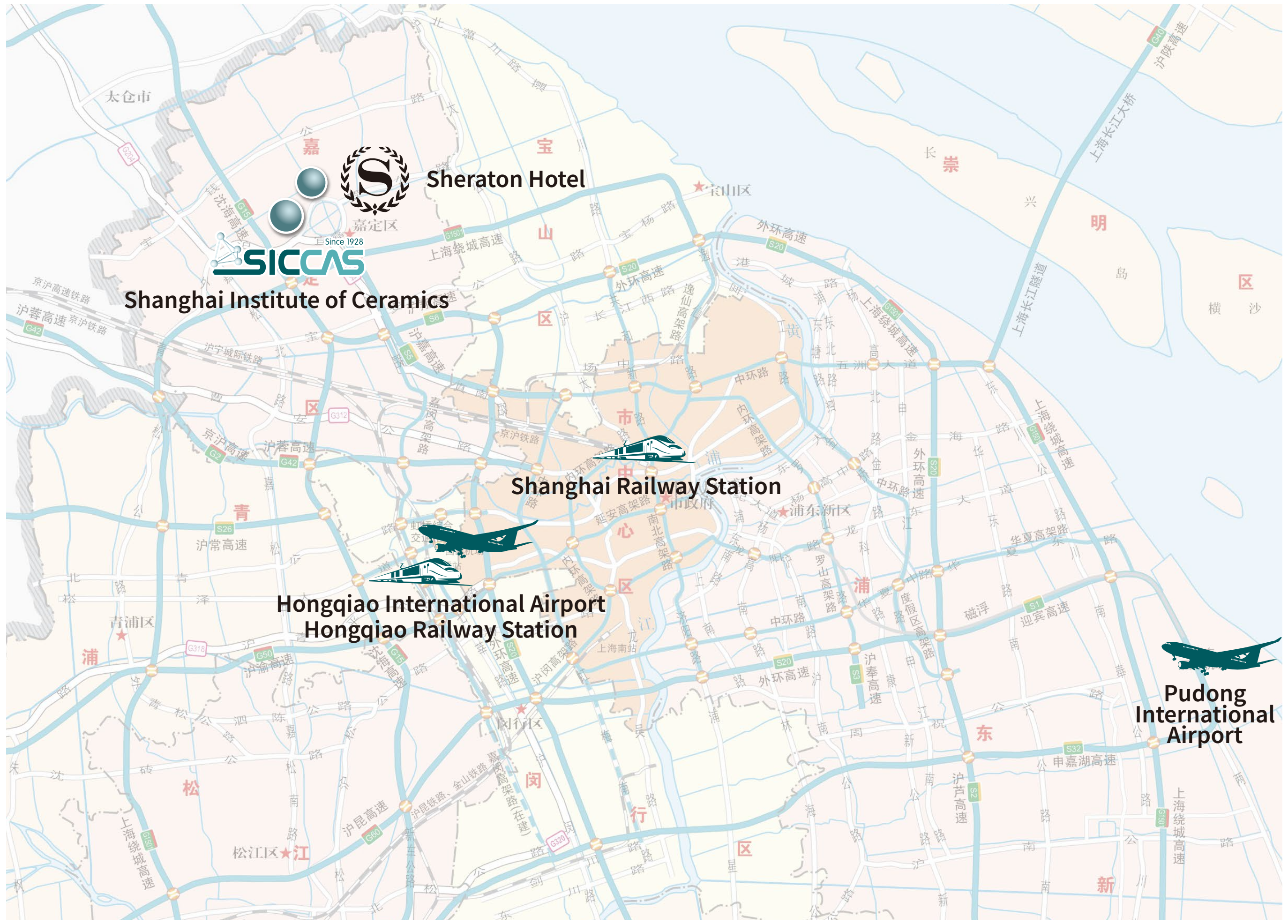

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第五届中俄介电铁电材料国际研讨会

The 5th China-Russia Workshop on Dielectric and Ferroelectric Materials

2024年5月11日~14日 中国 · 上海
May. 11-14, 2024, Shanghai, China

CONTENTS

The 5th China-Russia Workshop on Dielectric and Ferroelectric Materials

May. 11-14, 2024, Shanghai， China

The China-Russia Workshop on Dielectric and Ferroelectric Materials aims at providing a platform to enhance the bilateral communication, exchange and collaboration among the researchers working on fundamentals and applications of dielectric and ferroelectric materials. The first workshop was held in 2013 in Xi'an, China, the second one in in 2015 in Voronezh, Russia, the third one in 2017 in Wuhan, China, the fourth one in Yekaterinburg, Russia in 2019, and the fifth workshop will be held in Shanghai Institute of Ceramics, Chinese Academy of Sciences, in Shanghai, China, in May, 11-14, 2024.

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Topics:
1. High-performance piezo-/ferroelectric materials and devices
2. Structure and dynamics of piezo-/ferroelectric materials
3. Thin films, interfaces and nanoscale materials

4. Multiferroic materials and devices

4. Advanced processing techniques and characterization

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Please find the webpage of workshop:

https://www.diaochapai.com/survey3853739

or use the following

Workshop Location:

Conference hall of G3 building，Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Tentative Schedule:

	May 11	May 12	Oct 13	Oct 14
Morning	Registration and Reception	Invited Talks and Discussion	Invited Talks and Discussion	Industrial Tour
Afternoon		Invited Talks and Discussion	Panel Discussion	

Invited speakers:

To be announced.

Important Dates: (Scheduled)

1st announcement:	Jan. 15th, 2024
2nd announcement:	Feb. 20th, 2024
Abstract submission deadline:	March 31st, 2024
Program online:	April 25th, 2024
Final announcement:	April 30th, 2024
Manuscript submission:	on site

Full Programme-TBC

2024.5.11			
09：00-17：00	Registration		
18：00-20：00	Welcome reception		
2024.5.12			
09：00-09：10	Session 1： keynote speech （Chair:王根水）	局领导、所领导	Opening speech
09：10-09：40		Alexander S. Sigov 院士	Ferroelectric thin films: what is important in electrical measurements analysis
09：40-10：10		待定	
10：10-10：40	Photo & Coffee break		
10：40-11：00	Session 2： domain engineering （Chair:TBD）	Vladimir Shur	Recent achievements in nanodomain engineering in ferroelectrics
11：00-11：20		Zuo-Guang Ye	Polarization Rotation, Triclinic Phase and Domain Engineering in Relaxor-Based Piezocrystals
11：20-11：40			
11：40-12：00		Andrei Ushakov	Recent achievments of the domain engineering in ferroelectric materials in Russian-Chinese projects
12：00-13：40	Lunch break		
13：40-14：00	Session 3： single crystal, thin film, nanostructures （Chair:TBD）	Elena Charnaya	NMR studies of nanostructured ferroelectrics
14：00-14：20		李振荣	Giant piezoelectric properties of the PZT-5H single crystals grown by solid state crystal growth
14：20-14：40		M.V.Talanov(临时增加)	$Bi_2Ti_2O_7$ single crystal as a material candidate for geometrically frustrated relaxor
14：40-15：00		李降龙	Giant ferroelectric polarization in fluorite-structure zirconia thin films
15：00-15：20		孟祥达-哈工大	Piezoelectric Properties of Potassium Niobite based Single Crystal
15：20-15：40	Coffee break		
15：40-16：00	Session 4： Ferroelectrics in THz range; Defects （Chair:TBD）	Elena Mishina	Ferroelectrics in strong THz field
16：00-16：20		Natalia Sherstiuk	Effect of a DC electric polarization induced by intense THz radiation in ferroelectric single crystals
16：20-16：40		TBD-SICCAS	
16：40-17：00		Kirill Brekhov	Optical parameters of ferroelectrics in THz range
17：00-17：20		王学云	Mechanical manipulation for ordered ferroelectric topological defects
17：20-17：40		Denis Alikin	Exploring Charged Defects in Ferroelectrics by the Switching Spectroscopy Piezoresponse Force Microscopy
17：40-18：00		Aleksandr Kamzin	Magnetic Phase Transition in Solid Solutions $xBiFeO_3 – (1- x)SrTiO_3$ ($x = 0÷1.0; Δx = 0.1$)
18：30-20：30	Banquet		

2024.5.13			
09：00-09：20	Session 5： Phase transition （Chair:TBD）	Alexander Vtyurin	Raman Spectra of Huntite-Like Multiferroics – Interpretation Using Angular Dependences and DFT Simulations
09：20-09：40		靳立	Ferroelectric-to-relaxor transition and ultrahigh electrostrictive effect in Sm^{3+}-doped $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ferroelectrics ceramics
09：40-10：00		Sergey Vakhrushev	Phase transitions in PMN-PSN solid solutions
10：00-10：20		Alexander Krylov	Raman spectroscopy of phase transition in multiferroics with huntite structure.
10：20-10：40	Coffee break		
10：40-11：00	Session 6： dielectrics，piezoelectrics, pyroelectrics （Chair:TBD）	Ekaterina Koroleva	Electric field-induced transformation of dielectric spectra of PMN
11：00-11：20		张晨波	Enhanced electricity generation and long cycle pyroelectric energy conversion by reversible phase transformation in lead-free ferroelectric materials
11：20-11：40		Liudmila Kamzina	Influence of the Degree of Phase Transition Diffuseness on the Depolarization Temperature in Relaxors of Different Types
11：40-12：00		何子晨	The Effects of Ca substitution on structure and dielectric properties of $BaTiO_3$ ceramics
12：00-13：40	Lunch break		
13：40-14：00	Session 7: multiferroic materials and devices （Chair:TBD）	李法新	Linear and nonlinear electro-elastic/electro-damping effect in ferroelectric ceramics
14：00-14：20		A.A.Vasiliev(临时增加)	LTCC and screen-printed glass-ceramic MEMS
14：20-14：40		高翔宇	High performance actuators based on piezoelectric crystals and metamaterials
14：40-15：00		王春明	Textured calcium bismuth niobate exhibiting superior piezoelectric properties
15：00-15：20		刘博	The Intrinsic Variation of the Two-Dimensional Materials based Electronic Devices and their Novel Applications
15：20-15：40	Coffee break		
15：40-16：00	Session 8： modelling，energy storage，new frontiors （Chair:TBD）	田博博	In-memory sensing and computing based on ferroelectrics
16：00-16：20		牛刚	Hafnia based memristors artificial synapses for neuromorphic computation
16：20-16：40		孙梓雄	Cellulose-based energy storage dielectrics—the next-generation green capacitors
16：40-17：00		杨敏铮	Polymer sub-nanocomposite dielectrics for high temperature capacitive energy storage
17：00-17：20		赵诗博	High energy storage performance of KNN-based transparent ceramics
17：20-17：40		叶鹭	Preparation and research of polymer nanocomposites with high energy storage
17：40-18：00		秦锦成	Structure and microwave dielectric properties of gillespite-type $ACuSi_4O_{10}$ (A = Ca, Sr, Ba) ceramics and quantitative prediction of the Q × f value via machine learning
18：00-18：10	Closing （Chair:李国荣）	TBD	
		TBD	

In-plane anisotropic mechanical and piezoelectric properties of $NbOI_2$

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Two-dimensional niobium oxide diiodide ($NbOI_2$) has recently attracted extensive attention due to its highly anisotropic band structures and rich physical characteristics in electronics. Nevertheless, the mechanical properties of $NbOI_2$ have not been investigated systematically, which are critical parameters for applications. Meanwhile, the exceptionally high lateral piezoelectric coefficient (~21.8 pm/V), makes it a promising candidate for energy conversion applications. Here, we determine the directional dependence of Young's modulus of thin $NbOI_2$ flakes by using an atomic force microscopy-based nanoindentation technique. We then report the experimental observation of anisotropy in-plane piezoelectricity in multilayer $NbOI_2$. The determination of Young's modulus and the discovery of piezoelectricity in $NbOI_2$ opens up new avenues for the development of flexible and wearable electronic devices and provide valuable insights for further exploration in this field.

