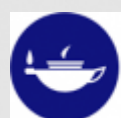




7th International Workshop on Relaxor Ferroelectrics

Programme and abstracts



Taylor & Francis Group
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7th—12th of
August 2022



Go Vilnius

7th International Workshop on Relaxor Ferroelectrics

Abstract book



7th – 12th of August 2022

Vilnius, Lithuania



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WELCOME WORD

Dear Colleagues,



On behalf of the Local Organising and Programme Committees we are delighted to welcome you to the 7th International Workshop on Relaxor Ferroelectrics (IWRf) in Vilnius.

The 7th IWRf supposed to be held in 2020, but the pandemic situation left the organizing committee no other option but to postpone the workshop for two years. Finally, the in-person meeting will be held in the Lithuanian Academy of Sciences.

The regular meetings were reestablished in 2013 in St. Petersburg although the first meetings were organized as early as 1996 and became biannual event. Later on it was held in Stirzín (Czech Republic), Matsue (Japan), Vancouver (Canada).


Laboratory of Microwave Spectroscopy of Vilnius University is honored to host this event. Vilnius University is the oldest university in the region. Its history dates back to 16th century. It is the largest university of Lithuania with long lasting traditions. We hope that the organization will meet the high standards which were set by the previous meetings.

This meeting will be concentrated on the further understanding of relaxor ferroelectrics and bridging theory and experimental results to be able to connect the microscopic picture to its unique macroscopic properties.

We wish you a pleasant stay in Vilnius and a fruitful scientific discussions during the conference!

Conference Chair

Prof. Jūras Banys

A handwritten signature in blue ink, likely belonging to Prof. Jūras Banys. The signature is stylized and cursive, written in a professional manner.

Conference committees

International advisory board

Jan Dec	Poland
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Peter Gehring	USA
Jirka Hlinka	Czech Republic
Kenji Ohwada	Japan
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Jūras Banys – chairman	Martynas Kinka	Eglė Šlinkšytė
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Mantas Šimėnas	Žygimantas Logminas	

General Information

Venue

The scientific programme of International Workshop on Relaxor Ferroelectrics 2022 will be held in **Lithuanian Academy of Sciences, Gedimino av. 3, Vilnius, Lithuania**. It is situated in Gedimino avenue – the main street of Vilnius city center. The venue is near the Cathedral Square and historical UNESCO heritage old town. It can easily be reached by foot. It takes 20 – 30 minutes to get to the city center from the Vilnius International Airport. Many hotels are situated in the vicinity of the Academy.



Academy of sciences is in ideal place to enjoy the scientific programme and cultural experience of Vilnius.

Practical Information

The official language of the conference is **English**. There will only be oral presentations. Invited speakers are given 40 minutes for their talk. Regular presentations are 20 minutes.

Meeting hall will be equipped with PC, LCD projector and microphones. The date/hour/room of your presentation(s) is available in the Conference Program. If you are using a slide presentation make sure that you bring it on the USB stick. Supported file types: ppt, pptx, pdf, avi.

Note! If you are planning to use your own computer for presentation, please inform secretariat about that in advance.

Detailed programme

Monday (8th of August)

8:30	Registration		
8:45	Welcome word		
Oral session 1			
Chairman: prof. Jūras Banys			
9:00	Peter Gehring <i>Anharmonicity and Polar Nanoregions in Photovoltaic Hybrid Organic-Inorganic Perovskites</i>	I1-1	
9:40	Chris Stock <i>Broadband critical dynamics in organic-inorganic lead-halide perovskites</i>	I1-2	
10:20	Mantas Šimėnas <i>Suppression of phase transitions and glass phase signatures in mixed cation halide perovskites</i>	O1-1	
10:40	Yulian Vysochanskii <i>On the origin of relaxor behavior in 3D and 2D MM'P₂S(Se)₆ferroics</i>	O1-2	
Coffee Break			
Oral session 2			
Chairman: Elena Buixaderas			
11:20	Marco Deluca <i>Origin of relaxor behavior in BaTiO₃-based lead-free perovskite ceramics</i>	I2-1	
12:00	Jirka Hlinka <i>Polarization relaxation: about the shape, dynamics and role of coherently flipping nanoregions in Ba(ZrTi)O₃</i>	I2-2	

