. This required huge energy is then stored within the material and released as it turns into antiferroelectric phase again. For an antiferroelectric ceramic to be commercially used in a capacitor it should preferably be free from toxic elements such as lead, the phase transition from antiferroelectric to ferroelectric should be reversible and the ceramic should be able to withstand a million of cycles, the critical electric field that phase transition occurs should be lower than breakdown voltage and it needs to have comparable recoverable energy density with the lead-based antiferroelectric capacitors. A promising lead-free candidate is $NaNbO_3$ (NN), but this material suffers from irreversible antiferroelectric-ferroelectric phase transition. In this study, pure and doped $NaNbO_3$ (NN) ceramics will be fabricated. The effect of microstructure on the electrical properties mentioned above for capacitor performance will be presented.

Role of A site stoichiometry and Na/Bi ratio on piezoelectric and ferroelectric properties of 0.94($Na_{0.5}Bi_{0.5}TiO_3$)-0.06($BaTiO_3$) ceramics

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Comprehending the chemistry of defects in functional material provides an advantage in effectively adjusting its properties [1]. The 0.94(Na0.5Bi0.5TiO3)-0.06(BaTiO3) (NBT-6BT) is potential lead-free material with properties comparable to commercial PZT. Despite their vast potential as a promising material for hard-type piezoelectric applications, the defect chemistry of NBT-6BT based materials is little known. The Na/Bi and A/B ratios in perovskite NBT-6BT have been found to have a substantial impact on its piezoelectric response and microstructure. The non-stoichiometric A site in NBT-6BT can affect its electronic structure, causing variations in ionic and electronic conductivity, and impedance.

Morphotropic phase boundary (NBT-6BT) solid solutions with A-site non- stoichiometry, along with different Na/Bi ratios, were synthesized and examined to comprehend how defect chemistry affects the microstructure and electro-mechanical characteristics of the ceramics. The deficiency of Bi in the solid solution of NBT-6BT leads to 12% decline in piezoelectric and dielectric response whereas deficient of Na at A site causes sharp decline in ferroelectric and piezoelectric properties. It is evident that an excess of Na causes an 15% increase in piezoelectric response compared to pure NBT-6BT, which is consistent with existing studies [2][3]. Bi deficiency and excess Na in NBT-6BT result in an increase of 8-9% and 14-15% in the depolarizing temperature and coercive field, respectively, as well as increase the grain size compared to pure one. These findings are valuable for further development of hard piezoelectric materials for ultrasonic applications.

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Synthesis and characterisation of TMCM-$MnCl_3$ hybrid perovskite

Chithra Kandappanthodi[1], Sobhan M. Fathabad[1], Doru C. Lupascu[1], Vladimir V. Shvartsman[1]
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Organic-inorganic hybrid halide perovskites have garnered significant attention in the realm of material science due to their environmentally friendly, cost-effective fabrication processes and exceptional optoelectronic properties. In this study, we have synthesized trimethyl chloromethyl ammonium manganese trichloride (TMCM-MnCl3) perovskite single crystals, featuring TMCM+ organic cations at the A-site and chloride ions at the X-site within the ABX3 perovskite structure. We demonstrate that TMCM-$MnCl_3$ exhibits a monoclinic crystal structure at room temperature, which upon heating undergoes a transition to a hexagonal structure with space group P63/mmc, as evidenced by temperature-dependent X-ray diffraction. The phase transition at 408 K was further confirmed by differential scanning calorimetry and dielectric impedance measurements. Piezoelectric response force microscopy measurements reveal a relatively high piezoelectric response and the presence of regular ferroelectric domains in the material. Additionally, the vibrational modes of the crystal were identified using Raman spectroscopy. This comprehensive characterization underscores the potential of TMCM-$MnCl_3$ perovskites for advanced ferroelectric and electrocaloric applications.

Central peaks, damped acoustics, and relaxation dynamics in lead organic-inorganic perovskites

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The organic-inorganic lead-halide perovskites are composed of organic molecules imbedded in an inorganic framework. The compounds with general formula $CH_3NH3PbX_3$ ($MAPbX_3$) display large photovoltaic efficiencies for halogens X=Cl, Br, and I in a wide variety of sample geometries and preparation methods. The organic cation and inorganic framework are bound by hydrogen bonds that tether the molecules to the halide anions, and this has been suggested to be important to the optoelectronic properties. In this poster we present results analyzing the dynamics that drive the structural distortions in these materials. In particular, we will discuss the unusual central peak that characterizes the structural transition and the molecular and acoustic dynamics defining the ground state of these compounds.

Characteristic Material Behavior of Lead-Free and Lead-Containing Piezo Ring Ceramics in Ultrasonic Transducers

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Legal requirements demand that hazardous substances such as lead should be replaced by lead-free materials in the future. This also affects the use of lead-containing piezo ceramics (e.g., PZT), which are used as a standard in ultrasonic transducers. Thus, lead-free ceramics are in the focus of research since a couple of years. Some ceramics are already commercially available, but the development of the new materials has not been completed yet: There is still some effort to be spent on making mass production efficient and as well more experience on the application in technical products is needed. For the optimal design of ultrasonic high-power transducers based on lead-free piezo ceramics precise material parameters are needed, that do not only describe small signal characteristics, but also the behaviour under pre-load, high power, heat impact and long-term operation.

This contribution reports on experiments done on ring-shaped lead-free and PZT ceramics, like they are used in standard bolted Langevin transducers. The measurements were done under free vibration and under pre-load in order to gain detailed insight into the performance of the lead-free ceramics. To ensure comparability of the results, all ceramics were pre-loaded in the same way. Therefore, the mechanical pre-load was measured by a strain gauge integrated in the transducer. Differences in the piezoelectric effect between lead-free and PZT ceramics were figured out by adopting material parameters used in FE-simulation. This will provide important insights for the future design of lead-free ultrasonic transducers.

HFO$_2$-Based Femfet electrical characterization and modelling

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New applications like artificial intelligence require to store and manage huge quantity of data, with growing interrogation about their energetic cost. Therefore, new low-power memory technologies and new architectures where memory and computing are brought together and even combined are necessary. HfO$_2$-based ferroelectric memories are good candidates with their CMOS compatibility, their very low energy consumption and high endurance. Ferroelectric field effect transistors (or FeFETs) allow non-destructive readout and multilevel programming but show limited endurance and retention in comparison with FeRAM. This work focuses on FeFETs with an HfO2-based BEoL ferroelectric capacitor separated from the MOSFET. This type of device, called FeMFET for Ferroelectric Metal FET, is studied because it is expected to overcome the reliability weaknesses of conventional FeFETs for which the ferroelectric material is integrated directly into the transistor gate. The FeMFET also provides more flexibility to store several bits of information since it allows to decouple the ferroelectrical capacitor area from the MOSFET gate area.

The first step is to develop a model of the FeMFET device based on the calculation of the floating potential between the MOSFET transistor and the ferroelectric capacitor. In a second step, we experimentally demonstrate its ferroelectric behavior with counter-clockwise hysteresis cycles measured on devices integrated at 130nm CMOS node. Based on the model and in-depth electrical characterizations, we describe the behavior of these components for different MOSFET and ferroelectric capacitor surfaces and highlight the role of the capacitance ratio between the MOS and the
ferroelectric capacitor.

Modelling of metamaterial response in ferroelectric periodic shell-based structures

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This poster will present the metamaterial response observed and modelled in shell-based ferroelectric structures of 3D printed $K_{0.5}Na_{0.5}NbO_3$ (KNN) ceramics via digital light processing. Unusual electromechanical response is obtained by placing the two electrodes on the main surfaces of the periodic structure, such that the transversal electrostrictive and piezoelectric effect cause a contraction in the external cubic volume encompassing 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. Properties of $KNbO_3$ 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 2 x 2 x 2 shell-structured unit cells where the ceramic polarization direction, determined using by solving a diffusion partial differential equation, specifies the main direction of the transversely isotropic elasticity tensor. Finally, a model displaying the electromechanical response of a cylindrical sample of the same material is presented for comparison, and figures of merit are used to assess the electromechanical metamaterial performance.

Tuning ferroic-structural and magnetic orders in Van-Der-Waals 2D magnets

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There has been a constant effort and tremendously growing interest in the discovery and design of novel magnetoelectric multiferroics[1-3] with strong magnetoelectric coupling and substantial polarization[4,5]. In this study, a novel class of 2D magnetic materials, CuVP2*X*6 (*X*=S, Se) with weak van der Waals (vdW) interactions has been explored. These materials are held by strong covalent bonds in two dimensions, but relatively weaker vdW interactions along the third. This weak stacking of vdW layers has a significant impact on the excitation energy bandwidth – an important gauge of correlations. One unique feature of these materials is the presence of 3*d* transition metal ions where spin-orbit coupling (SOC) has an accessible energy scale coupling magnetic spins and orbital order which is naturally tied to the local nuclear structure. Here we use neutron diffraction to investigate the magnetic and nuclear structure at several temperatures. This study is complemented by electromechanical resonance response measured using dielectric spectroscopy. This experimental evidence supporting the presence of strong magnetoelectric coupling in 2D layered compounds would open a promising direction to experimentally probe the co-existence of magnetism and ferroelectricity in real materials.