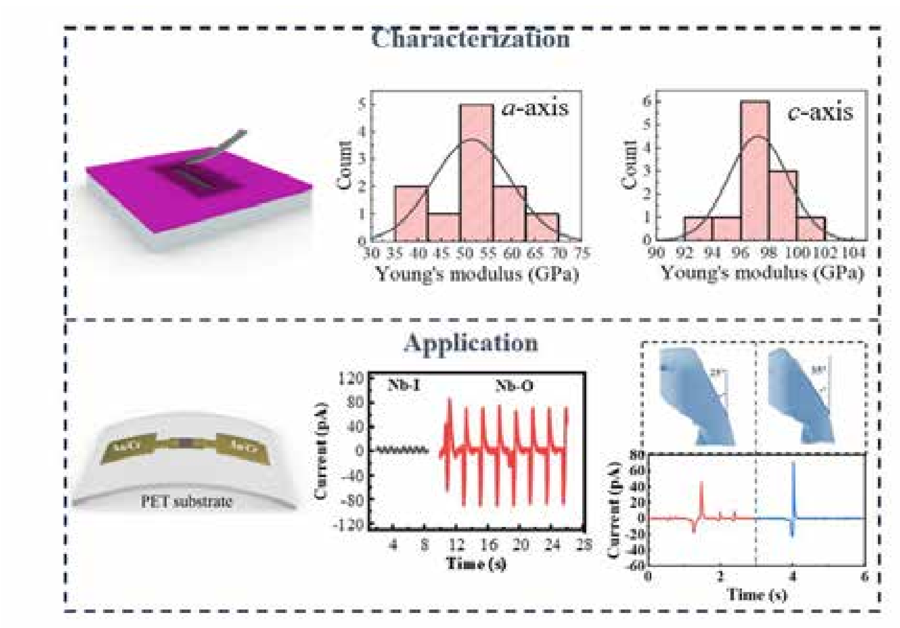

Figure 1. Characterization and application of $NbOI_2$.

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Shear horizontal guided wave transducer based on a novel piezoelectric crystal: $KCsMoP_2O_9$ with strong face shear vibration mode

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The fundamental shear horizontal (SH_0) wave transducer shows unique promise for structural health monitoring in oil pipelines, railway tracks, solar power plants and beyond due to its nondispersive characteristics. Under this background, there is a pressing need for the exploration of high-performance piezoelectric materials to advance SH_0 wave transducers. Herein, a new piezoelectric crystal $KCsMoP_2O_9$ (KCMP) with dominant face shear mode d_{14} is proposed to excite and receive the SH_0 wave based on the finite element simulation. The results demonstrated the exceptional ability of KCMP-based guided wave transducer to generate and detect obvious SH_0 waves in two orthogonal principal directions over a wide frequency range (140-380 kHz). Additionally, the KCMP-based SH_0 wave transducer showcases its excellent defect localization ability over a wide frequency range (160-360 kHz), demonstrating its great potential for application in non-destructive testing and structural health monitoring.

High performance actuators based on piezoelectric crystals and metamaterials

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High-performance piezoelectric actuators and ultrasonic motors are featured with quick response and accurate output micro/nano-scale displacements. They have become key electronic components in many equipments and technologies, which are widely used in optical collimation equipment, adaptive optical telescope systems, micro-nano processing and manufacturing equipment, etc. Traditional PZT ceramic actuators are restricted by the intrinsic piezoelectric properties of ceramics, and their performance has been close to the bottleneck for a long time. In recent years, researchers have developed new piezoelectric materials such as relaxor ferroelectric single crystals with excellent piezoelectric performance, piezoelectric metamaterials, etc. Their piezoelectric coefficients are 5-10 times higher than that of PZT ceramics, so the development of actuators and piezoelectric motors based on high-performance piezoelectric materials is an important method in the enhancement of piezoelectric devices, and great progress has been made in miniaturization and high precision. This report mainly introduces our research work of piezoelectric actuators and ultrasonic motors developed with new piezoelectric materials, including shear-bending mode micro ultrasonic motors, piezoelectric motion platforms, bending-bending composite mode piezoelectric motors, etc., as well as new piezoelectric actuation systems for small bio-inspired robots and adaptive optical systems.

Design, Screening, and Performance Evaluation of β-$A^{I}B^{III}O_2$-Type Ferroelectric Materials: An In-depth Investigation

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In ferroelectric materials, the alignment of dipole moments due to non-overlapping positive and negative charge centers within the lattice results in internal polarization even in the absence of an external electric field, facilitating the separation of positive and negative charges.[1] β-$CuGaO_2$ is a ferroelectric semiconductor with a narrow bandgap and strong polarization.[2] Based on this, we have expanded the Cu position to include 11 monovalent cations (Li^+, Na^+, K^+, Rb^+, Cs^+, Cu^+, Ag^+, Au^+, Pd^+, Hg^+ and Tl^+) and replaced Ga^{3+} with various trivalent cations, constructing a series of β-$A^{I}B^{III}O_2$-type ferroelectric materials. Different B-site ions determine the distinct characteristics of the materials, and by studying their structural and electronic properties, as well as their relevant performance, materials with unique potential applications can be screened. When B^{III} = P^{3+}, As^{3+}, Sb^{3+}, Bi^{3+}, the presence of ns^2 lone pair electrons creates a unique local polar environment within the system. Combined with the bulk polarization induced by the crystal structure along the [001] direction, these two polarizations synergistically promote the separation and transport of photoexcited charge carriers, which is of significant importance in addressing the recombination issue of photogenerated electron-hole pairs in the field of photocatalysis. Based on this, a series of efficient ferroelectric photocatalysts can be developed and designed. When B^{III} =trivalent transition metal cations, the unfilled d orbitals confer different magnetic structures to the materials. The coupling of magnetism and ferroelectricity can lead to the development of novel multiferroic materials. These materials exhibit multi-field responses, and the involvement of transition metals facilitates the reduction of the material's bandgap, potentially giving rise to ferroelectric metal materials, which is advantageous for the development of efficient electrocatalysts. Matching different application prospects according to the characteristics of different systems is of great significance for the exploration of new ferroelectric materials.

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The Effects of Ca substitution on structure and dielectric properties of $BaTiO_3$ ceramics

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$Ba_{1-x}Ca_xTiO_3$ (BC100xT) and $BaTi_{1-x}Ca_xO_{3-x}$ (BTC100x) ceramics were synthesized via the solid-state reaction method. The effect of Ca substitution occupation on the structure and dielectric properties of $BaTiO_3$ ceramics was systematically investigated. The c/a ratio increased with the increase of Ca substitution in BC100xT ceramics while in reverse BTC100x. It was found that pure $BaTiO_3$ (BT) and BC100xT ceramics had similar structural and dielectric properties, whereas BTC100x ceramics showed much difference. BTC100x ceramics were in the tetragonal phase when x ≤ 0.02, but transformed to cubic at x>0.02. With increasing x, the Curie temperature decreased from 128 ºC (BT) to 54 ºC (BTC4). XRD patterns, Raman spectrum, impedance spectra, and dielectric-temperature spectra provided strong evidence of Ca^{2+} substitution at Ti site in BTC100x.

Ferroelectric-to-relaxor transition and ultrahigh electrostrictive effect in Sm^{3+}-doped $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ferroelectrics ceramics

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Rare-earth Sm^{3+}-doped $Pb(Mg_{1/3}Nb_{2/3})O_3$-0.25$PbTiO_3$ (PMN-0.25PT) ferroelectric ceramics with doping amount between 0–3% were developed via a conventional solid-state method. The doping effect of Sm^{3+} ions on the PMN-0.25PT matrix was systematically investigated based on the phase structure, temperature-dependent dielectric, ferroelectric and electrotechnical properties. Due to the disruption of long-range ferroelectric order, the addition of Sm^{3+} ions effectively lowers the T_m (temperature corresponding to maximum permittivity) of the samples, leading to enhanced relaxor ferroelectric (RFE) characteristic and superior electric field-induced strain (electrostrain) properties at room temperature. Intriguingly, a considerable large-signal equivalent piezoelectric coefficient d_{33}* of 2376 pm/V and a very small hysteresis were attained in the PMN-0.25PT component doped with 2.5 mol.% Sm^{3+}. The findings of piezoelectric force microscopy indicate that the addition of Sm^{3+} increases the local structural heterogeneity of the PMN-0.25PT matrix, and that the enhanced electromechanical performance is due to the dynamic behavior of polar nanoregions. Importantly, strong temperature-dependent electrostrain and electrostrictive coefficient Q_{33} are observed in the critical region around T_m in all Sm^{3+}-modified PMN-0.25PT ceramic samples studied. This work elucidates the phase transition behavior of Sm^{3+}-doped PMN-0.25PT and reveals a critical region where electrostrictive properties can be greatly improved due to a strong temperature-dependent characteristic.

Linear and nonlinear electro-elastic/electro-damping effect in ferroelectric ceramics

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The linear piezoelectric and nonlinear hysteresis behavior of ferroelectrics are well known and have been extensively studied. However, less attention has been paid to the variations of their mechanical properties under electric loading. In this work, using tube and cylinder specimens, three independent elastic coefficients and the related internal frictions of PZT-5H ferroelectric ceramics are measured by using a quantitative electromechanical impedance method (Q-EMI) under an electric field E3 along the poling direction. Results show that, under low electric fields, the elastic coefficients s_11^E, s_66^E and all the internal frictions decrease linearly with E3, whereas s_44^E increases linearly with E3. Thus, two five-order tensors are defined, i.e., linear electro-elastic tensor (p_ikl) and linear electro-damping tensor (q_ikl), among which p_311, p_366, p_344 and q_311, q_366, q_344 are obtained in this work. When the applied electric field exceeds the coercive field (~500V/mm), the nonlinear electro-elastic/electro-damping effect dominates, resulting in reversed butterfly curves for s_11^E and s_66^E, and butterfly curves for s_44^E. As to the internal frictions under large bipolar fields, they seem to be a superposition of the reversed butterfly curves and a peak or valley at the coercive field. The linear electro-elastic effect in ferroelectric ceramics is caused by the reversible domain wall motions while the nonlinear electro-elastic effect is caused by the irreversible non-180° domain switching. The linear and nonlinear electro-elastic and electro-damping results obtained here renovated the electromechanical coupling behavior of ferroelectric materials.

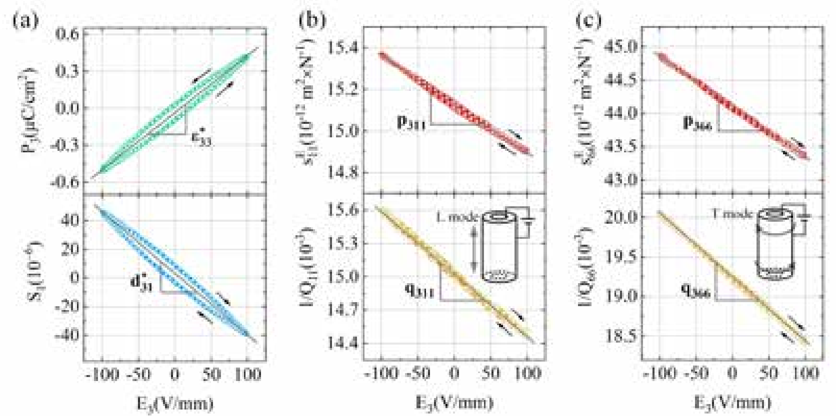

Fig.1 Linear properties of radially poled PZT-5H ceramic tubes under a low radial electric field

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[1] M. Xie, Q.Z. Wang, F.X. Li*. Journal of Applied Physics 132, 195105 (2022)

Giant Piezoelectric Properties in PZT-5H Single Crystal Grown by Solid State Crystal Growth

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The growth of PZT single crystals is an area of special interest because single crystals with specific orientations possess better piezoelectric properties than ceramics. However, the growth of PZT single crystals is limited by their high melting point and incongruent melting behavior. In this work, the PZT-5H single crystals are grown by the solid-state crystal growth (SSCG) method with excess PbO addition. An ultra-high piezoelectric performance (d_{33}~1800 pC/N, d_{33}^*~2400 pm/V at 3 kV/cm and k_{33}~87%) was achieved in [110]-oriented PZT-5H single crystal with excess 4 wt% PbO addition in the growing process. The variation of piezoelectric coefficients is explained by the ferroelectric phase coexistence adjusted by the excess PbO induced chemical composition fluctuation in the PZT-5H single crystals, which results in flattening of the free energy profile and improving piezoelectric performance. With the increase of the PbO liquid phase, the composition of PZT-5H single crystal shifts to promote the monoclinic and rhombohedral phases. This research paves the way for designing high-performance piezoelectric material by manipulating ferroelectric phase coexistence with SSCG.