12:40	Jürgen Spitaler <i>Advanced ab-initio approaches for the characterization of relaxor ferroelectrics</i>	O2-1	
Lunch			
Oral session 3			
Chairman: Peter Gehring			
15:00	Andrew Rappe <i>Relaxing in Weird Places</i>	I3-1	
15:40	Alexei Gruverman <i>Direct Observation of Ferroelectricity in Two-Dimensional MoS₂</i>	I3-2	

Tuesday (9th of August)

8:30	Registration		
Oral session 4			
Chairman: Jirka Hlinka			
9:00	Elena Buixaderas <i>What the hell is a uniaxial relaxor?</i>	I4-1	
9:40	Igor Levin <i>Unraveling correlated disorder in relaxor Sr_{0.61}Ba_{0.39}Nb₂O₆</i>	I4-2	
10:20	Jūras Banys <i>Dielectric spectroscopy and piezoelectric properties of lead-free BaTiO₃-xBi(Zn_{2/3}Nb_{1/3})O₃</i>	O4-1	
10:40	Monica Pinto Salazar <i>²³Na Nuclear Magnetic Resonance Longitudinal and Transverse Spin Relaxation times (T₁, T₂) Study of Na_{1/2}Bi_{1/2}TiO₃-6mole%BaTiO₃</i>	O4-2	

11:00	Coffee break		
Oral session 5			
Chariman: Brahim Dkhil			
11:20	<i>Petr Ondrejko</i> <i>Neutron backscattering studies of relaxor ferroelectrics</i>	I5-1	
12:00	<i>Mojca Otoničar</i> <i>About the origins of the large nonlinear response in relaxor ferroelectrics</i>	I5-2	
12:40	<i>Chae Il Cheon</i> <i>Phase Evolution and Ferroelectric Properties of BiFeO₃-BaTiO₃ Ceramics around Morphotropic Phase Boundary</i>	O5-1	
Lunch			
Oral session 6			
Chairman: Krystian Roleder			
15:00	<i>Vladimir Shvartsman</i> <i>Relaxor terpolymers P(VDF-TrFE-CFE) for electrical energy storage</i>	I6-1	
15:40	<i>Zuo-Guang Ye</i> <i>Relaxor to Ferroelectric Crossover in the Lead-Strontium Zirconate-Titanate Perovskite Solid Solution System</i>	O6-2	

Wednesday (10th of August)

8:30	Registration		
Oral session 7			
Chairman: Igor Levin			
9:00	<i>Zuo-Guang Ye</i>	I7-1	

	<i>Optimization of Piezoelectric Properties of Relaxor-based Crystals via Domain Engineering</i>		
9:40	Martin Kempa <i>Broadband dielectric properties of the BaTiO₃-BaZrO₃ solid solutions</i>	I7-2	
10:20	Piotr Czaja <i>Influence of dopant ions on mechanical and dielectric properties of K_{0.5}Bi_{0.5}TiO₃ ceramics</i>	O7-1	
10:40	Šarūnas Svirskas <i>Dielectric and NMR studies of BaTi_{1-x}Sn_xO₃ solid solutions</i>	O7-2	
Coffee Break			
Oral session 8			
Chairman: Mojca Otoničar			
11:20	Brahim Dkhil <i>Relaxors for neuromorphic computing</i>	I8-1	
12:00	Krystian Roleder <i>Domains populations and piezoelectric properties in PZT single crystals</i>	I8-2	
12:40	Annette Bussmann-Holder <i>Complex symmetry of phases and magnetic properties of the oxide perovskite EuTiO₃</i>	O8-1	
Lunch			
Banquet to the Palace of Grand Dukes			
Banquet in the Palace of Grand Dukes			

Thursday (11th of August)

10:00	Excursion around the historical Vilnius University ensemble
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Abstracts

Anharmonicity and Polar Nanoregions in Photovoltaic Hybrid Organic-Inorganic Perovskites