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A new mechanism of relaxor ferroeloectric system for neuromorphic computing

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As an attractive alternative to memristor, memcapacitor offers the possibility of building ultra-low power brain-inspired neural networks[1]. Realistic memcapacitive neural networks are based on ferroelectric materials[2], ion migration[3], or charge-shielding devices[4]. Here, we propose a novel memcapacitor mechanism for neuromorphic computing. Our approach utilizes a relaxor ferroelectrics (RFE) system that exhibits neuromorphic features. Basic synaptic learning rules, such as long-term potentiation/depression (LTP/LTD) and spike-timing-dependent plasticity (STDP), are reproduced on various relaxor ferroelectrics (PMN-28PT, PZN-4.5PT) under customized pulse trains. Furthermore, a nonlinear model representing PZN-4.5PT's neuronal behavior is used to construct a fully connected neural network and a reservoir computing system. These PZN-4.5PT-equipped networks show enhanced accuracies compared with their memristive counterparts.

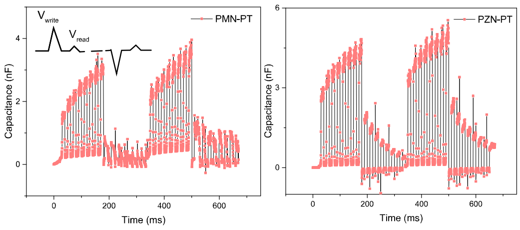

Fig. 1: Evolution of capacitance as a function of voltage pulse sequences for different materials, showing LTP/LTD behaviors.

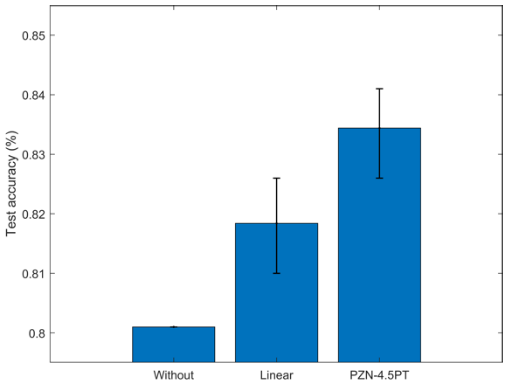

Fig. 2: Comparison of the recognition accuracies for the simplified SVHN dataset with three different neural networks. Without: test accuracy of the network without dendrite, Linear: test accuracy of a referential memristive network[5].

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Mechanical pressure effects on ferroelectric Hafnium Oxide thin films

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Ferroelectric hafnium oxide is one candidate material for next-generation memory devices such as FeRAM and FeFET. When the material is grown to thin films, the orthorhombic phase can be stabilized, exhibiting ferroelectric properties. Zirconium doping enhances the stability of the orthorhombic phase. We expect that applying non-uniform mechanical stress to the thin films will not only induce the flexoelectric effect, which is a switching of ferroelectric polarization by strain gradients, but also induce phase transitions or changes in physical properties. Here, we use cantilevers with a high spring constant in an atomic force microscope to explore the possibility of mechanical switching in epitaxial $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films. Piezoresponse force microscopy is also employed to visualize ferroelectric domains and characterize their mechanical switching behaviors. Furthermore, we investigate how structural phases compete and are controlled by mechanical stress or electrical poling, using X-ray diffraction, Raman spectroscopy, and transmission electron microscopy. This study provides useful insight into mechanical pressure effects on phase competition properties in hafnium oxides.

Observation of charged domain walls in antiferroelectric-like $K_3[Nb_3O_6(BO_3)_2]$

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Antiferroelectric materials exhibit an anti-polar alignment of electric dipoles, giving rise to intriguing physical properties and functional behaviours. In this work, we apply different scanning probe microscopy techniques to image and investigate the domains and domain walls in the ferroelectric model system $K_3[Nb_3O_6(BO_3)_2]$, which exhibits a canted anti-polar arrangement of electric dipoles that leads to an intriguing coexistence of ferroelectric and antiferroelectric-like properties. Using piezo response force microscopy, we show that the domains exhibit a pronounced piezo response, consistent with the non-centrosymmetric crystal structure. At the nanoscale, a chevron-like pattern of twin domains develops, where the crystallographic structure changes by 120° across the domain walls. Interestingly, we observe the formation of charged twin walls with distinctly different piezoelectric and electrostatic responses, arising from a small canted electric moment of the otherwise anti-polar arrangement of electric dipoles. Furthermore, the charged domain walls can be controlled by local electric fields. Our findings provide insight into novel types of ferroic domain walls with unusual mechanical and electronic properties.

Investigation of energy storage properties of $Pb(Fe_{0.5}Nb_{0.5})O_3$–$BiFeO_3$ bulk ceramics and thick films

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Energy storage is the ability to collect and store energy for use at another time. Dielectric capacitors are good candidates for energy storage in pulsed systems. Among energy storage devices, dielectric capacitors have higher power density compared to batteries and are good candidates for energy storage in pulsed power systems. Different classes of dielectric materials result in different energy storage capabilities. The most promising are dielectric materials with slim and pinched polarization versus electric field (P–E) hysteresis loops. Such properties are obtained in $(1–x)Pb(Fe_{0.5}Nb_{0.5})O_3–xBiFeO_3$ (PFN–100xBFO) solid solutions. Compared to bulk ceramics, thick films withstand higher electric fields, which makes them even more promising for energy storage applications.

In this work, we investigated the energy storage properties of PFN–100xBFO bulk ceramics and thick films. PFN–100xBFO ($x = 0–0.5$) powders were prepared by mechanochemical synthesis, isostatically pressed into pellets and sintered in an oxygen atmosphere at 900 °C or 950 °C for 2 h. The best energy-storage properties were determined for the composition $x = 0.3$. The recoverable energy storage density (U_{rec}) and efficiency (η) values were 1.0 J/cm^3 and 91 % at 70 kV/cm, respectively. After that, thick films of the composition $x = 0.3$ were screen-printed on gilded Al_2O_3 substrates. The samples were sintered in an oxygen atmosphere at 800 °C, 850 °C and 930 °C for 2 h. The samples sintered at 800 °C withstood the highest electric fields and were selected for further investigation of the energy storage properties. The U_{rec} value of the PFN–30BFO thick films reached 2.8 J/cm^3 at 400 kV/cm and the η value was ~80 %. The samples were additionally cycled by an electric field and survived 10 million cycles. The achievement of good energy storage properties and fatigue resistance of the PFN–30BFO thick film samples shows the possibility for applications in energy storage systems.

Design and mechanical characterization of lead-free piezoelectric ceramics

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Piezoelectric materials for electromechanical devices such as lead zirconate titanate based ceramics (PZT), have nowadays dominated the industrial market thanks to their piezoelectric properties.However, the lead contained in these ceramics known for its toxicity, has become an issue for their use in the European Union following its banishment in electronic devices in 2003. Therefore, research in alternative lead-free piezoelectric materials have been investigated while still not being introduced at an industrial scale on account of manufacturing processes or inequivalent response values of PZT. Among
lead-free ceramics composition, the (K,Na)NbO3 system has been one of the most investigated and promising candidate that needs to be further investigated in order to introduce it at an industrial scale. For producing high quality ceramics, chemical modification such as doping is used, in addition to Spark Plasma Sintering (SPS) in order to limit alkali volatilization or excessive grain growth. It also allows a faster sintering step that gives time and energy consumption gain. However, it remains a lack of data on
the mechanical behaviour in order to scale-up this material and to push forward its introduction at an industrial scale to fulfil European directives. The aim of this study is to investigate the design of lead-free piezoelectric ceramics in order to obtain high quality, homogeneous, and dense materials with different grains sizes and piezoelectric performances, using conventional sintering and spark plasma sintering. Microstructure and mechanical characterizations have shown the high potential of spark plasma sintering technique in addition to the effect of tantalum doping in KNN-based ceramics for the strengthening of KNN which is important for applications.

On the Solid-State Synthesis Of BiFeO3 Ceramic Powders by *in-situ* High-Temperature X-Ray Diffraction and Related Methods

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Bismuth Ferrite ($BiFeO_3$ - BFO) has been the subject of materials research for over 50 years due to its unique combination of ferroelectric, antiferromagnetic, and piezoelectric properties. Its high Curie and Néel temperatures, along with its multiferroic properties at room temperature, make BFO highly suitable for advanced technological applications, including novel memory devices, sensors, transducers, and actuators. These applications span various fields, from consumer electronics to aerospace and defense.

As a lead-free piezoelectric material, BFO has garnered significant attention due to environmental and health concerns associated with its lead-based counterparts, such as $Pb(Zr,Ti)O_3$ (PZT). Its simple perovskite structure and diverse physical properties have led to intense study, aiming to optimize its piezoelectric and magnetic behaviors through doping and defect engineering.