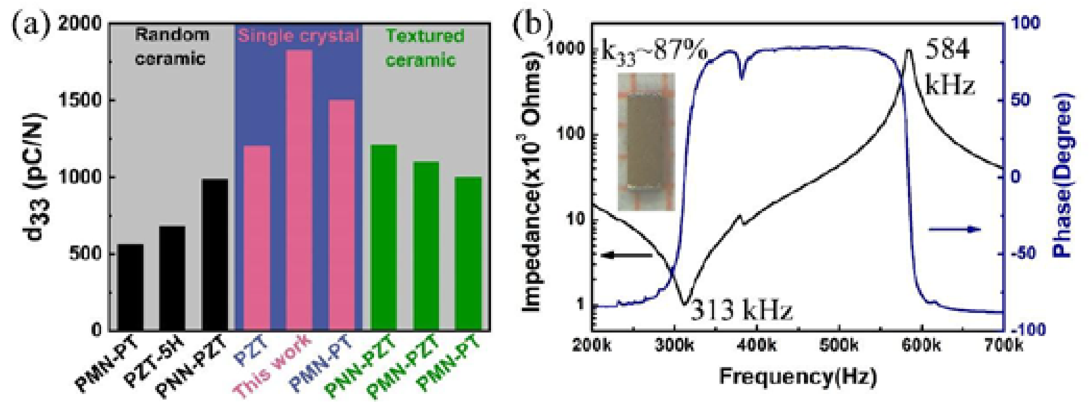

Figure 1. (a) The d_{33} comparation of PZT-5H single crystal, typical piezoelectric and texture ceramics, (b) k_{33} PZT-5H single crystal

Giant ferroelectric polarization in fluorite-structure zirconia thin films

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[†] **These authors contributed equally to this work**

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Abstract:

Owing to their compatibility with the silicon-based technology, ferroelectric fluorite oxides are considered to be one of the most potential candidates for modern large-scale integrated-circuits (ICs). While both hafnium (HfO_2) and zirconia (ZrO_2)-based fluorites materials show decent in ferroelectric properties, ZrO_2 is usually though to be anti- or week ferroelectric. In this study we have successfully obtained the ferroelectric orthorhombic ZrO_2 with a giant remanent polarization amounted to ~53μC/cm² growing on $SrTiO_3$ (110) substrates, which is comparable with the most outstanding HfO_2-based ferroelectric oxides. We believe that this giant remanent polarization stems from the irreversible antiferroelectric-to-ferroelectric phase transition driven by electric field, which converts those as-grown antiferroelectric-ferroelectric blends into purely ferroelectric ZrO_2. Our studies pave the way understanding the ferroelectricity in ZrO_2-based fluorites for ICs.

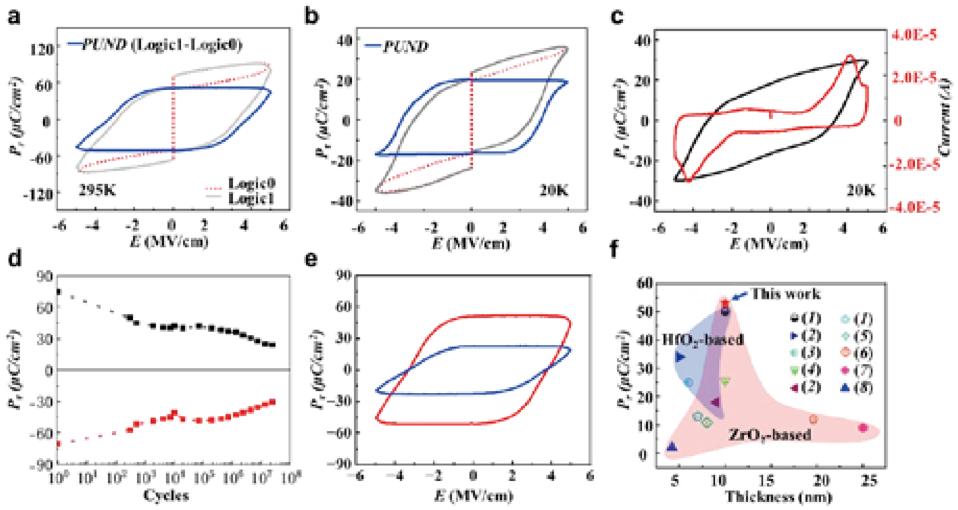

Figure1. (a)-(c) Ferroelectric properties of LSMO/ZrO_2/Pt capacitor. (d) The fatigue of LSMO/ZrO_2/LSMO capacitor under 5*MV*/cm.（e）The *P-E* loops under

PUND recipe before and after the fatigue test.（f）Reported P_r in HfO_2 or ZrO_2-based thin films.

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We apply for reporting our work.

The Intrinsic Variation of the Two-Dimensional Materials based Electronic Devices and their Novel Applications

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The intrinsic variations, such as device-to-device variations, cycle-to-cycle variations, and time-to-time variations (e.g. the noises) are considered detrimental to electronic device performances[1]. The intrinsic variation is in turn a treasure stone for some emerging applications. The author takes two-dimensional materials-based electronic devices as an example, mainly memristors[2], to demonstrate multiple novel applications based on the intrinsic variation of two-dimensional materials-based electronic devices, including true random number generators (TRNG)[3], generative adversarial networks (GAN)[4] and physical unclonable functions (PUFs)[5]. Moreover, the author proposed a serial analysis tool including state-of-the-art AI computing to analyse the physical-based stochastics.

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May 11-14, 2024, Shanghai, China

Large Shear-Mode Electro-optic Coefficient in Single-domain PIN-PMN-PT Single Crystal

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Due to the excellent shear-mode piezoelectric properties, single-domain tetragonal $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O3$-$PbTiO_3$ (PIN-PMN-PT) crystals are believed to possess giant shear-mode electro-optic (EO) coefficients as well. However, the EO properties of single-domain PIN-PMN-PT crystals have not been systematically studied because of the difficulties in the single-domain sample preparation. Here, by our proposed method, optical grade single domain crystal with good transparency and high shear mode EO coefficient (γ_{51}~2800 pm V^{-1}) has been achieved. This work confirms the giant EO performance of domain-engineered PIN-PMN-PT single crystals mainly comes from the contribution of shear-mode EO property of single domain crystal other than the domain wall or domain switching related mechanisms.

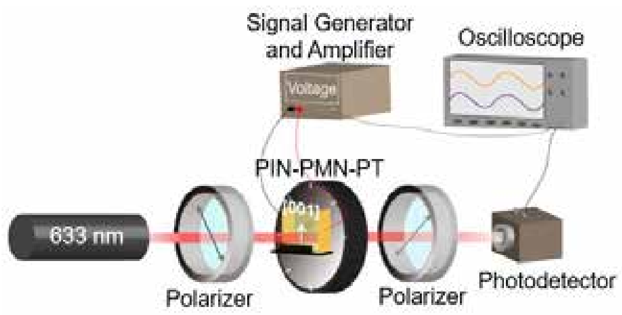

Figure 1 Illustration of the sample orientation with the direction of the poling field and the direction of the applied AC field.

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Piezoelectric Properties of Potassium Niobate based Single Crystal

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Due to the excellent piezoelectric performance and nontoxic character, potassium niobite (KN) based materials have attracted a great amount of attention since the report of Saito et al. in 2004. In order to increase the piezoelectric properties of KN-based ceramics, the grains were oriented in a preferred direction with reactive templated grain growth method[3]. The KNN-based single crystals therefore also exhibit excellent performance along certain crystal directions and absence of grain-boundaries. With the purpose of studying the potential of KN-based materials in piezoelectric field, we grew a few of KN-based single crystals with large size and high quality via top-seed solution growth (TSSG) method and carried out investigations of their performance. The as-grown crystal displayed outstanding properties at room temperature without annealing, including the low loss (0.007), a saturated hysteresis loop, as well as a high piezoelectric coefficient (strain~ 0.9 % @1kV/mm and d33* ~9000 pm/V), which also exhibit an excellent temperature stability. In addition, the domain structure was also studied via polarized light microscope.

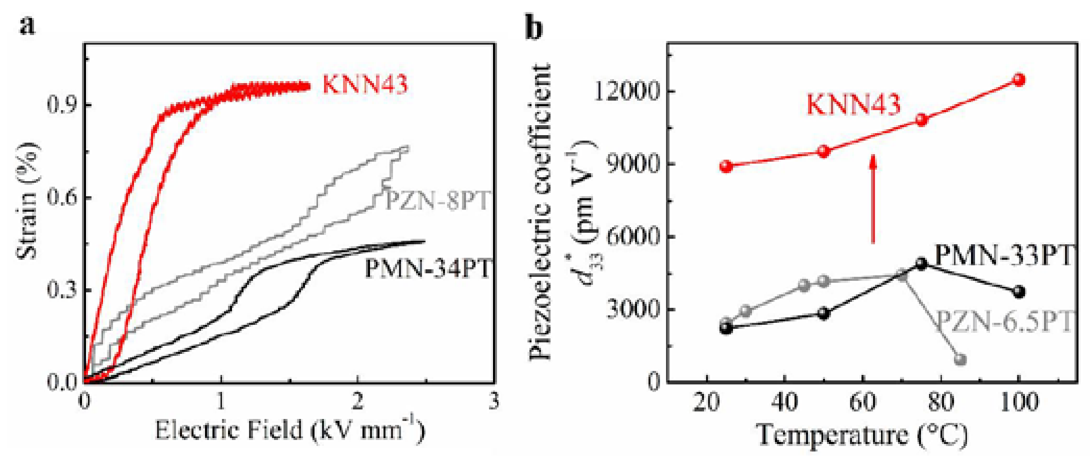

Figure 1. Strian of KNN43 single crystal

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Realization of excellent piezoelectricity and high Curie temperature in BF-BT ceramics via structural regulation and domain engineering

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The pure $BiFeO_3$ (BF) ceramic has good piezoelectric properties (piezoelectric constant d_{33} ~ 70 pC/N) and high Curie temperature (T_C~ 830 ℃), but its leakage current is large and is difficult to polarize due to mixed Fe^{3+}/Fe^{2+} valence states and the volatilization of Bi^{3+}.[1-3] In this work, the effects of $(Bi_{0.5}Li_{0.5}Ti)^{2+}$ (BLT) doping on the phase structure, microstructure, electrical properties, and conductance mechanism of BF-BT ceramics are investigated. The better comprehensive properties are obtained: d_{33} ~ 130 pC/N, ρ ~ 1.49 × 10^6 Ω·cm at 300 ℃, T_C ~ 632 ℃, S ~ 0.168%. We hope that our research can provide good inspiration for the research of high-temperature lead-free piezoelectric.

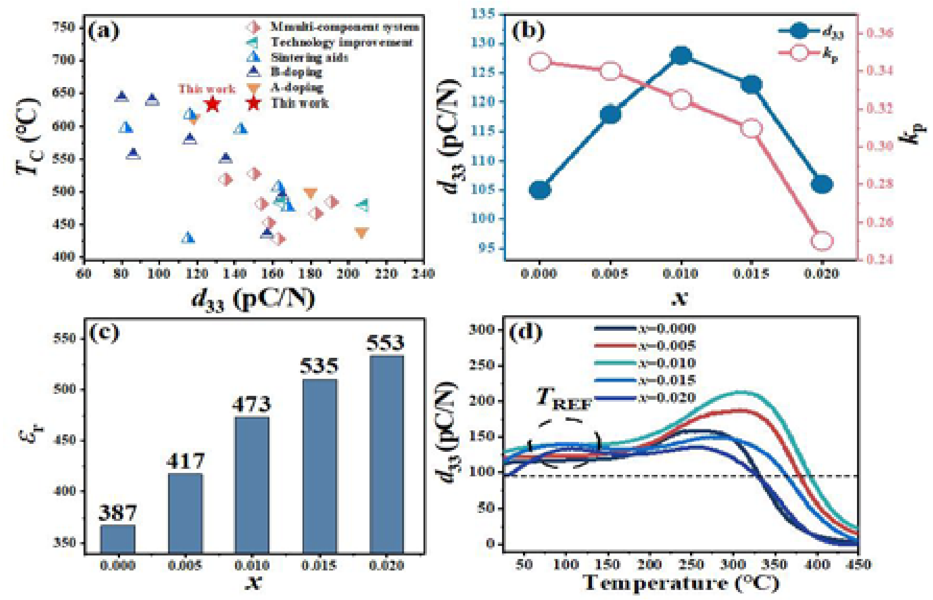

Fig. 1 (a) d_{33} values and T_C values of BF-BT piezoceramics prepared by different methods; (b) d_{33}, k_p values; (c) ε_r values; (d) in-situ d_{33} values

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Hafnia based memristors artificial synapses for neuromorphic computation

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Future information society featuring with the Internet of Things (IoTs), big data and artificial intelligence (AI) urgently requires the integrated circuit with non-von Neumann architecture and thus higher energy efficiency and lower power consumption. Massive edge-side smart devices have even higher requirements for power consumption of AI chips. Hafnia based resistive and ferroelectric memristors are one of the strongest candidates for the computing-in-memory (CIM) technology thanks to their various virtues like high speed, low power consumption, high endurance and retention, continuous conductance regulation and the compatibility with Si based semiconductor fabrication process. In particular, hafnia-based ferroelectric tunneling junction (FTJ) is considered to be the candidate for artificial synapses probably with the lowest power consumption due to the tunneling current mechanism. Different from the conventional bi-resistance-state resistive random-access memory (RRAM) devices, hafnia based memristors for artificial synapses require the continuous and symmetric regulation of the multi-resistance-state. Therefore, the regulation mechanism needs to be clarified and the materials as well as the integrated device fabrication technology need to be further optimized. We clarified the key impact of the carbon residues and the interface oxygen migration in the 1-transistor-1-resistor (1T1R) integrated RRAM arrays by combining the statistic electrical measurements, operando synchrotron radiation examination and the theoretical calculation. The materials and fabrication techniques were subsequently improved and thus significantly increase the device reliability of the 1 Mbit artificial synapses arrays. The recognition accuracy of the MNIST handwriting dataset using our devices is as high as 95.6%. We will also show the recent results on the epitaxial hafnia FTJ memristors. The ferroelectricity of the hafnia was realized and optimized using the Zr doping and the strain from the bottom electrode. Our hafnia FTJ memristors show a large On/Off ratio of >500 and continuous conductance regulation of 1-250 nS. Such devices achieve a high recognition accuracy of the MNIST handwriting dataset. These results will provide the technology accumulation for AI chips with low power consumption.

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Structure and microwave dielectric properties of gillespite-type $ACuSi_4O_{10}$ (A = Ca, Sr, Ba) ceramics and quantitative prediction of the Q × *f* value via machine learning

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Structure and dielectric properties of gillespite-type ceramics $ACuSi_4O_{10}$ (A = Ca, Sr, Ba) were investigated. A series of $(Ca_xSr_{1-x})CuSi_4O_{10}$ (0 < x < 1) ceramics with relative permittivities of 5.70−5.82, Q×*f* values of 20391−48794 GHz (@ ~13.5 GHz), and τf of −46.3 to −38.9 ppm/°C were synthesized at sintering temperatures of around 1000°C. By Ca^{2+} substitution for Sr^{2+} at the A-site, the rigid double-layered copper silicate framework remains stable, resulting in the nearly unchanged relative permittivity; While the $[(Ca,Sr)O_8]$ dodecahedron undergoes shrinkage and distortion, which is correlated to the changes in the Q×*f* and τ_f values. The normalized bond valence sums indicate that almost all ions are rattling, weakening the bond strengths and enlarging the molecular dielectric polarizability. The fitting of far-infrared reflectivity spectra reveals that the local structure changes suppress the intermediate and low-frequency vibrational modes significantly and improve the contribution from electronic polarization to permittivity. Symmetry breaking of the $[(Ca,Sr)O_8]$ dodecahedron conforms to the elevated restoring forces acting on the ions and improves the τ_f value. The large span in the Q×*f* value may have intricate correlations to local structure changes and defects. Machine learning methods were introduced to explore the decisive structural factors for the Q×*f* value. A Q×*f* value prediction model correlated with the A−O2 bond length and the variance of A−O bond lengths was established. The Q×*f* values of isostructural $(Ba_ySr_{1-y})CuSi_4O_{10}$ ceramics were predicted and verified by experiments.

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Cellulose-based energy storage dielectrics—the next-generation green capacitors

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As one of the alternatives to petroleum-based polymers, cellulose with low cost and biodegradability has noticed by lots of researchers. Due to the effect of strong hydrogen bond between molecular chains, the cellulose films prepared by the conventional tape-casting technology is easy to shrink during the drying process, bringing difficulties on preparing the lamellated structure. In this study, natural cotton wool was dissolved and regenerated in DMAc/LiCl solution, during which a small amount of PVDF was added. Due to the strong electronegativity of F^-, the inter-chain hydrogen bond in the network was destroyed, and the self-assembly behavior of the hydrogen bond network structure was effectively reduced, weakening the shrinkage of the cellulose films. After embedding the ceramic powders and regulating the structure, high energy storage performance that can be competitive with petroleum-based polymers was achieved. By employing the band theory, the shifting of Fermi level and the electric redistribution were revealed to be the main reasons. In addition, the excellent intrinsic insulation also benefited its good energy storage performance.

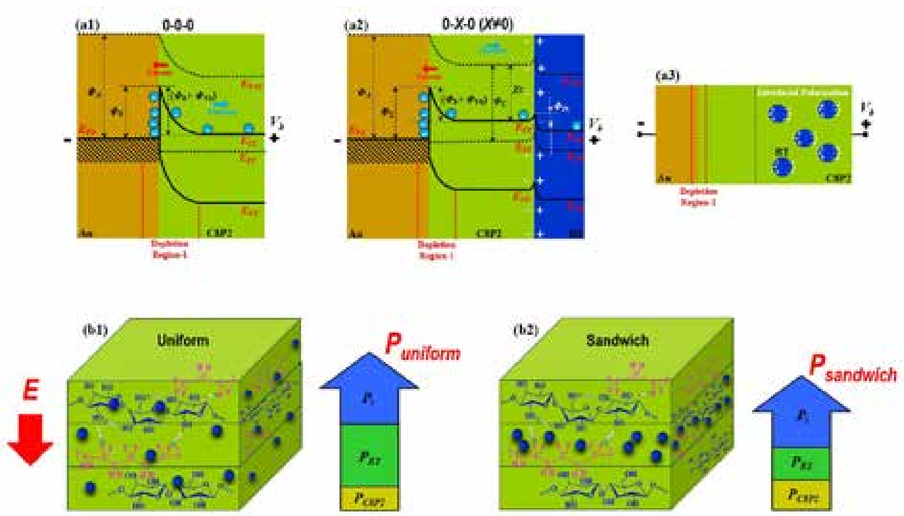

Figure 1. Effect of organic-inorganic interfacial polarization on the band structure of cellulose-based dielectric films

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In-memory sensing and computing based on ferroelectrics

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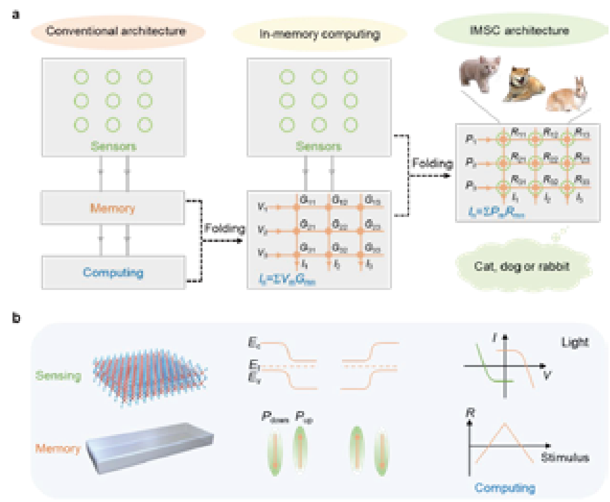
Rapid developments in Internet of Things (IoT) and Artificial Intelligence (AI) trigger higher requirements for image perception and learning of external environments through visual systems. However, limited by von Neumann bottleneck, the physical separation of sensing, memory, and processing units in a conventional personal computer (PC) based vision system tend to consume significant energy consumption, time latency and additional hardware costs. The emerging bio-inspired neuromorphic visual systems, by integrating sensing, memory and computational tasks of multiple functionalities into one single namely retinomorphic device, provide an opportunity to overcome these limitations. An architecture for the in-memory sensing and computing (IMSC) paradigm that combines all three modules has been developed based on ferroelectrics. Here I summarize our recent work about ferroelectric-based in-memory sensing and computing[1,2,3,4].



The architecture for the in-memory sensing and computing (IMSC)

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Textured calcium bismuth niobate exhibiting superior piezoelectric properties

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High-temperature piezoelectric materials are required for piezoelectric sensors under critical conditions in the nuclear power plants, aerospace, and energy industries. To meet the requirements of these applications, piezoelectric materials must possess high piezoelectric performance and high Curie temperature T_C. Bismuth layer-structured ferroelectric calcium bismuth niobate, $CaBi_2Nb_2O_9$, is considered to be one of the most promising high-temperature piezoelectric materials because of its high T_C of 940 °C, but the drawbacks of low electrical resistivity at elevated temperature and low piezoelectric performance limit its applications at elevated temperature. Therefore, many efforts have been made to improve the piezoelectric performance of $CaBi_2Nb_2O_9$ ceramics. The prototype $CaBi_2Nb_2O_9$ ceramic exhibits very low piezoelectric performance, with a low piezoelectric constant d_{33} value of 5 pC/N. By compositions adjusting, it is found that the d_{33} value can be promoted to >16 pC/N, while the T_C remains ~900 °C. Texture technologies, such as hot-forging, templated grain growth, and spark plasma sintering, are good methods to further enhance the piezoelectric performance of $CaBi_2Nb_2O_9$ ceramics. The d_{33} value can be promoted to higher than 30 pC/N through spark plasma sintering. The results indicate that the $CaBi_2Nb_2O_9$ ceramics are promising materials for high-temperature piezoelectric sensor applications.

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High-Throughput Screening Thickness-Dependent Oxide Thin Films

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Abstract. Artificial synaptic devices have the potential to accelerate high performance parallel and low power in-memory computation, artificial intelligence, and adaptive learning. For fabricating artificial synaptic devices with high performance, oxide thin film is an ideal choice due to its advantages of oxygen migration, easy adjustment of components and fast switching speed. In the oxide thin film-based artificial synaptic device, the thickness of the oxide thin films plays an important role, since it is a critical parameter that can directly determine devices' physical properties and functional performance. However, precisely control of thickness in local regions of film and devices under similar growth conditions is a challenge, since the preparation parameters and processing conditions is difficult to maintain consistency. To address this challenge, the as-proposed synthesis strategy is demonstrated based on high-throughput pulsed laser deposition technology, and a high-throughput $SrTiO_3$ thin films with nine gradient thicknesses ranging from 10.1 to 30.5 nm are fabricated. Notably, the screening of $SrTiO_3$ thin films with different resistive switching behaviors revealed that the $SrTiO_3$ thin film with a thickness of 20.3 nm exhibit excellent conductance modulation properties under the application of electrical pulses as well as significant reliability for the emulation of various synaptic functions, rendering it a promising material for artificial neuromorphic computing applications. Besides electrical pulse modulated of artificial synaptic devices, other external filed of stress or heating also would disturb the performance neuromorphic computing, especially for flexible electronic synapse. In our work, an all-inorganic flexible artificial synapse enabled by a ferroelectric field effect transistor based on mica also have been demonstrated. This flexible device not only exhibits excellent electrical pulse modulated conductance updating for synaptic functions but also shows remarkable mechanical flexibility and high temperature reliability, making robust neuromorphic computation possible under external disturbances such as stress and heating.