Despite its immense potential, synthesizing pure-phase BFO is challenging due to the thermodynamic stability of intermediate phases, such as Sillenite ($Bi_{25}FeO_{39}$) and Mullite ($Bi_2Fe_4O_9$). A recent study by Wesley *et al.* (2023) has shown that BFO forms via the Sillenite intermediate phase during synthesis, as confirmed through *in-situ* Powder X-Ray Diffraction (PXRD) analysis.

My current research in the Jacob Jones Research Group at North Carolina State University focuses on expanding upon the observations by Wesley *et al*. (2023) and leveraging *in-situ* PXRD analysis to investigate whether aliovalent doping of the Sillenite intermediate phase can thermodynamically avoid the formation of unwanted secondary phases. Thereby producing a single-phase aliovalent doped BFO product upon reaction with Fe_2O_3. My research also includes the detailed structural characterization of both the aliovalent doped intermediate phase and the aliovalent doped BFO product to understand their macroscopic properties.

By optimizing the synthesis of aliovalent doped BFO and understanding its structural properties, our research aims to enhance BFO's performance across a wide range of applications, contributing to the development of an environmentally friendly, high-performance multifunctional material.

Phase identity and microstructure-property relationships in $BiFeO_3$-$BaTiO_3$ ceramics

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Lead free bismuth ferrite-barium titanate (BF-BT) is a promising material for high temperature piezoceramic applications such as sensors, transducers, actuators. The demand for lead-free materials is increasing as it has environmental features. Incorporating minor dopants and ternary perovskite components, as well as modifying the heat treatment method, can indeed enhance the properties of BF-BT ceramics. Issues arising due to the controversial identification of tetragonal phase and lack of recognition for chemically heterogeneous core-shell microstructural features in previous reports on BF-BT based materials are highlighted in the present work. In this poster, the effects of processing parameters on the structure and functional properties of $Bi(Mg_{1/2}Ti_{1/2})O_3$ (BMT)-modified BF-BT ceramics are evaluated, with particular emphasis on crystal structure refinement by XRD and micro-chemical analysis by EDX, together with temperature-dependent dielectric and ferroelectric property measurements.

Functional characterization of piezoelectric materials by non-destructive techniques

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For 20 years now, EU laws restrict the use of certain hazardous substances in electrical and electronic equipment through the RoHS Directive. In the field of piezoelectric materials, an exemption for the use of PZT exists but may not be reconducted as soon as a replacing solution will be found. The aim of the european SCUALE project (Sustainable Components for Underwater Application in Lead-free materials in Europe) is to study, develop, and produce advanced lead-free materials and components to replace PZT (Plomb Zirconate Titanate) existing ceramics with improved performance for underwater acoustics applications.Nowadays, Finite Element Methods (FEM) are intensively used to dimension devices using piezoelectric materials particularly for ultrasonic transducers. Thus, an accurate and consistent dataset of characteristics of piezoelectric materials is crucial (elastic, piezoelectric and dielectric tensors) to simulate properties of such transducers. To deliver the complete dataset, the well-known IEEE standard is mainly used but its procedure uses several samples which could meet the dimensions ratio imposed for the vibration of a favor mode. The use of multiple samples can imply inaccuracies and consistency errors.

To avoid these possible errors which can subsequently have significant consequences on the simulated properties of the devices, only one sample can be used using the resonant ultrasound spectroscopy technic with electrical impedance measurements to detect eigenfrequencies of a parallelepiped shape piezoelectric sample. Small electrodes judiciously placed are used to respect as well as possible the theoretical stress-free hypothesis. Eigenmodes of a 10x15x30mm parallelepiped of PZT-4 were computed as a numerical phantom in the frequency range of [20kHz;200kHz]. 80 eigenfrequencies were exploited which allow a complete characterization by using the Rayleigh-Ritz method which was implemented as a first step. A new inverse problem with an optimization hybrid method (genetic algorithm coupled to a gradient method) was specifically developed as a second step to deduce the material characteristics from the impedance signature. Accurate results were obtained showing the effectiveness of this method. Mean error on the parameter values is less than 4%. In the near future, implemented method will be experimentally applied to lead-free BT-based materials.

Growth of piezoceramic films on glass via flash lamp annealing

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Piezoelectrics integrated on glass will bring new functionalities, including advanced haptics and loudspeakers, which could be part of future flat panel displays, mobile phones, windows, etc. With its large piezoelectric coefficient and transparency, lead zirconate titanate (PZT) is widely used in industry and an obvious candidate for integration on glass. However, its major drawback is its crystallization temperature above 650 °C, beyond the processable limit of most commercial glasses. Flash lamp annealing is a powerful tool to thermally treat samples through the absorption of broad-spectrum light. Due to its geometry, flash lamp annealing allows treatment of large area oxide thin films on temperature-sensitive substrates, which is particularly suited for industrial applications.

In this work, we demonstrate crystallization and macroscopic properties of PZT thin films (with morphotropic phase boundary composition) grown directly on various glasses, including alumina-borosilicate and soda-lime, through flash lamp annealing. The achieved films crystallize in perovskite phase and demonstrate macroscopic properties. They exhibit an in-plane permittivity of 450 with dielectric losses below 5% and a remanent polarisation larger than 12 µC·cm-2. We also demonstrate a surface haptic device fabricated with a 1 µm-thick film (piezoelectric e33, f of -5 C m-2) on alumina-borosilicate glass. With an ultrasonic surface deflection reaching 1.5 μm at 60 V, this device is sufficient for surface rendering applications. Furthermore, we will show the implementation of this process on thinner and flexible glasses, such as Corning Willow glass.

Pyroelectric Effect Enhancement by Poling in PZT Thin Films

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Ferroelectric thin films offer numerous applications, such as nonvolatile memories, piezoelectric sensors, and actuators. It is also noteworthy that significant pyroelectric and electrocaloric effects have been reported in ferroelectric thin films, providing potential applications to infrared sensors, energy harvesting, and electrocaloric cooling. Electrical poling with DC or AC voltages enhances remanent polarization and piezoelectric coefficient. Although the pyroelectric coefficient also increases with increasing poling voltage [1], its relationship with a degree of poling is not straightforward [2].

Here, we investigate the impact of poling on the pyroelectric effect. In this study, using lead zirconate titanate (PZT) with morphotropic phase boundary composition prepared by sol-gel method, we simultaneously measured the pyroelectric effect and the remanent polarization by varying DC poling time. We measured the pyroelectric current via local AC heating at 220 Hz with a Pt thin film heater stacked on the PZT, and the remanent polarization by applying a triangular pulse at 1 kHz. The results show an increase in both the pyroelectric current and the remanent polarization with increasing DC poling time as shown in Figure. With the same poling time, the pyroelectric current increased more rapidly than the remanent polarization did, suggesting the importance of poling in enhancing pyroelectric effects and the significance of direct evaluation of pyroelectric properties.

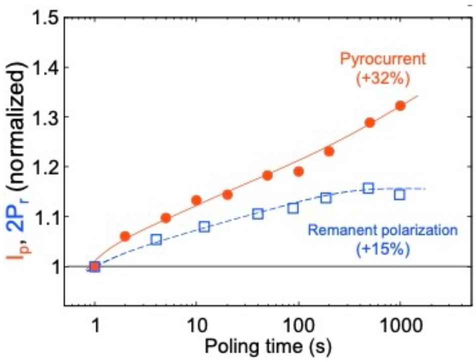

Figure Poling time dependence of pyrocurrent and remanent polarization, which are normalized at 1 s.

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Spin coating behaviour on patterned substrates for selective area deposition of oxides from aqueous solution

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Selective Area Deposition (SAD) is an alternative to conventional litho-etch techniques for the fabrication of devices from thin films. In SAD, a film is shaped through selective deposition rather than etching it post deposition. SAD can be achieved using solution-based deposition techniques, like Chemical Solution Deposition (CSD), by manipulating the wetting behaviour of the precursor solution on substrates. By locally altering the wettability of the substrate, it is possible to selectively deposit the precursor solution and control where a film is deposited. Unlike etching, this method requires no high energy plasma or hazardous corrosive chemicals, does not damage the substrate, and does not introduce contaminants to the film.

In this research, the wettability of platinised silicon substrates was successfully manipulated using octadecanethiol Self-Assembling Monolayers (SAMs). The SAMs were fully removed and the platinum was oxidised after 40 minutes of exposure to DUV generated reactive oxygen species. After exposure, a water contact angle difference of ~100\deg was achieved, resulting in complete wetting on hydrophilic regions and complete dewetting on hydrophobic regions when applying aqueous solutions. The patterning of complex 2D structures was achieved using a standard photolithography mask compatible with DUV exposure. The patterning of both the SAM and the precursor solution was imaged using 3D optical profiling. High resolution height mapping of the SAMs revealed a non-uniform coating of the substrate, limiting the resolution that can be achieved. Imaging of the patterned precursor film revealed that a minimum feature size of 40 um has been achieved. Additionally, it was revealed that the confinement of the precursor solution during spin coating alters the mechanics of the spin coating process, resulting in uneven thickness of the deposited film. As such, proof of concept of solution-based SAD has been achieved, but further research is required to improve the quality of the deposited structures.