High temperature piezoelectric properties and conduction mechanism of bismuth titanate-ferrite

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Bismuth titanate-ferrite ($Bi_5Ti_3FeO_{15}$), a typical bismuth layer-structured ferroelectric, has attracted considerable interest for high-temperature applications due to its high Curie temperature T_C of 760 °C. However, no extensive studies have been carried out on the high-temperature piezoelectric properties of $Bi_5Ti_3FeO_{15}$. Herein, the piezoelectric performance of $Bi_5Ti_3FeO_{15}$ is significantly enhanced with the lanthanum substitutions, and the conduction mechanism of $Bi_{5-x}La_xTi_3FeO_{15}$ (abbreviated as BTF-100*x*La) is investigated in detail. As a result, BTF-6La exhibits a large piezoelectric constant d_{33} of 24.3 pC/N, which is three times larger than that of prototype $Bi_5Ti_3FeO_{15}$ (7.1 pC/N), whereas the Curie temperature T_C is almost unchanged, ~756 °C. The dc and ac electrical conduction behaviors indicate that the conduction mechanism of BTF-100*x*La has a strong relation with oxygen vacancies. Benefiting from the reduced oxygen vacancy concentration, BTF-6La exhibits a large dc electrical resistivity of 3.16×10^5 Ω cm and a low dielectric loss tanδ of <5% at 500 °C, thereby leading to thermal-stable electromechanical coupling properties up to 400 °C. These results suggest that the lanthanum substituted $Bi_5Ti_3FeO_{15}$ ceramics are promising candidates for high-temperature piezoelectric applications.

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Mechanical manipulation for ordered ferroelectric topological defects

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Randomly distributed ferroelectric domain in hexagonal manganites are geometric topological vortex structure, though the electric field can tune the ferroelectric domain wall, the effective mean to manipulate the topological vortex into ordered form is elusive due to the topological protection. Here, we establish a strategy to effectively align the topological domain networks through a mechanical approach. It is found that the nanoindentation strain gives rise to a threefold Magnus-type force distribution, leading to a sixfold symmetric domain pattern by driving the vortex and antivortex in opposite directions. On the basis of this rationale, sizeable mono-chirality topological stripe is readily achieved by expanding the nanoindentation to scratch, directly transferring the randomly distributed topological defects into an ordered form.

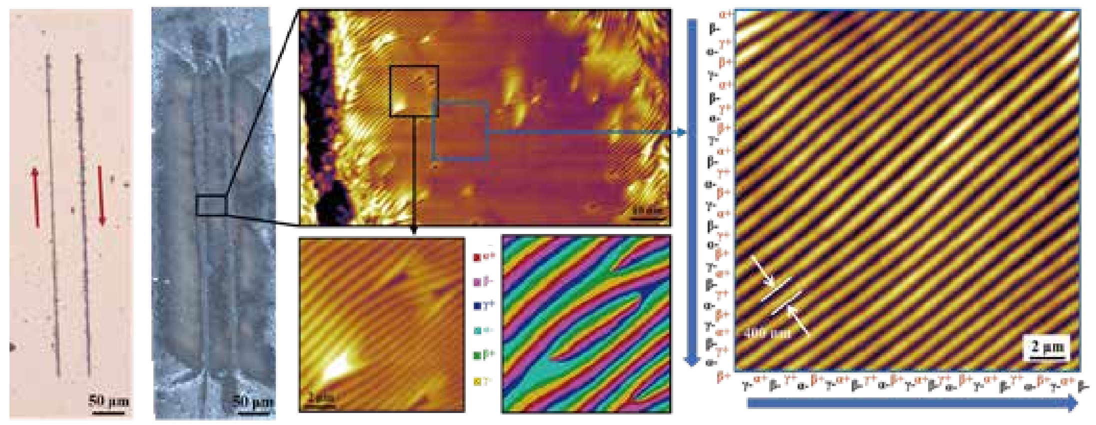

Figure 1. Scratch induced unfolding of vortices into topological stripes

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Ultra-High Performance Hafnium-Based Capacitors: Synergistic Achievement of High Dielectric Constant and Low Leakage Current（做报告）

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abstract

The relationship between the dielectric constant and leakage current of materials often exhibits a negative correlation. However, to sustain Moore's Law, the semiconductor industry necessitates novel materials that simultaneously possess a high dielectric constant and low leakage current, meeting the shrinking demands of electronic components. In this study, a high-performance hafnium-based thin film capacitor achieved through the collaborative effects of bottom electrode engineering and ion doping. Tungsten (W) as the bottom electrode, with its chemically inert nature and low thermal expansion coefficient, proves advantageous in improving interface quality and promoting the generation of the high-*k* phase in HfO_2. Concurrently, yttrium (Y) ion doping contributes to stabilizing the high-*k* phase of HfO_2, reducing non-lattice oxygen, and enhancing the disorderliness of the dielectric thin film. By synergistically integrating these factors, the hafnium-based thin film capacitor achieves a high dielectric constant of 36.6 while maintaining minimal leakage current (Electric field ~ 6 MV/cm, J ~ 10^{-8} A/cm^2) and a high charge storage capacity (U_{rec} ~ 104.4 J/cm^3). These research findings open a promising pathway for the development of novel hafnium-based materials with broad applicability and exceptional dielectric performance.

Design of Polymer-inorganic Ferroelectric Composite Materials for Antibacterial Applications

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The ferroelectrics, renowned for their multifaceted properties encompassing piezoelectricity, pyroelectricity, ferroelectricity, etc., have garnered widespread attention in recent years across diverse biomedical and antibacterial applications[1]. Especially, polymer-inorganic ferroelectric composites have emerged as a strategic solution that seamlessly integrates ferroelectricity with biocompatibility. In this work, a series of innovative inorganic ferroelectric materials were screened out as fillers, characterizing narrow bandgaps and strong intrinsic polarization[2]. Subsequently, the composite materials were fabricated by electrostatic spinning with polymer ferroelectric matrix as the carriers. As a result, the ferroelectric thin films showcased excellent antibacterial effect under indoor lighting conditions, with the best antibacterial rate reaching 99% against *S. aureus*. The mechanism of ferroelectric antibacterial activity has been further analyzed, emphasizing its association with reactive oxygen species and charge distribution. This exploration provides insight into the intricate interplay between ferroelectricity and antibacterial effects, thereby expanding the application of ferroelectricity in medical antibiotics.

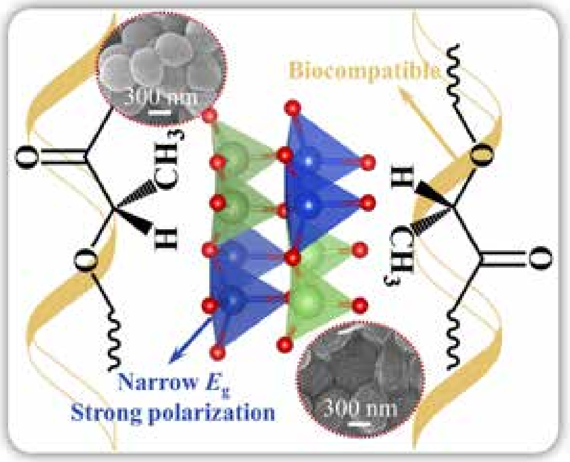

Figure 1. Design of polymer-inorganic composite ferroelectric materials for antibacterial applications.

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Polymer sub-nanocomposite dielectrics for high temperature capacitive energy storage

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Polymer dielectrics possess significant advantages in electrostatic energy storage applications such as ultrahigh power density and self-healing capability, while their discharged energy density (U_d) is limited by the low dielectric constant and breakdown strength especially at high temperature. And the performance improvement bottleneck of nanofiller incorporation strategies has been encountered. We proposed two novel incorporation strategies involving sub-nanosized fillers, i.e., inorganic sub-nano inorganics and aromatic molecules. In the first strategy (Figure 1a)[1,2], the hydroxyapatite sub-nanowires and phosphotungstic acid sub-nanosheets possess ultralarge specific surface area, which enables them to effectively reinforce the polymer matrix and trap the charge-carriers at an ultralow loading (<1 wt%). And the grafted organic surfactants enhance the interfacial compatibility. As for the second strategy (Figure 1b)[3], the aromatic molecules contain negatively charged phenyl groups, which can form electrostatic interaction with the positively charged phenyl groups on aromatic polyimide chains. Therefore, a physical crosslinking network in polymers can be formed. These two strategies both avoid the inherent shortcomings of nanofiller incorporation, such as fragile organic-inorganic interfaces and filler aggregation, thus considerably improve the U_d of polymer dielectrics.

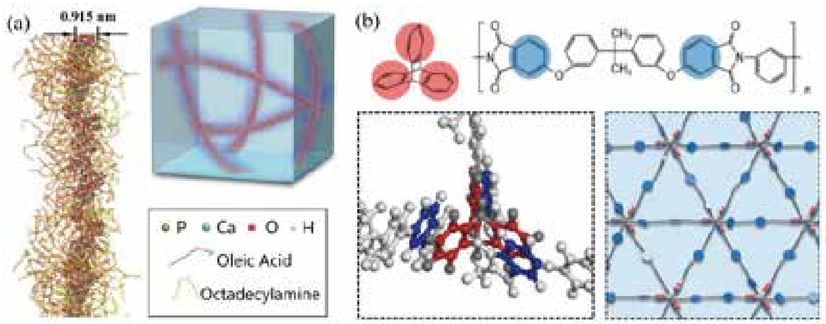

Figure 1. Schematic diagram of polymer sub-nanocomposite dielectrics

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Preparation and research of polymer nanocomposites with high energy storage

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Dielectric materials with high energy density are key to the development of adaptable energy storage and conversion devices to address the growing demand for electrical energy[1,2]. Polymer dielectric materials have significant advantages in the design and preparation of energy storage devices due to their excellent mechanical flexibility, high breakdown strength and good moldability[3]. And it is still challenging to improve their energy storage capability by simple and effective methods. In this work, the complementary effects of embedding highly polarized nanoparticles and wide bandgap nanosheets in ferroelectric polymer and the influence of interfacial interactions on the energy storage performance of polymer nanocomposites are investigated, especially on the energy density of new energy vehicles, capacitors, and other energy storage and conversion devices when operating at high temperatures. Due to the complementary effect of the dual fillers and the mutual coordination with the matrix, the polymer nanocomposites exhibit good synergistic effects, interfacial interactions, and attractive energy densities, especially at high temperatures where high energy densities can be maintained or even slightly increased. This has good application prospects in energy storage and conversion devices and microelectronic devices.

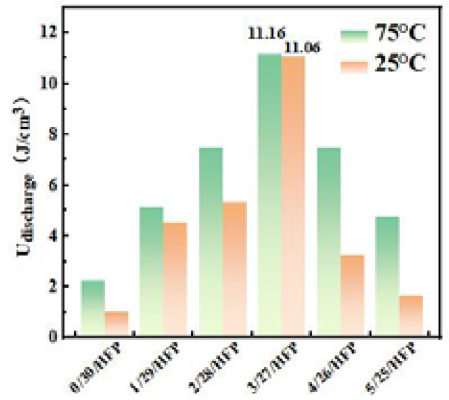

Figure 1. Maximum energy density of polymer nanocomposites at different temperatures

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Enhanced electricity generation and long cycle pyroelectric energy conversion by reversible phase transformation in lead-free ferroelectric materials

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Ferroelectric materials with temperature dependent spontaneous polarization can be used to directly convert heat to electricity. At phase transformation, the pyroelectric coefficient (dP/dT) is 1-2 orders of magnitude higher than non-transforming regime. A tri-doped Barium Titanate single crystal produces 1.93μC/cm^{2}K pyroelectric coefficient at ferroelectric-to-paraelectric transformation within 5°C narrow temperature range. By proposed bias-free thermodynamic model, the material generates 15μA electricity around transformation temperature without connecting to any external power source. By lattice tuning and grain engineering, the tri-doped lead-free material satisfies the lattice compatibility condition, which exhibits exceptional fatigue-resistance, with stable pyroelectric current over 3,000 energy conversion cycles. These results not only open a new way to design high-performance ferroelectric materials, but also advances the pyroelectric energy conversion for practical application in engineering.