Towards high-end photonics: enhancing orientation in novel $Ca_xSr_yBa_{1-x-y}Nb_2O_6$ thin layers

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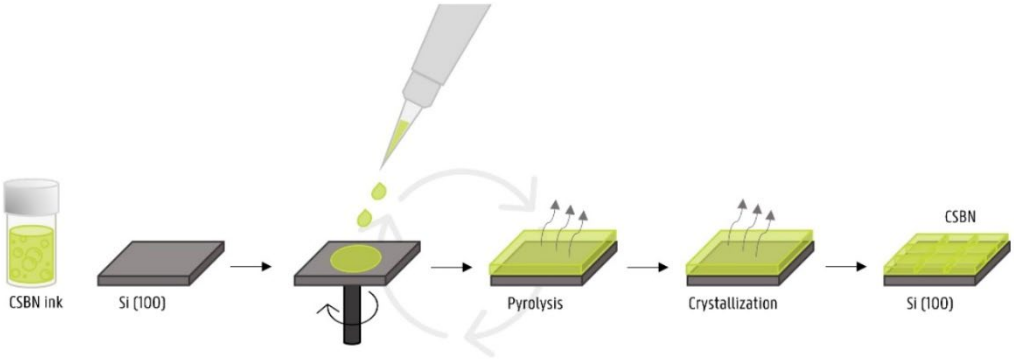
In our modern society people are able to communicate, generate and store enormous amounts of data. As a result, the amount of data traffic worldwide is increasing exponentially and outgrowing the available technology. Therefore, high-speed data communication has become a necessity. By integrating both electronic and photonic functions on a single chip, photonic integrated circuits (PICs) could function as a platform for data communication via optical means. Today, silicon and silicon-nitride materials are mostly used for integrated photonics. The possibilities of these platforms can be further enhanced by the addition of a ferroelectric layer as an active device for a hybrid system. Tuning of the signal can be accomplished by changing the refractive index of the active device via the application of an electric field. The most efficient way to integrate this ferroelectric layer is via direct layer growth on PICs. In this work, calcium strontium barium niobate (CSBN) with promising ferroelectric properties is used. For the direct integration of $Ca_xSr_yBa_{1-x-y}Nb_2O_6$ on Si substrates, we have introduced a wet chemical solution deposition approach by means of spin-coating technique. The implementation of this wet chemical method facilitates molecular level control and low-cost production of highly oriented ferroelectric thin films for integrated electro-optic devices.



Bismuth ferrite-lead titanate thin films for an investigation of the effects of the morphotropic phase transition on magnetic properties

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x$BiFeO_3$-(1-x)$PbTiO_3$ (BFPT) is a ferroelectric perovskite for all values of x, and antiferromagnetic at certain values of x. The material properties depend on the crystal symmetry, which in turn depends on the ratio of $BiFeO_3$ to $PbTiO_3$ [1]. For $x > 0.7$ the crystal structure is rhombohedral (R), with the ferroelectric saturation polarisation (Ps) // [111], while for $x < 0.7$ it is tetragonal (T), with Ps // [001]. At room temperature, the R phase is G-type antiferromagnetic while the T phase is paramagnetic [2]. At x=0.7 BFPT exhibits a morphotropic phase boundary (MPB) between T and R structures [3], accompanied by an enhancement in the ferroelectric and piezoelectric properties. There's the potential to manipulate the phase transition by applied stress or electric field, and hence switch between antiferromagnetic and paramagnetic behaviour [4].

Here we deposit BFPT films for an investigation of the effect of the phase transition on the magnetism. Figure 1 demonstrates the effect of changing the chamber temperature during deposition. The splitting of the diffraction peak seen at 22° is synonymous with the (100) lattice plane splitting into (001) and (100), indicating the T crystal symmetry. This is useful for controlling whether BFPT is R or T without changing the composition. An optimum deposition temperature was investigated regarding thin film topography.

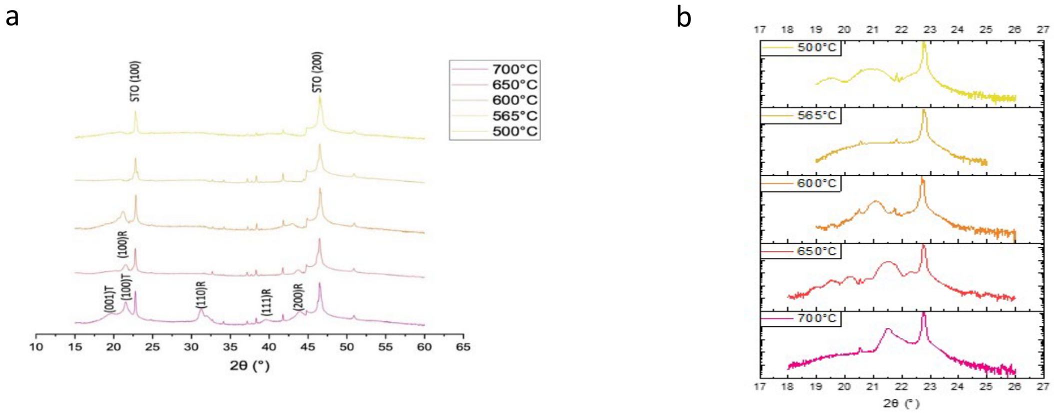

Figure 1: XRD data collected for x=0.65 (x)BF-(x-1)PT where deposition chamber temperature varied. a) shows the 2θ range of 15° to 60° and b) narrowed 2θ range, across the (100) peak, 18° to 26°

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Towards artificial magnetoelectric composites using Ce_2Fe_{17}-based intermetallics

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Compared to single-phase magnetoelectric (ME) materials, magnetostrictive-piezoelectric composites demonstrate stronger ME coupling mediated by interfacial elastic deformation. Most often the choice of the magnetic system is limited to ferrite and manganite spinel or perovskite oxides and terfenol-D or metglas alloys. The design of new magnetoelectric composites using novel magnetic materials like the Ce_2Fe_{17}-based family is of significant interest to look for better ME responses and the emergence of exotic coupling behaviours.

Ce_2Fe_{17} is particularly notable for its complex and diverse magnetic ground states (ferromagnetic, helimagnetic, antiferromagnetic…) and its behaviour along with the application of magnetic fields and across varying temperatures, making its magnetism a compelling subject for further investigation [1-2].

Due to the computational challenges of modelling full composites, we applied the strain directly to the Ce2Fe17 unit cell to mimic the stress effect arising from an adjacent piezoelectric material, and performed Density Functional Theory (DFT) calculations using VASP code to explore its structural, electronic and magnetic properties under epitaxial and uniaxial strains. Additionally, we are assessing the magnetocrystalline anisotropy energy to identify the most energetically favourable magnetic orientations under different strain conditions.

While these DFT calculations were limited to collinear magnetism, the results show that strain application can significantly alter the Ce_2Fe_{17} magnetic properties, suggesting such material, we successfully succeeded to fabricate exhibits a strong potential for the design of ME composites.

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Piezoelectric properties of $Na_{0.5}Bi_{0.5}TiO_3$-based ceramics for sonar applications

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Underwater sonars are devices that use sound waves to detect objects in oceans and have thus proved very useful in marine biology and defense systems. The functional component of a sonar consists of a piezoelectric ceramic material that can serve as an active or passive component, meaning it can transmit and receive sound waves, or only receive them, respectively. While sonar technology is well developed, scientists are still searching for and developing lead-free piezoelectric ceramics due to European Union legislation according to which all lead-containing materials should be replaced by lead-free ones.

Promising lead-free piezoelectric materials can be obtained by compositional design, by creating solid solutions with coexisting symmetries (e.g., tetragonal and rhombohedral), a so-called morphotropic phase boundary composition, where competing phases allow increased polarization and strain responses. To optimize the piezoelectric response and mechanical quality of ceramic samples, microstructure (grain size and density) needs to be appropriately adjusted, which can be achieved by optimizing the sintering conditions.

In this work, solid solutions between rhombohedral sodium bismuth titanate (NBT) and tetragonal potassium bismuth titanate (KBT) or barium titanate (BT) were produced using the solid-state synthesis method. The influence of processing parameters such as sintering time and temperature on the microstructure and piezoelectric properties were investigated. The material composition was determined by X-ray powder diffraction (XRPD) and the microstructure was analyzed by field emission scanning electron microscopy (FE SEM). The piezoelectric properties were measured with the Berlincourt d_{33} piezo meter, while electrical measurements were performed to obtain dielectric permittivity and resonance frequencies, from which the elastic compliance, coupling factors and mechanical quality factor were calculated. We find that NBT-KBT/BT solid solutions hold promise for their use on sonar devices not necessarily from their modest d_{33} values, but rather due to their appropriate elastic compliance values, which can surpass the values of lead zirconate titanate (PZT) compositions.