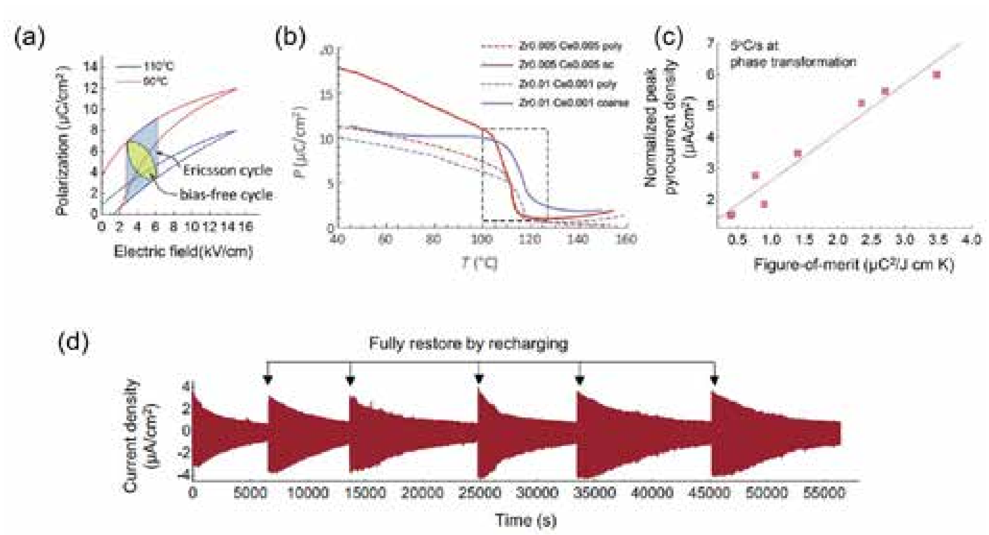

Figure 1 (a) proposed bias-free thermodynamic cycle; (b) temperature dependent polarization in a tri-doped single crystal; (c) Figure-of-merit in the design of high-performance material; (d) long cycle pyroelectric energy conversion.

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High energy storage performance of KNN-based transparent ceramics by multiscale designing

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Dielectric capacitors show significant advantages of faster charge-discharge time over the solid oxide fuel cells, Li-ion batteries, and electrochemical capacitors, and has been considered to be the best candidate next-generation high-performance pulsed power system.Considering the advantage of feasibility of efficient multifunctional coupling, which meets the integration trend of electronic devices and relies on the excellent transmittance of KNN-based ceramics, we chosen the KNN-based systems in this work. The (1-x)($K_{0.5}Na_{0.5}$)NbO_3-$x$$Ba_{0.9}Ca_{0.1}Zr_{0.15}Ti_{0.85}O_3$ ceramics were fabricated by employing the conventional solid state technology, and as expected, the the substitution of Ba/Ca by K/Na in the A-site and the substitution of Zr/Ti by Nb in the B-site, strongly decreased the leakage current of pristine KNN. By multiscale designing, the W_{rec} of 7.83 J/cm^3 with η of 81.02%, which has huge advantages over both BCZT-based systems and KNN-based systems, was finally achieved when the x equals 0.30, and such an excellent energy storage performance was caused by both high maximum polarization and high large electric breakdown strength.The work offered new concept in designing energy storage capacitors with high overall performance.

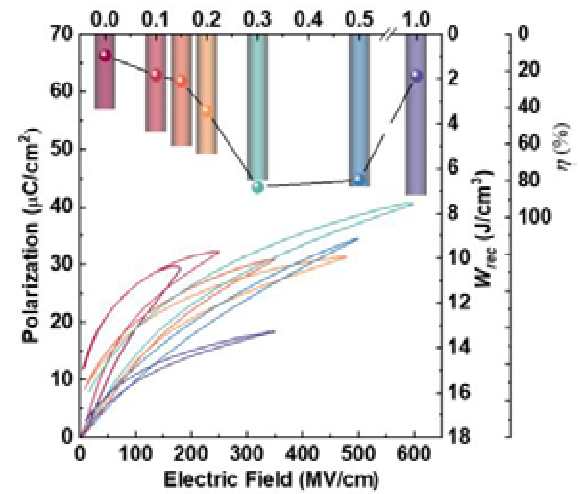

Figure 1. The P-E loops at E_b of all the ceramics are summarized at the bottom, and the W_{rec} and η of each ceramic are plotted on the top

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Investigation of ferroelectric crystal based whispering gallery mode resonator

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Whispering gallery mode resonators (WGMR) have garnered significant interest due to their potential applications in the fields of electro-optic modulation and microwave to optical photon conversion. In this study, we have leveraged the ferroelectric crystal lead indium niobate-lead magnesium niobate-lead titanate (PIN-PMN-PT), to fabricate a high-quality WGMR. Our investigation revealed that the crystal composition used in this work is 0.24PIN-0.45PMN-0.31PT, and each element of the whole sample is homogeneously distributed. The dielectric properties of the sample revealed the necessity of limiting the temperature and external electric field frequency to below 100 °C and 106 Hz, respectively. The obtained optical quality factor value (Q value) of the PIN-PMN-PT based resonator is larger than 10^5. Impressively, our resonator could be conveniently tuned by exploiting the enormous inverse piezoelectric effect d_{31} of the crystal, alleviating the need for precise fabrication. Furthermore, a theoretical analysis of our resonator revealed that a calculated resonance wavelength shift is within a broad range of 2.16 nm. Intriguingly, if the surface roughness of the resonator is reduced tenfold, we can increase the calculated Q value dependent on surface scattering by 10^4. Our finding showcase the tremendous potential of ferroelectric crystal-based WGMR as versatile building blocks for a variety of applications in the burgeoning field of photonic technology.

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Ferroelectric films: what is important in electrical measurement analysis?

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Ferroelectrics are highly nonlinear media with exciting properties for many applications in electronics, optics, etc. For thin ferroelectric films, the interpretation of physical processes is complicated by various reasons occurring simultaneously, such as leakage currents, relaxation, interfaces, and grain boundaries. As a result, the interpretation of experimental data may lead to numerous errors and ambiguous conclusions. In this report, we have performed an analysis of methods that could provide a correct physical interpretation of experimental data obtained by the most widespread measurement techniques, including dielectric hysteresis, current-voltage dependences, and others. The parameters, such as the remanent polarization and the coercive voltage obtained from the hysteresis loop, do not reflect the real ferroelectric behavior of the material in the presence of leakage currents and dielectric losses. We will discuss this issue and describe techniques that provide the real value of the spontaneous polarization, the ohmic and relaxation components, as well as the correct estimation of the dead layer thickness in metal-ferroelectric-metal capacitor structures.

Measurement of the leakage current is often performed by applying a linear voltage sweep to a pre-polarized sample. However, the registered current value, in addition to the steady-state ("true") leakage current, includes transient current and the ferroelectric polarization recovery current arising from the fast depolarization of pre-polarized film. For this reason, to obtain a steady-state current, a voltage step technique may be used. This technique involves registering the current versus time J(t) dependence at each constant voltage value applied to the sample. This requires quite a long observation (tens of minutes) and may be accompanied by time-dependent dielectric breakdown. Some relaxation models can be utilized to decrease the observation time. An exponential function with varying relaxation times offers a better fit for PZT films compared to the commonly used Curie-von Schweidler model. We demonstrate that the steady-state leakage current in PZT films is controlled by the redistribution of oxygen vacancies under an external electric field and the formation of an induced p-n junction. Leakage current in this case is well described by a modified equation for a p-n diode, which takes into account a counter field generated by electrons injected into the film volume.

Proposed experimental techniques and physical models could be useful for engineering FRAM and MEMS devices based on PZT films.

Ferroics in strong THz fields

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Terahertz radiation and the effects induced by it can have great potential for practical application both for the development of new generation photonic and electronic devices and for fundamental research aimed at revealing new properties of well-known functional materials. For ferroelectric materials, the advantage of using THz radiation lies in the possibility of an electrodeless application of an electric field to a ferroelectric and thus affecting its polarization in the pico(femto)second time range.

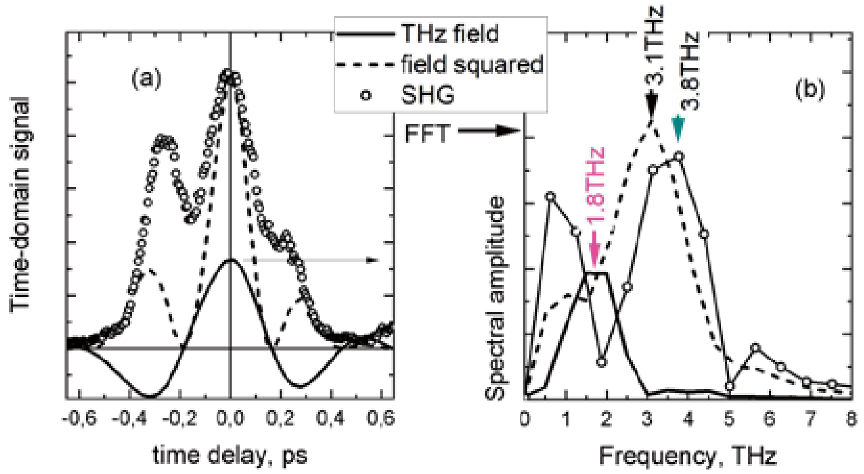

Figure 1. Time-domain (a) and spectral (b) shape of THz field, THz field squared and SHG intensity, generated in $Bi_4Ti_3O_{12}$ film under THz pulse with amplitude of 1 MV/cm.

In this work, we report the results of experimental studies of polarization modulation induced by strong picosecond THz pulse in several ferroelectric materials: Si:PbGeO and TGS crystals, $BaSrTiO_3$ and $Bi_4Ti_3O_{12}$ films. Optical second harmonic generation (SHG) as a measure of polarization is used. SHG provides information on the dielectric polarization (re-)orientation (switching) under the action of ultrashort electric field pulse due to the general proportionality of the SH field to the ferroelectric polarization vector. The dependences of the SHG intensity on the THz field, as well as polarization hysteresis loops, are discussed.

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Effect of a DC electric polarization induced by intense THz radiation in a ferroelectric single crystals

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One of the first experimentally discovered nonlinear optical effects is the effect of optical rectification (OR), which consists in the fact that when a sufficiently powerful laser pulse passes through a nonlinear optical crystal, a dielectric polarization is formed in it, the shape of which reproduces the laser pulse envelope [1]. This effect is widely used in terahertz electronics [2], as well as in a number of optoelectronic and photonic applications. Despite the apparent simplicity of its practical implementation, the effect of rectification in the terahertz range has not yet been studied.

Here we present the effect of terahertz wave rectification in a triglycine sulphate single crystal. Analogously to the OR, the effect consists in the appearance of a dc voltage induced by a THz radiation pulse on the faces of the crystal. Experiment was made using the FLARE FELIX free electron laser system (Radboud University, the Netherlands) at the frequencies of 1,57 and 1,96 THz. It was shown that the THz-induced dc voltage depends on the polarization of the THz radiation and ensures a maximum conversion efficiency of about 444 mV/mW at a frequency of 1.96 THz. The developed approach based on the known fundamental nonlinear optical relations makes it possible to obtain the values of the nonlinear susceptibilities of crystals directly from the approximation of the experimental polarization dependences of the THz-induced voltage. This demonstration adds to the growing number of reports highlighting the promise of THz techniques for studying the properties of functional materials, and also reveals additional opportunities for the practical implementation of photoconversion in the THz range.

This work is supported by the Russian Ministry of Science and Higher Education (075-15-2022-1131).

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MAGNETIC PHASE TRANSITION IN SOLID SOLUTIONS $x\mathrm{BiFeO_3} – (1\text{-} x)\mathrm{SrTiO_3}$ ($x = 0 \div 1.0$; $\Delta x = 0.1$)

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Materials that have two coexisting order parameters (magnetic and electric polarizations) were first created by G.A. Smolensky. with co-authors (see [1] and references there). Such materials are the subject of intense research for their applications in new types of next-generation multifunctional devices. Later, such materials were called multiferroics (MF) [2].

This paper presents the results of systematic Mössbauer studies of the evolution of the properties of $x\mathrm{BiFeO_3}$-(1- x)$\mathrm{SrTiO_3}$ solid solutions (SS) when x is varied from 0.1 to 1.0 (in steps of 0.1). Interest in the $x\mathrm{BiFeO_3}$-(1-x)$\mathrm{SrTiO_3}$ (BFO-STO) SS system was caused by the facts that in this SS: 1) at room temperature the appearance of magnetic properties at $0.7 \le x \le 0.9$ was found [3], and 2) at $x > 0.6$ an AFM transition occurs [4]. Mössbauer spectroscopy was widely used to study the BiFeO3−BaTiO3 SS, but there are no Mössbauer study of the BiFeO3−SrTiO3 system.