Unraveling Crystal Lattice of Cold Sintered Lead-Free Perovskites

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In pursuit of designing environmentally friendly materials and processes, our work focuses on the cold sintering process (CSP) of lead-free ferroelectric perovskites, namely $BiFeO_3$ (BFO) and $K_{0.5}Na_{0.5}NbO_3$ (KNN), with a strong emphasis on understanding the influence of CSP on their structural and functional behaviour. Unlike traditional sintering methods, which require temperatures around 1000°C, CSP is an innovative technique that uses a transient liquid phase, high pressures (~ 600 MPa), and significantly reduced temperatures (≤ 300°C). This approach not only densifies the material but also enables control of the microstructure [1].

To investigate the nano- to atomic-scale characteristics of cold-sintered perovskites, scanning transmission electron microscopy (STEM) is employed, allowing the visualization and detailed analysis of defects that arise during CSP. Such defects include a high-density of dislocations that strongly affect the electrical and mechanical properties of these materials. To provide insights to understanding the functional behavior of defected perovskite ceramics from strain and charge perspectives, image processing techniques such as atomic-scale polarization mapping and geometric phase analysis (GPA) are performed. Furthermore, charge density calculation from electron diffraction patterns obtained from novel the 4D STEM technique is utilized [2].

In order to validate the experimental findings from the STEM technique, image simulations are conducted using abTEM, a powerful tool that enables the comparison of simulated and experimental results, offering a more comprehensive understanding of the behavior of the cold-sintered material. Through this multi-faceted approach, the research aims to advance the development of environmentally friendly cold-sintered perovskite materials.

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Thin Films of Quinuclidine-Based Molecular Ferroelectric with Preferred Orientation

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Ferroelectricity continues to fascinate materials science researchers, as new ferroelectric hybrid materials and unique aspects of the phenomenon continue to be discovered, highlighting its potential for innovative technological applications.[1,2] In this study, a novel inorganic-organic hybrid material consisting of 3-quinuclidinone cations and a tetrachlorocobaltate(II) anion is synthesized using a green, solvent-free mechanochemical approach.[3] Two forms of this compound (anhydrous and hydrate) can be prepared depending on the reactants used. These two forms can be converted into each other under humid or dry conditions. In addition to humidity-induced transformations, the material also exhibits several phase transitions triggered by temperature changes. Ferroelectric phases have been observed for the anhydrous phase at low, room and high temperatures. The occurrence of multiple transformations reflects the soft crystal packing of the 3-quinuclidinone cations and the tetrachlorocobaltate(II) anion, which is controlled by non-covalent interactions. The structural flexibility of this material makes it ideal for deposition on substrates achieved by the dip-coating method. The resulting metal–organic thin films grow in a specific crystal orientation on Si(100) and ITO-coated glass substrates and yield uniform and crystalline films. According to remanent polarization measurements, these films show stable ferroelectric switching under ambient conditions.

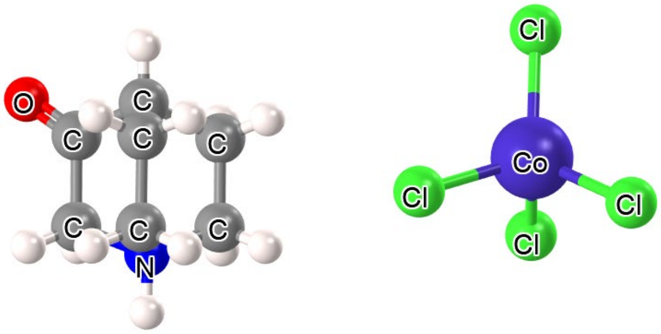

Figure 1. Molecular ferroelectric composed of organic 3-quinuclidinone cation (left) and inorganic tetrachlorocobaltate(II) anion (right).

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Shape-memory effect study on thin film piezo-ferroelectric actuators

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Piezo-ferroelectric materials are prominent candidates for highly valued applications such as sensors and actuators for microelectromechanical systems (MEMS). The integration of these materials in multicomponent actuators represents a technological advantage over electrostatic or magnetic actuation [1]. Piezoelectric actuation displayed a larger stroke – or maximum displacement – at lower voltages, which made it attractive to applications where the power consumption and scaling effect are one of the most important limitations. One interesting phenomenon observed in piezoelectric actuators is the shape-memory effect [2,3]. The shape memory effect is observed when there is a remanent strain -at E=0- in the material after electric field application. This effect could be related to the imprint effect [4], which surges from the domain wall pinning due to dipole defects ($V\ O..-DTi''$)[5] in doped ferroelectric materials. Shape memory effect in ferroelectric materials could then be exploited for fine positioning systems since the remanent deformation of the micro actuator is about units to hundreds of nm for thick films. Since the study of this phenomena poses an important technological contribution for novel smart systems, the aim of this research is to establish the compositional, crystalline, and morphological features that promote this effect in ferroelectric actuators. In this regard, doped- PZT and PZT-thin films will be developed by chemical solution deposition. Their composition and deposition parameters will be optimized to obtain dense, secondary-phase free and thick films which will be further characterized by XRD, EBSD, SEM, Ferroelectric and Piezoelectric behavior (P-E and S-E loops), Piezo-response Forcemicroscopy and ferroelectric fatigue.

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3D HfO_2-based FeCAPs for advanced FeRAMs

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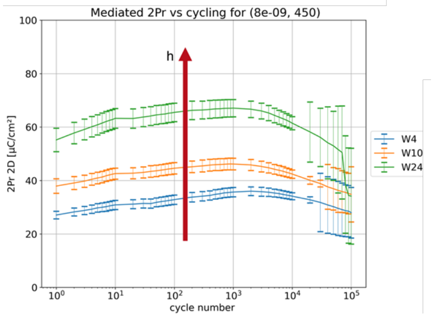
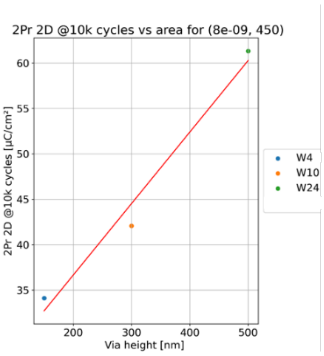
Thanks to their excellent CMOS compatibility and potential for scalability, ferroelectric HfO_2-based materials have been intensively studied in emerging memory field. Recently, TiN/$Hf_{0.5}Zr_{0.5}O_2$ /TiN ferroelectric capacitors were successfully integrated in the Back-End-Of-Line (BEOL) of 130 nm CMOS technology [1]. $Hf_{0.5}Zr_{0.5}O_2$ (HZO) has shown robust ferroelectricity, high dielectric constant and low-temperature preparation, which is a crucial aspect for its integration into the semiconductor-based industry and a promising material for the non-volatile memories [1]. Among the methods for depositing thin films, ALD (Atomic Layer Deposition) is unique for its capability of growing conformal thin films with a controled composition and thickness [2]. In order to surpass 130 nm node, it is imperative to reduce devices footprint scaling it down to tenths of nm. The only way to achieve this without losing ferroelectric properties is to develop 3D ferroelectric capacitors (FeCAPs).

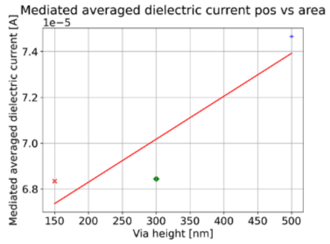
The scope of this study is to understand 3D FeCAPs electrical performances and the underlying physical phenomena governing their properties. This will lead to optimized HfO2-based 3D-FeCap for advanced FeRAM integrated at 22nm FDSOI node and below. Electrical characterization was made through Positive-Up-Negative-Down technique, which is specifically designed to isolate ferroelectric and dielectric response of a material. Thanks to these measurements, hysteresis loop for polarization can be retrieved and subsequently endurance for remnant polarization (fig 1.a) can be extracted as well as dielectric current (fig 1.c). Then the impact of via height (or of a different parameter) on ferroelectric properties can be estimated (fig 1.b). In particular first set of measurements clearly indicate how the out of plane surface contribution boosts ferroelectricity, although its gain is not exactly equal as the gain in surface.

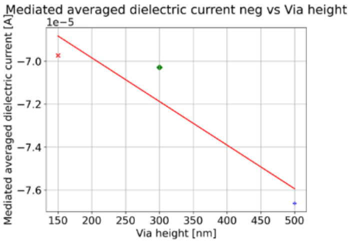
h(W4) = 150 nm h(W10) = 300 nm h(W24) = 500 nm

8 nm hzo thickness , T_{ann} = 450 °C









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Nanoscale Polar Order in Relaxor Ferroelectrics and its response to external stimuli

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Relaxor Ferroelectric (RFE) materials exhibit unique characteristics, including a slim polarization-electric field hysteresis loop, diffuse phase transitions, frequency dispersion of maximum permittivity, and exceptional electro-mechanical responses [1]. Since their discovery in 1958, these extraordinary properties have been hypothesized to originate from polar states which correlate at the nanoscale. Although this idea remained speculative for decades, recent advances in high-resolution electron microscopy have enabled the direct detection of polar nanodomains and their spatial correlation with chemically ordered regions [2-3].