The experimental Mössbauer spectra (MS) were mathematically processed using a specialized program. At analysis of the HFS parameters, it was shown that when $x\mathrm{BiFeO_3}$-(1- x)$\mathrm{SrTiO_3}$ in the solid solution contains from 20% to 40% ferro-antiferromagnetic BiFeO3, only a single peaks or doublet is observed on the MS, indicating paramagnetic solid solution state in a given $\mathrm{BiFeO_3}$ content region. When the amount of $\mathrm{BiFeO_3}$ in a solid solution reaches 50%, lines of Zeeman splitting of low intensity appear on the MS spectrum. As the $\mathrm{BiFeO_3}$ content increases, the intensities of the Zeeman splitting lines increase and their widths decrease. A further increase in the amount of $\mathrm{BiFeO_3}$ from 80% in the BFO-STO solid solution leads to the fact that on the MS there are clear Zeeman lines belonging to the ferro-antiferromagnetic phase of $\mathrm{BiFeO_3}$, against which lines are observed indicating the presence of the paramagnetic phase. At $x = 1.0$, the spectra show lines of the ferroelectric ferromagnetic phase of $\mathrm{BiFeO_3}$ against the background of which there are lines of a paramagnetic doublet of low intensity (~ 5%).

Thus, the work for the first time presents direct experimental observations in xBiFeO3-(1-x)SrTiO3 solid solutions of the magnetic phase transition and there evolution.

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Influence of the Degree of Phase Transition Diffuseness on the Depolarization Temperature in Relaxors of Different Types

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The relationship between the temperatures of depolarization (T_d) and morphotropic phase transition ($T_{\mathrm{F-R}}$) in crystalline relaxor solid solutions of various types, such as $\mathrm{PbMg_{1/3}Nb_{2/3}O_3}$−29$\mathrm{PbTiO_3}$ (PMN−29PT), $\mathrm{PbZn_{1/3}Nb_{2/3}O_3}$−9$\mathrm{PbTiO_3}$ (PZN−9PT) and $\mathrm{NaBi_{1/2}Ti_{1/2}O_3}$−5$\mathrm{BaTiO_3}$ (NBT−5BT) has been studied. For this purpose, dielectric measurements of polarized samples were carried out, and the process of induction of the ferroelectric phase in an electric field applied below the $T_{\mathrm{F-R}}$ temperature was also studied. It was found that the structure of the low-temperature phases in these compounds is different, which leads to significant differences not only in the induction of the ferroelectric phase, but also to different relative positions of the temperatures T_d and $T_{\mathrm{F-R}}$. In PMN−29PT, the formation of ferroelectric phases is preceded by some delay time, which is one of the hallmarks of a non-ergodic glassy phase, and in this case the temperatures T_d and $T_{\mathrm{F-R}}$ coincide. In PZN−9PT and NBT−5BT, the ferroelectric phase is induced immediately after the field is applied without a delay time, which indicates that below the $T_{\mathrm{F-R}}$ temperature the non-ergodic glassy phase does not appear, and the temperatures T_d and $T_{\mathrm{F-R}}$ do not coincide in them. The results obtained are discussed from the point of view of different degrees of diffuseness of the phase transition and different sizes of the polar regions. It is suggested that the coincidence of temperatures T_d and $T_{\mathrm{F-R}}$ is a consequence of the non-ergodic glassy phase and the small sizes of the polar regions.

Electric field induced transformation of dielectric spectra of PMN

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One of the key points in the physics of the relaxors is their response to the applied DC field. The application of the external electric field higher than E_{th} to PMN single crystal in <111> or <110> directions induces the ferroelectric phase transition. The application of electric field along <100> direction does not induce ferroelectric phase transition and leads to a decrease of dielectric response magnitude only. Ceramics is a system of randomly oriented crystallites and the behavior of PMN ceramics under external electric fields may differ from that of a single crystal. The question of the possibility of inducing a ferroelectric state in ceramics by external field has been discussed for a long time.

We have studied the behavior of the dielectric response of a PMN single crystal in the applied external electric field in (111) direction range from 0 to 7 kV/cm at 246 K crossing the glass/paraelectric (G/P) and paraelectric/ferroelectric (P/F) lines. The evoluting of the dielectric spectra in the frequency range 0.1Hz to 1 kHz was followed. For the first time, the measurements were made by scanning the E-T phase diagram along the line of constant temperature. The analysis of the frequency response within the framework of the Cole-Cole model was carried out. Clear indication of the G/P transition was found. In the paraelectric phase, field increase from 1.3 kV/cm to 4 kV/cm results in strong fastening of the relaxation with relaxation time changing from about 10 s to nearly 10^{-4} s. Obtained results allows to explain the contradiction between different papers about the sign of the C-V effect.

The transitions from the glass-like into the ferroelectric phase were found in PMN polycrystalline ceramics both in field cooling and zero field heating after field cooling regimes under the fields above 3 kV/cm. The hysteresis loops, obtained in the low-temperature region, unambiguously confirm the phase transition of ceramics into the ferroelectric state. The behavior of the low-frequency relaxation process in ceramics has been studied under electric fields from 0 kV/cm to 6 kV/cm. The relaxation dynamics of polycrystalline ceramics and the single crystal under field are generally similar, but all dependences for ceramics dependent weaker on the field. This fact confirms also our assumption that due to the random orientation of grains in ceramics, the magnitude of critical fields in ceramics is much larger.

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Phase Transitions in PMN-PSN Solid Solutions

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Relaxor ferroelectrics are known for more than 70 years. Despite their extensive studies the microscopic nature of the relaxors remains questionable. One of the major problem is the control of the chemical order in relaxors. It can be achieved, albeit not completely in the 1:1 compounds like PbSc1/2Nb1/2O3 (PSN), however in more physically and practically interesting 1:2 (PbMg1/3N2/3O3 (PMN) - like) compounds is quite difficult. One of the most effective way of order controlling is by solid solution of 1:1 and 1:2 compounds, PMN1-xPSNx serves as an example. In the present work structure rearrangement processes and accompanying changes in dielectric response in a series of PMN-PSN crystals with x=0.35 (PMN-35PSN), 0.55 (PMN-55PSN), x=0.8 (PMN-80PSN) x=1 (PSN) have been studied.

Superstructural peaks indicating compositional ordering were detected for all crystals. The analysis showed that in all cases the order parameter S was close to 1, indicating almost complete ordering on scales of the order of 30 nm. However sharp phase transitions was observed only in PSN and PMN-80PSN. This shows that the ordering in PMN- and PSN-type crystals is significantly different.

We have traced the temperature evolution of unit cell parameters of PSN, PMN-80PSN and PMN-35PSN single crystals. In PSN, PMN-80PSN crystals in the region of existence of cubic phase, the behavior characteristic for relaxors was found. The temperature dependence of the CTE in PMN-35PSN is similar to that of disordered PSN. In the region $T \geq 325$ K, one can expect that the correlated ferroelectric displacements play a determining role. However below this temperature antiferroelectric correlations develops playing the decisive role in the CTE(T) dependence.

The behavior of diffuse scattering (DS) in the vicinity of the ZB center and the M-point of the ZB was followed. The DS in the neighborhood of M points (h+1/2 k+1/2 l was fundamentally different for the case h=k "symmetric point" and $h \neq k$ “asymmetric point” indicating an important role of the antiferrodistortive (AFD) oxygen mode. The lineshape of the DS was quantitatively described by the coupling of the TA and AFD modes. The consequences of this coupling wil be discussed in the report.

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Recent achievements in nanodomain engineering in ferroelectrics

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We present the achievements in fabrication of effective nonlinear frequency converters by creation of the stable domain structure with nanoscale period reproducibility by various methods of the domain engineering in single crystals of lithium niobate, lithium tantalate and potassium titanyl phosphate families. The promising applications of femtosecond laser irradiation for all-optical creation of the periodical domain structure in the crystal bulk are demonstrated [1-3].

The obtained achievements are based on complex study of the domain structure evolution in various uniaxial ferroelectrics with high spatial and temporal resolution. The realized methods of domain engineering are based on application of the electric field using: (1) periodical stripe electrodes [4], (2) biased tip of scanning probe microscope (SPM) [5,6], (3) focused electron and ion beams [7], (4) pulse heating by IR laser irradiation [1]. The created precise tailored domain structures allowed to realize the highly effective optical parametric oscillation (OPO) and out-of-cavity second harmonics generation. The periodical poling has been carried out also in thin single-crystalline ion sliced films of lithium niobate on SiO_2 isolation layer (LNOI) by conductive tip of SPM. The stable domain structures with period less than 200 nm have been created [5,6]. The periodical domain structures were produced at the surface and in the bulk of single-domain MgO doped lithium niobate using irradiation by femtosecond laser emitting pulses at the 1030 nm wavelength with energies from 0.7 to 6.7 μJ in filamentation regime with duration 240 fs [8].

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Recent achievements of the domain engineering in ferroelectric materials in Russian-Chinese projects

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Oxides with a perovskite structure based on the ferroelectric relaxor sodium-bismuth titanate $Bi_{0,5}Na_{0,5}TiO_3$ (BNT) are among the most promising lead-free piezoelectric and ferroelectric materials since the introduction of various additives makes it possible to change their functional properties in a wide range [1]. BNT-based ceramics near the morphotropic phase boundary (MPB) have significant electrostrictive performance but a rather small residual piezoelectric response associated with a heterophase relaxor state [2]. Though the structural and electrical properties of BNT-based ceramics have been studied in detail, the local structural distortions and nanodomains have not yet been studied.

The domain structure of $Bi_{0,5}Na_{0,5}TiO_3$–$PbTiO_3$ (BNT-PT) ceramics was studied by the piezoresponse force microscopy (PFM) for compositions near the MPB. It was shown that ceramics of all compositions exhibit a ferroelectric nanodomain structure. The minimum average domain size of about 4 nm was detected in BNT-4PT. The fraction of the area occupied by macroscopic domains increases along with the PT concentration. Quantitative estimations of PFM data showed that the ceramics with low PT concentrations have the minimum piezoelectric coefficient. In the range from 2 to 12% PT, three types of domains coexist: nanosized rhombohedral domains, as well as macroscopic domains of the rhombohedral and tetragonal phases [3].

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Exploring Charged Defects in Ferroelectrics by the Switching Spectroscopy Piezoresponse Force Microscopy

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Monitoring the charged defect concentration at the nanoscale is of critical importance for both the fundamental science and applications of ferroelectrics. However, up-to-date, high-resolution study methods of the investigation of structural defects, such as transmission electron microscopy, X-ray tomography, etc., are expensive and demand complicated sample preparation[1,2]. With an example of the lanthanum-doped bismuth ferrite ceramics, we propose a novel method based on the switching spectroscopy piezoresponse force microscopy (SSPFM) that allows probing the electric potential from buried subsurface charged defects in the ferroelectric materials with a nanometer-scale spatial resolution[3]. When compared with the composition-sensitive methods, such as neutron diffraction, X-ray photoelectron spectroscopy, and local time-of-flight secondary ion mass spectrometry, the SSPFM sensitivity to the variation of the electric potential from the charged defects is shown to be equivalent to less than 0.3 at. % of the defect concentration. Additionally, the possibility to locally evaluate dynamics of the polarization screening caused by the charged defects is demonstrated, which is of a significant interest for further understanding defect-mediated processes in ferroelectrics.

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Raman spectroscopy of phase transition in multiferroics with huntite structure

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The ferroborates with the huntite structure with the general formula of LnMe3(BO3)4 (Ln = rare-earth cation, Me = Fe, Ga) are the objects of many studies because of the wide range of promising physical properties. These materials exhibit multiferroic properties, as they combine the mutual influence of magnetic and electrical subsystems, and the transition points can be varied by substituting a magnetic ion as the rare earth element. [1] We present the Raman spectroscopy result of the investigation of single crystals and a solid solution.

Temperature measurements performed in the temperature range 10–400 K. We performed high-pressure experiments. We conducted measurements under pressure and high temperature simultaneously, covering the range of 0-8GPa and 300-600 K. This study aims to investigate the possible existence of a soft mode related to structural order parameter and effects of magnetic transitions on Raman spectra. Our analysis included examining the experimental Raman spectra, the temperature dependences of the centers of lines, their width, and relative intensity. We also conducted a theoretical temperature approximation for some lines. Some anomalies in the temperature dependences of the spectral lines associated with the occurrence of magnetic order. The spectrum of the low-frequency range (below 100 cm-1) shows significant changes - observed a mode corresponding to two-magnon scattering was observed. The structural phase transition accompanied condensation of soft mode. [2].

The phase diagram Temperature–Composition and Pressure–Temperature has been acquired for several systems. Structural transitions manifest clearly by soft mode restoration, and abnormal changes of line position indicate a temperature of magnetic ordering. [3] Increasing temperature and pressure increases the stability of the R32 phase. There are no new phases found during investigations.

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Raman Spectra of Huntite-Like Multiferroics – Interpretation Using Angular Dependences and DFT Simulations

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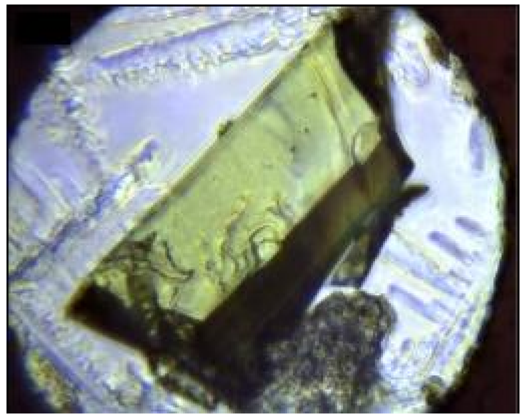
Ferroborates $ReFe_3(BO_3)_4$ (*Re* – rear earth ion) are piezoelectric crystals with two types of magnetic ions in the structure demonstrating sequences of structural and magnetic phase transitions. Restoring soft modes were found in Raman spectra at these transitions [1], but no structural interpretation was proposed.



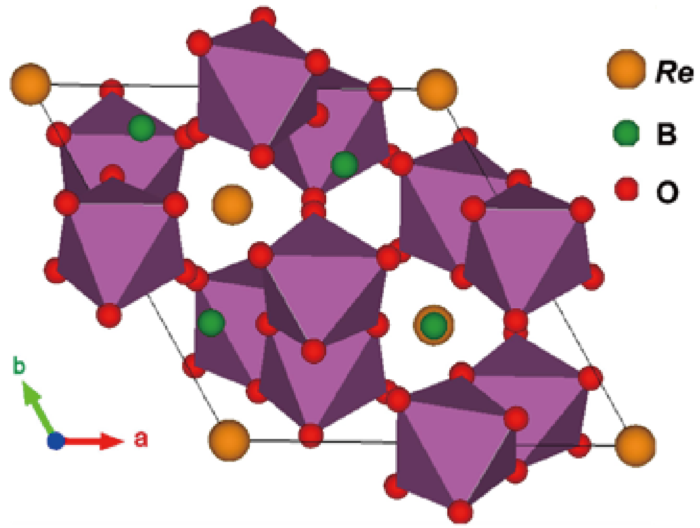


Figure 1. Typical as grown sample of $TbFe_3(BO_3)_4$ and *R*32 crystal structure.

To perform symmetry attribution of Raman lines obtained with unoriented samples angular dependences of scattering intensities have been measured [2]. The results are interpreted using *ab initio* lattice dynamics simulations.

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NMR studies of nanostructured ferroelectrics

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We present a short review of our studies of ferroelectric nanostructures using NMR, which is sensitive to local properties. The main attention is focused on the impact of size reduction and nanoconfinement on structural phase transitions in ferroelectric nanoparticles embedded into porous matrices (opals, porous glasses, molecular sieves, and porous alumina). The samples are nanostructured sodium nitrite and its mixtures [1], Rochelle salt [2], KDP and DKDP with different levels of deuteration [3], organic ferroelectrics DIPAC, DIPAB, and DIPAI [4,5] in comparison with their bulk counterparts. The variations in the NMR lineshape, chemical shifts, and spin-lattice relaxation rate were observed within large temperature ranges covered the ferroelectric phase transitions. For the organic ferroelectrics we used a standard ^{13}C cross-polarization MAS pulse sequence.

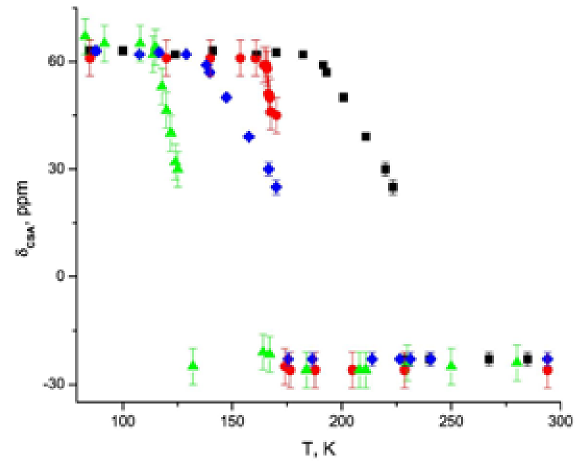

Figure 1. ^{31}P chemical shift anisotropy for two DKDP samples, bulk (squares and diamonds) and embedded into opals (circles and triangles), calculated from NMR measurements.

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Polarization Rotation, Triclinic Phase and Domain Engineering in Relaxor-Based Piezocrystals

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Piezo-/ferroelectric materials play a crucial role in electromechanical sensors and actuators for a wide range of applications. Significant progress has been made in the past decades in the research and development of relaxor-based piezoelectric single crystals, represented by the $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMN-PT) solid solution, with outstanding piezoelectric and electromechanical properties. An important tool for improving the properties of ferroelectric crystals is domain engineering, in which special conditions are applied to create a preferable domain structure. In particular, it was commonly believed until recently, that increasing the domain wall concentration enhances the piezoelectric coefficients because the wall motion contributes to piezoelectric effect. However, in 2010 we studied flat engineered domain walls inclined to the surface of PMN-PT single crystal with the help of piezoresponse force microscopy and found that d_{33} piezoelectric coefficient is significantly reduced around the wall [1]. We suggested that "to increase macroscopic d_{33} it would be useful to fabricate the crystals oriented and poled along a nonpolar direction but free from uncharged walls; the method of such a fabrication process needs to be developed." [1]. Later, the AC poling method was used to eliminate inclined (71° degree) walls from (001) -oriented $0.72Pb(Mg_{1/3}Nb_{2/3})O_3$ – $0.28PbTiO_3$ crystals of rhombohedral symmetry, and ultrahigh piezoelectricity was really obtained [2]. Interestingly, application of AC field to pole relaxor-based rhombohedral crystals was earlier reported to increase piezocoefficients (as compared to traditional DC poling method) [3], but the effect was explained by an *increase* in the concentration of domain walls or by the transformation from the rhombohedral to the monoclinic phase.

Here, we report the investigations of the influence of poling conditions on dielectric and piezoelectric and properties of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ single crystals with a composition close to the morphotropic phase boundary (MPB), and of the relationship between the properties and the structural symmetry of these crystals. We studied monoclinic PMN-PT crystals with the morphotropic phase boundary composition (PMNT-C Type crystals according to the IEEE standard classification) and found that, similar to rhombohedral (PMNT-A and B) crystals, AC poling improves significantly (up to ~50 % compared to DC poling) their piezoelectric and dielectric properties and makes the crystal transparent. By X-ray diffractometry and polarized light microscopy, the mechanisms of this effect are determined, which involve elimination of inclined domain walls and incomplete reorientation of spontaneous polarization in monoclinic domains. The domain wall relaxation is characterized by means of dielectric spectroscopy. Temperature-dependent investigations of the domain structures and birefringence allow us to discover a new phase of triclinic (Tr) symmetry, which was not reported previously in relaxor-based ferroelectrics. It is located between the low-temperature monoclinic M_B phase and the high-temperature monoclinic M_C phase. The temperature-induced rotation of spontaneous polarization direction is found in the Tr and M_C phases.

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LTCC and screen-printed glass-ceramic MEMS

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We present the results obtained with the application of alternative technology for the fabrication of MEMS devices based on thin dielectric membranes and cantilevers. Among these devices are high temperature gas sensors of semiconductor and thermocatalytic types, gas flow meters, high temperature pressure sensors requiring for there operation thermal isolation of the sensing element.

Usual silicon MEMS technology applicable for the fabrication of mass produced devices has limitations, when is used for the fabrication of high temperature sensors because of very specific requirements to the technology (good adhesion of platinum, long term operation at temperature up to 500^0C) and of very large variety of sensors needed by electronic instrument produces.

We developed a new approach to the fabrication of such devices based on two approaches. The first one consists in the application of thick film sacrificial material consisting of unsiterable at 900^0C microparticles and polymeric binder [1] followed by the screen printing of functional materials (Pt based resistive material [2], body of the membrane or cantilever, sensing material, etc. The sacrificial material becomes powder after firing and can be removed from under the cantilever in ultrasonic bath. Another approach consists in the application of very thin LTCC membranes (20 micron thick) and in the screen printing of functional materials. To reinforce thin membrane during printing, the cavity under the membrane is filled by the same sacrificial material.

Sensing materials are deposited by robotic system onto the pre-sintered cantilever. The tests of both semiconductor and thermocatalytic sensors demonstrated high performance of the approach: power consumption of the microheater at 450^0C is of 120 mW, response to H_2 of the Pd thermocatalytic nanomaterial made by spark discharge is ~ 30 mV/percent, response (R_{air}/R_{gas}) of semiconductor SnO_2 nanomaterial made also by spark discharge is of about 10 at H_2 concentration of 200 ppm.

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$Bi_2Ti_2O_7$ single crystal as a material candidate for geometrically frustrated relaxor

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For more than a hundred years, materials science has been dedicated to the comparative study of magnetism and ferroelectricity, uncovering similarities in terms of ordering types, domains, hysteresis, and responses to external stimuli. The outstanding physical properties of magnets often stem from frustration, which can be induced by a number of effects such as site disorder and lattice geometry. While disordered relaxor ferroelectrics showcase remarkably high dielectric and piezoelectric properties, displaying behavior akin to spin glasses, ferroelectric materials exhibiting clear geometrically frustrated states have not been previously identified. In this study, we introduce a novel class of relaxor materials which can be named as geometrically frustrated relaxors, with a $Bi_2Ti_2O_7$ single crystal featuring a compositionally ordered pyrochlore structure as a prime example [1].

Our research reveals the classic relaxor behavior of this material, characterized by dielectric anomalies, dipole freezing, non-ergodicity, and the absence of spontaneous phase transitions. Additionally, we observe the emergence of a unique dipole ice state upon cooling, that is a consequence of conflicting order parameters leading to geometric frustration within the crystal lattice. These findings introduce a new perspective on the manifestation of geometrical frustration in non-magnetic media, paving the way for the exploration of exotic ground states and advanced functionalities in dielectric materials.

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Structural tuning of transition metal-doped $SrTiO_3$ single crystals

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The influence of doping on the chemical and physical characteristics of semiconductors, alloys, ferroelectrics, glasses, and other materials has been a long-standing focus in the field of materials science, spanning centuries. Strontium titanate, $SrTiO_3$, serves as a quintessential perovskite with significant relevance in fundamental science as a quantum paraelectric, showcasing a myriad of exceptional physical properties and applications such as dielectrics, tunable microwave and photovoltaic devices, superconductors, thermoelectrics, and potential multiferroics. The introduction of chemical dopants, especially transition metals, introduces novel functionalities to $SrTiO_3$. However, the intrinsic mechanisms governing structural responses triggered by impurities have not been meticulously explored [1,2]. The present study elucidates a comparative analysis of the crystal structure, vibrational spectra, and dielectric properties of single-crystalline $SrTiO_3$ doped with transition metals M (M = Mn, Ni, and Fe at 2 at. %). The investigation reveals distinct tendencies of impurities towards off-centering and dipole formation within the crystal lattice: Mn and Fe atoms exhibit clear off-centered displacement, whereas Ni atoms maintain an on-centered position. Consequently, even minor chemical doping exerts a profound impact on the dielectric behavior through diverse structural mechanisms, including the pseudo-Jahn-Teller effect, the first-order Jahn-Teller effect, and defect-induced distortion. These findings not only shed light on the intricate interplay between dopants and structural properties, but also present novel opportunities for addressing complex challenges in the practical applications of doped $SrTiO_3$ and related materials.

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