Despite these advances, the complex polar arrangement and its role in the functionality of RFE are still a matter of debate and especially how the polar disorder responds to external stimuli, such as the electric field [4]. This thus requires in situ high resolution techniques to directly probe it at the atomic scale.

In this work, we investigate the relaxor ferroelectric composition $0.72Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.28PbTiO_3$ by using atomic-resolution Cs-corrected Scanning Transmission Electron Microscopy (STEM) coupled with in situ heating and electric field application. Our findings reveal a hierarchical polar arrangement, where short-range and long-range order coexist. We discuss the response of this complex polar environment to external electric fields and present the temperature-dependent evolution, where the short-range order responds initially, followed by the long-range order, in correlation with the macroscopic diffuse phase transition. Finally, a critical discussion on the capabilities, challenges and limitation of using in situ STEM for the investigation of relaxor ferroelectrics will be provided.

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Synthesis and Characterization of a Platelike Aurivillius Compound

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Aurivillius structure materials consist of a Bi-layers (Bi_2O_2) separated by layers of perovskite. Hence, they have great potential for designing novel property combinations. The Aurivillius material $Bi_6Fe_2Ti_3O_{18}$ (BFTO18) is potentially multiferroic and due to its large c/a lattice parameter ratio has a tendency to form platelike particles; these may be suitable for producing crystallographically textured materials. We have employed a molten salt method, with a NaCl-KCl eutectic, to produce BFTO18 particles with large aspect ratio. Synthesis variables included dwell temperature and BFTO18/Cl ratio. The particles have been characterized employing X-ray diffraction and electron microscopy and their suitability for forming textured materials via tape-casting has been explored.

Getting in contact with ferroelectric domain walls

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Ferroelectric domain walls represent functional interfaces with unique electronic properties. For more than a decade, their physical properties have been studied intensively, and a wide range of applications towards beyond-silicon nanoelectronics have been proposed. For example, it has been demonstrated that ferroelectric domain walls can be used to rectify or control the flow of electrical currents at length scales approaching the unit cell level. Despite their outstanding application potential, little is known about the performance of the domain walls in actual device geometries and the contact phenomena that co-determine the current injection.

In this study, we perform a systematic analysis of the transport behavior of ferroelectric domain walls in the vicinity of different electrode materials with varying work functions. By applying electron beam lithography and evaporation, we design electrode patterns with gaps ranging from some hundred nanometers to several micrometers on the ferroelectric p-type semiconductor ErMnO3, and measure the impact on the transport behavior of different types of domain walls within the gap. For this purpose, we use a suite of scanning probe microscopy techniques, including conductive atomic force microscopy (cAFM) and Kelvin probe force microscopy (KPFM), as well as mesoscopic probe techniques. Based on our experiments, we gain quantitative insight regarding the distinct barrier that locally forms at the electrode–domain wall contact. We show that key parameters, such as the barrier height and emergent depletion regions, are distinctly different from the domains, which we explain within the framework of classical semiconductor physics. The results are of fundamental importance for the integration of ferroelectric domain walls and the general understanding of applying scanning probe microscopy for contact formation characterization.

Electromechanical and energy storage properties of $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ thin films by Chemical Solution Deposition

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Lead-free $0.5Ba(Zr_{0.2}Ti_{0.8})O_3$-$0.5(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT–BCT) bulk ceramic is one of the potential environmental-friendly alternatives of PZT ceramics for piezoelectric applications, especially at ambient environment conditions, and energy storage applications due the high piezoelectric coefficient d_{33} and saturated polarization (P_s). Considering the miniaturization of electronic components, the use of materials in the form of thin films is a viable solution. However, thin films prepared by Chemical Solution Deposition (CSD) using the conventional carboxylic acid-based synthesis route are often characterized by fine-grained and porous microstructure, resulting in inferior functional properties.

By introducing alternative solvents, ethylene glycol, and ethanol, and multistep annealing at 850 °C, we obtained dense BZT-BCT films on platinized silicon substrates (Pt/Si). Here, we present the design of the thermal processing, aiming to obtain the films with a columnar microstructure. However, the films on Pt/Si with thicknesses exceeding about 120 nm contained intergranular cracks. The crack evolution was attributed to the thermal expansion mismatch between the film and the substrate; therefore, another substrate, platinized sapphire (Pt/Sapp), with a larger thermal expansion coefficient than silicon was introduced. Excellent energy storage properties of 46 $J \cdot cm^{-3}$ of recoverable energy and energy storage efficiency of 89 % are measured in the 340 nm thick BZT-BCT thin films on Pt/Sapp compared to 10 $J \cdot cm^{-3}$, and 69 %, respectively, measured in the 120 nm thick BZT-BCT films on Pt/Si. A similar trend is observed with electro-mechanical properties measured by a double-beam laser interferometer. The piezoelectric d_{33} coefficient and the electric field-induced strain (S) of 40 pm/V and 0.77 % were measured in the film on Pt/Sapp, while the 120 nm-thick film on Pt/Si exhibited d_{33} of about 20 pm/V and S of 0.18 %, respectively.

Model for the Effect of Pyroelectricity on Schottky Barrier Height

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Schottky diodes are made of the contact between a semiconductor and a metal. While silicon isn't pyroelectric and so are all metals, recent studies have shown that silicon-based Schottky diodes do exhibit pyroelectric behavior [1].

Previous studies have shown that if the Schottky barrier height is determined by the I-V curve, it increases as the temperature increases. However, the opposite trend is found if it is extracted from C-V measurements [2]. While there is well excepted explanation to the I-V behavior (interface inhomogeneity), to the best of our knowledge no such explanation exists for the C-V behavior.

We suggest a model to bridge this gap, which is based on the Bardeen model for Schottky barrier height non-idealities diodes, which includes an interfacial layer at the contact, and interfacial charges:

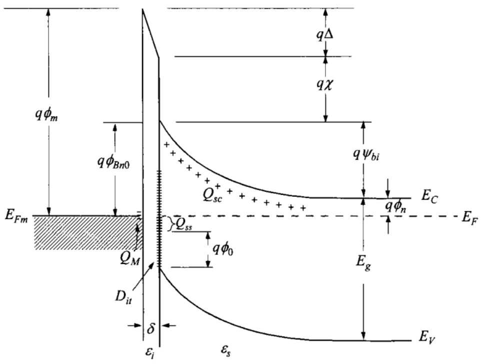

Figure 1 - band diagram of a Schottky diode according to the Bardeen model [3]

Assuming the device is pyroelectric, this interfacial layer serves as a capacitor which is charged by the temperature-induced polarization charge. This would bring the barrier height down by Δ_{ϕ_b} :

$$\Delta_{\phi_b} = \frac{2r_{Si}\cdot p}{\varepsilon_{Si}\cdot \varepsilon_0}\cdot \Delta T$$

Where $r_{Si}, p, \varepsilon_{Si}, \varepsilon_0$ and T are, respectively, the atomic radius, pyroelectric constant, dielectric constant, vacuum permittivity and temperature. For the pyroelectric coefficient found for these types of junctions, the barrier lowering as a function of temperature is at the same order of magnitude of that reported in the C-V measurements.

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Enhancing the Electrocaloric Effect in Sodium Bismuth Titanate-Based Perovskites for Environmentally Friendly Cooling Solutions

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The electrocaloric effect (ECE) refers to the isothermal entropy change or adiabatic temperature change observed in dielectrics when an electric field is applied or removed. The ECE holds potential for developing solid-state cooling technologies suitable for microelectronics, semiconductors, and industrial refrigeration. While lead-based ferroelectric materials have demonstrated high electrocaloric temperature changes, environmental and health concerns necessitate the exploration of lead-free alternatives. This study seeks to optimize the ECE in sodium bismuth titanate, $(Na_{0.5}\,Bi_{0.5})TiO_3$, based perovskites. These materials exhibit significant EC responses within a narrow temperature range associated with the depolarization. This research aims to adjust this critical temperature closer to room temperature using chemical additives and defect chemistry. Additionally, it aims to expand the temperature range of the large ECE by inducing relaxor behavior. The ceramic samples were synthesized using the solid-state reaction sintering method. The depolarization temperature was determined through pyrocurrent measurement, as well as from temperature dependences of dielectric loss of pre-poled samples. The depolarization mechanism was further investigated using X-ray diffraction and piezoresponse force microscopy. The ECE was directly measured using a quasi-adiabatic electrocalorimeter device. These data were compared with the indirect ECE estimation by the Maxwell relation.

Multicaloric composites prepared via the powder aerosol deposition method

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In recent years, alternatives to vapor compression cooling technologies have received increased attention. Among the most promising options are the ones based on the caloric effects which describe latent heat induced temperature changes of a material due to an external stimulus, such as an electric or magnetic field. In pursuit of an enhanced caloric output, research has been made on combining different caloric effects, namely the multicaloric effect. However, the combination of electrocaloric (EC) and magnetocaloric (MC) in composite materials remains mostly unexplored. In light of this, using the powder aerosol deposition method, also known as aerosol deposition (AD), we prepared multicaloric composites that combine both EC and MC phases. A suitable EC candidate is $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ (PMN–10PT), as it shows excellent electrocaloric change, ΔT_{EC}, of 1.5 K at 600 kV cm^{-1} and room temperature (RT) in thick film form [1]. While the MC material, is a La–based MC alloy which shows a temperature change of ~2.5 K at 1.5 T and at RT [2].

In this work, we prepared AD ~5 µm-thick films with 2 wt% to 12 wt% MC concentrations on a flexible gold-sputtered polymer substrate (Figure 1a). The films were then annealed at 400 °C in argon atmosphere. Due to the Maxwell-Wagner effect , the electrocaloric response (Figure 1b) enhances with increasing amounts of the MC phase, reaching up to ΔT_{EC} ~0.44 K at 250 kV cm^{-1} in the 7 wt% composite. In addition, both EC (measured via thermistor-in-calorimeter) and MC (via infrared camera) responses were directly characterized in composites with MC phase as low as 2 wt% (Figure 1c), being the first multicaloric composite thick-film observed at RT. The characterization of the caloric properties of the composites and the MC phase influence on the functional properties of prepared composite films will be discussed in the contribution.

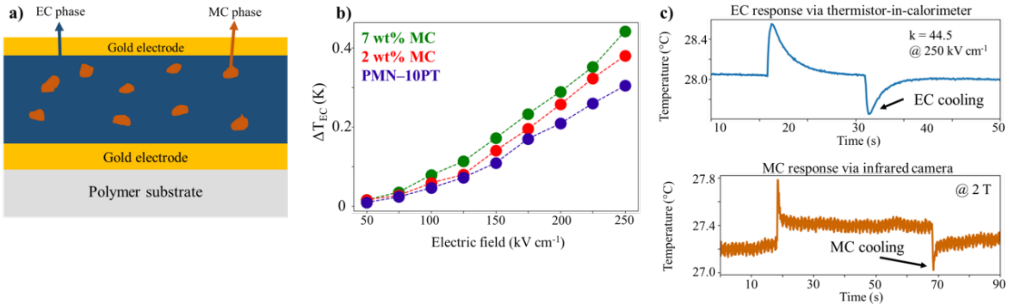

Figure 1. a) Schematic representation of a composite film. b) The electrocaloric output of composites with different amounts of MC phase measured at RT. c) EC response measured using thermistor-in-calorimeter at 250 kV cm^{-1} and MC (not-corrected data) measured using infrared camera at 2T. The EC response was corrected considering the thermal influences of the setup, the correction factor is k = 44.5.

References:

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Tunable thermal conductivity in $(Ba_{0.85}Ca_{0.15}Ti_{1-x}Zr_x)O_3$ ceramics under electrical field

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Thermal conductivity switches are essential for the development of high efficiency thermoelectric devices, thermal refrigeration systems and new computing paradigms, if they exhibit high switching ratio in the ON/OFF thermal conductivity, fast switching on a wide range of operating temperature. However, tuning the thermal conductivity over wide range of temperatures and phonon transport still remains a challenge to realize 'phononic devices'. Phonons (quantized lattice vibrations), being the primary heat carriers in insulators, cannot be directly manipulated by an external electric field due to their lack of mass and charge. Recently, a strategy based on ferroelectric and ferroelastic oxides materials has been suggested to obtain a dynamic heat flow control, considered as a new way for tuning thermal conductivity in a large temperature range. The ferroelectric domain walls (DWs), a special nanoscale interface that separates uniformly polarized domains, can be generated or annihilated by an external electric field and thus successfully tune the phonon transport. In this work, the structural, morphological, dielectric and ferroelectric properties of $(Ba_{0.85}Ca_{0.15}Ti_{1-x}Zr_x)O_3$ ceramics with x= 0.05, 0.1 were studied to analyze the thermal conductivity (κ) variations under electric field. The in-situ Laser Flash Analysis has been used to measure the thermal conductivity.

Hafnium Oxide Ferroelectric Films : from fundamental understanding to optimized low power device integration

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Neuromorphic systems are artificial neural systems inspired by the biological human brain, a marvellous data-processing and learning system. The human brain connections can be mimicked by artificial synapses between memory devices, forming neural networks for deep learning. Learning demands plasticity, which requires the possibility to analyse a large number of values stored in memory and allow changes in synaptic strength, while inference demands long-term stability. Currently, no memory technology offers both characteristics simultaneously. In the pursuit of a memory solution for simultaneous on-chip learning and inference, a hybrid FeRAM/OxRAM synapse circuit is proposed. Hafnium oxide-based ferroelectric memories (FeRAM) are used for learning due to their high endurance, ultra-fast, low-power (10-50 fJ/bit), and non-volatile character. However, they have a destructive read operation, which makes them unsuitable for inference. This is why Hafnium oxide-based non-volatile resistive memories (OxRAM) are used for inference. OxRAMs have long-term stability and non-destructive reading; they suffer from poor write endurance, which is why they are not used for learning [1]. If we combine advantages of these two devices, we can manage to achieve on-chip learning and inference. Therefore, we plan to develop and implement these two different resistive memory technologies (OxRAM/FeRAM) on a single CMOS substrate. For the success of the approach, it is important to improve the endurance of the recently developed HfO_2-based FeRAMs as much as possible. To do this, a better understanding of the fundamental properties of the ferroelectric material is necessary. Advanced in situ characterization techniques based on x-ray photoemission spectroscopy (XPS) will be useful to probe the concentration of oxygen vacancies in the HfO_2 ferroelectric film during electrical cycling.

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Giant Piezocatalytic Effect Triggered by Antiferroelectric-to-Ferroelectric Transition

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Piezocatalysis which is frontier technology for converting mechanical energy into chemical energy and harnessing physical force to drive redox reaction has been recently emerged to be an efficient means, and promising alternative to sunlight-driven photocatalysis.[1] To achieve a good piezoelectric catalyst, by selecting the model multiferroic $BiFeO_3$, our group has recently demonstrated that beyond the good piezoelectric properties (that should be conserved when reducing the particle size), low dielectric response (to favor the piezoelectric figure of merit), high polarization (to favor electron-hole separation) as well as nanosize (limiting the recombination of the electron and hole charge carriers which can reach the surface to trigger the redox reactions) are required.[2] Here, we consider antiferroelectric-to-ferroelectric transitions to produce enormous charges, strongly favoring the piezocatalysis process. Such strategy is inspired by the mechanism involved in explosive-driven short pulsed power sources used in high-voltage power supply technology.[3] The system we choose to fulfill these requirements is the solid solution of Sm-doped $BiFeO_3$ (Sm-BFO) because as already mentioned BFO displays a very high polarization (in addition of its good energy harvesting figure-of-merit) and shows antiferroelectric behavior

when about 16% of Sm is substituted to the Bi-site. Such original and new idea which provide exciting perspectives for the rational design of efficient piezocatalytic systems for wastewater treatment and H_2 production, will be presented in line with the physical properties of the nanoparticles at play in the mechanism [4].

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Investigation of the domain formation of layered ferroelectric Bi_2WO_6 thin films

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A polarization rotation inevitably deviates from the stable orientation in axial ferroelectrics. However, local energy losses compromise the global symmetry, resulting in a distorted shape of the topological vortex or inhibiting the vortex. Easy planar isotropy helps to promote rotating structures and to facilitate access to polar textures such as skyrmion, vortex, flux-closure. Recently, these structures emerged in the oxide thin films and actively studied [1]. Topological defects in ferroelectric materials exhibit stability against external perturbations while maintaining a smaller size compared to their magnetic counterparts. These interesting properties make them potential candidates for nonvolatile and high-density memories in the next generation [2,3]. Nowadays, research related to the above is being conducted in layered ferroelectrics, and one of the representative materials is the bismuth tungsten oxide (Bi_2WO_6) thin film. It spontaneously forms intriguing polar structures on flat surfaces [4]. Since the studies of phase evolution and competing domain textures in Bi_2WO_6 are still lacking, we investigate how the ferroelectric domain evolves with the film thickness in c-axis oriented epitaxial Bi_2WO_6 thin films grown on $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}$ substrates. By visualizing the spatial distribution of electric polarizations through angle-resolved piezoresponse force microscopy [5-7], we provide direct evidence for the spontaneous emergence of nontrivial topological polar structures. Moreover, we are currently exploring the relationship between local strain and domain formation thereby devising ways to control domain texture more effectively. These results provide useful insights into the domain behavior of layered ferroelectric thin films.

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TiN/$BiFeO_3$ Based Memristive Device with Valence Change Mechanism

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In this study, we have successfully fabricated Al/BiFeO3/TiN/FTO heterostructures employing a cost-effective chemical solution deposition method. X-ray diffraction and morphological studies validate the pure-phase growth of $BiFeO_3$ thin films with a uniform granular distribution on pre-sputtered TiN, FTO substrate. X-ray Photoelectron Spectroscopy (XPS) analysis indicates that Bi exhibits a 3+ oxidation state, while Fe is present in multiple oxidation states, specifically Fe^{3+} and Fe^{2+}. Additionally, the analysis reveals the presence of oxygen vacancies. These vacancies contribute to the leakage currents, which accelerate the formation of conductive filaments in bismuth ferrite (BFO) thin films. These heterostructures exhibit two distinct switching modes: filamentary and area-dependent switching. By systematically investigating physical cells of varying sizes, we compare the filamentary and area switching modes. Our findings reveal that these devices manifest area-dependent valence change mechanism switching, presenting a promising prospect for energy-efficient neuromorphic computing applications due to their area-scalable resistance with low variability. The devices demonstrate a memory window of 10 in both area-switching and filamentary-switching modes, achieved at a lower switching voltage of 0.5 V. Furthermore, the resistive cells' switching behavior and conduction mechanism are systematically investigated. Remarkably, the devices exhibit stable data retention up to 3×106 cycles at room temperature, displaying negligible resistance variation.

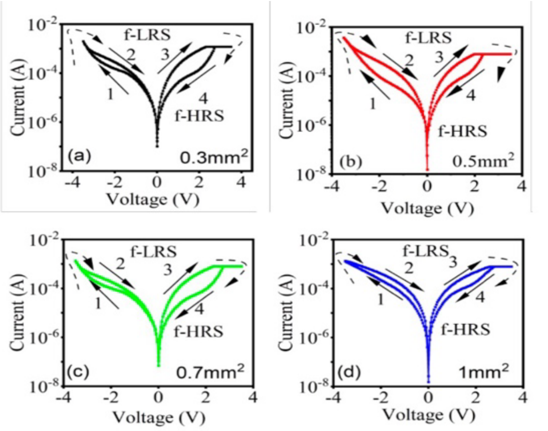

Fig. 1.(a)-(d): Filamentary switching behavior of Al/BFO/TiN/FTO devices with different device sizes. (a) 0.3 mm², (b) 0.5 mm², (c) 0.7 mm², and (d) 1 mm².

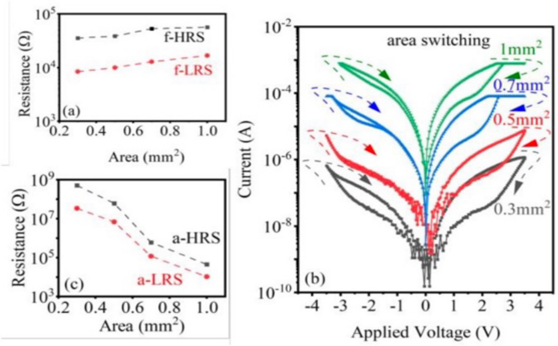

Fig. 2.: Switching behavior of Al/BFO/TiN/FTO devices. (a) area switching at varied device sizes (b) Variation of resistance with area for filamentary switching mode. (c) Variation of resistance with area for area switching mode.

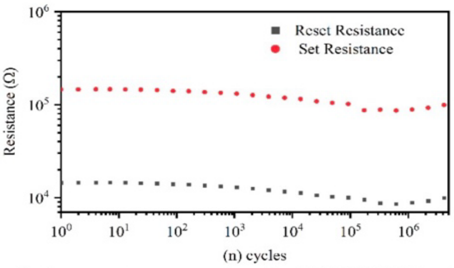

Fig. 3.: Endurance measurements of Al/BFO/TiN/FTO device executed at continuous voltage pulses at a frequency of 50 kHz.

Enhanced Piezoelectric Properties of $(Bi_{0.5}Na_{0.5})TiO_3$–$BaTiO_3$ Ceramics by Alternating Current Poling above Curie Temperature.

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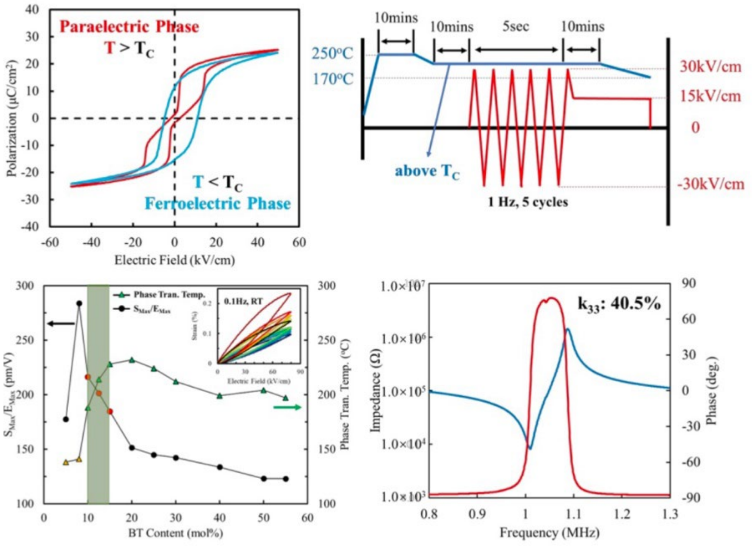
Nowadays, lead-free piezoelectric materials have attracted great research interest due to their environmentally friendliness. $(1\text{-}x)(Bi_{1/2}Na_{1/2})TiO_{3-x}$ $BaTiO_3$ ($(1\text{-}x)$BNT–$_x$BT) system, a potential lead-free piezoelectric material, has been studied intensively. And many researchers have focused on $x = \sim 0.06$, where in the morphotropic phase boundary (MPB) region. Although BNT–BT ceramics exhibit relatively superior dielectric and piezoelectric properties at MPB region, relatively low depolarization temperature (~140oC) limits their applications. Therefore, it is very promising if BNT–BT ceramics can be obtained both relatively high piezoelectric properties (d_{33} > 200 pC/N) and relatively high Curie temperature TC (~200oC).

In this experiment, various chemical composition of BNT–BT ceramics were synthesized by solid-state reaction. Their piezoelectric properties and TC were determined by Strain-Electric field (S-E) loop at room temperature and Polarization-Electric field (P-E) loop at high temperature, respectively. In addition, alternating current (AC) poling technique was applied above their TC to those BNT–BT ceramics with both relatively high piezoelectric property (d_{33} > 200 pm/V) and relatively high T_C (~200oC), aiming to obtain enhanced piezoelectric property compared with traditional direct current poling treatment.

By conducting AC poling treatment above their T_C, d_{33} values of BNT–BT ceramics were around 100 pC/N. Although this piezoelectric property has not been enhanced to 200pC/N yet, we still believe that using this poling strategy for textured BNT–BT ceramics in the future will get better results.



FINAL REMARKS

The organizers of Ferroschool 2024 would like to thank all speakers to accept their role of teaching younger colleagues about the complexity and importance of ferroelectrics. All Ferroschool participants are acknowledged for their invaluable contributions, which have made this event a resounding success. We hope that the participants gained valuable insights, made meaningful connections, and enjoyed the sessions as much as we enjoyed hosting the participants and the speakers.

Special thanks goes to the IEEE Ultrasonics, Ferroelectrics, and Frequency Control Society for their generous financial support, as well as JSI leadership for making it possible to organize the event at JSI, both of which played a vital role in making the Ferroschool 2024 memorable.

Ferroschool organizing committee

PROGRAMME

	DAY 1, 18.11.2024	DAY 2, 19.11.2024	DAY 3, 20.11.2024	DAY 4, 21.11.2024
8.00	*Registration*			
8.45	*Opening remarks*			
9.00	**Novak** Physics of ferroelectrics	**Elissalde** Conventional and unconventional sintering techniques of ferroelectric materials	**Buixaderas** Raman scattering and broadband dielectric spectroscopy: A useful combo for ferroelectrics	**Džeroski** Machine learning for material science
10.30	*Coffee break*			
11.00	**Iñiguez** Computational approaches dedicated to ferroelectric materials: first principles	**Glinšek** Solution-based processing of thin-film oxides for piezoelectric applications	**Garcia** Scanning probe microscopy for functional oxide thin films	**Stoica** Designing underwater devices with ferroelectric materials
12.30	*Lunch*			
14.00	**Iñiguez** Computational approaches dedicated to ferroelectric materials: second principles	**Rojac** Electrical and electromechanical responses in ferroelectrics	**Benčan** Local structure of ferroelectrics by electron microscopy techniques	**Webber** Mechanics of ferroelectrics
15.30	*Coffee break*			
16.00	**Gorfman** Introduction to crystallography of perovskites	**Glaum** Mechanisms of aging and fatigue in ferroelectrics	LAB VISITS	**Dkhil** Towards neuromorphic computing using ferroelectric and related materials
17.30	POSTER SESSION			
18.30	Welcome reception			
19.00			School dinner	Goodbye party