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Strong anharmonicity and dynamic A-site disorder are prominent features of ABO_3 perovskite relaxors such as $PbMg_{1/3}Nb_{2/3}O_3$ [1] and $PbZn_{1/3}Nb_{2/3}O_3$ [2]. These features are also characteristic of hybrid organic-inorganic perovskites such as $CH_3NH_3PbI_3$ (MAPI), a material that shows exciting promise in photovoltaic applications. I will compare the lattice dynamics of PMN and MAPI. I will also report recent measurements made on single crystal $CH_3NH_3PbX_3$ ($X=I, Br$) using x-ray and neutron diffuse scattering techniques, neutron inelastic spectroscopy, and molecular dynamics simulations [3]. The diffuse scattering data (Fig. 1) reveal a network of dynamic, two-dimensional disk-shaped regions of tilting lead-halide octahedra roughly 3 nm in diameter that induce intermolecular correlations within the polar $CH_3NH_3^+$ sublattice, which are reminiscent of the polar nanoregions observed in relaxors. The lifetime of the 2D and polar regions in the cubic phase of MAPI is > 3 ps. The nature of these previously unidentified structural correlations may have significant implications on charge carrier lifetimes and halide migration pathways, two properties that are considered critical to the development of stable and efficient optoelectronic devices based on hybrid lead halide perovskites.

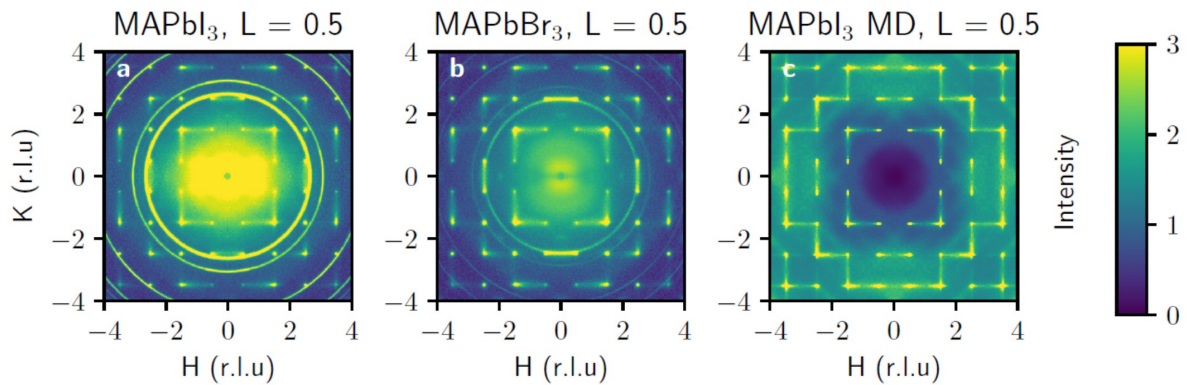


Figure 1: Neutron diffuse scattering in the $(H, K, L=0.5)$ plane measured for cubic (a) $CH_3NH_3PbI_3$ (MAPbI₃) at 335 K; (b) $CH_3NH_3PbBr_3$ (MAPbBr₃) at 250 K; (c) MD simulations of MAPbI₃ to compare to the data shown in (a).

References

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- [3] N. Weadock *et al.*, submitted.

Broadband critical dynamics in organic-inorganic lead-halide perovskites

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Organic-inorganic hybrid halide perovskites have been the subject of extensive theoretical and experimental work as promising materials for photovoltaic and optoelectronic devices [1]. These systems can be described with the well-known ABX_3 perovskite structure where the A site is occupied by a molecular cation (most commonly methylammonium or formamidinium), and B is a metal (typically Pb or Sn) located in an octahedral environment provided by the X-side (Cl, Br, or I), thus forming an inorganic framework (as shown in the figure below). We have applied high resolution neutron spectroscopy [2-4] to investigate the dynamics that drive the structural transitions in these materials, comparing organic-inorganic to the fully inorganic compounds to determine the role of the molecular dynamics in the structural phase transitions in these materials.

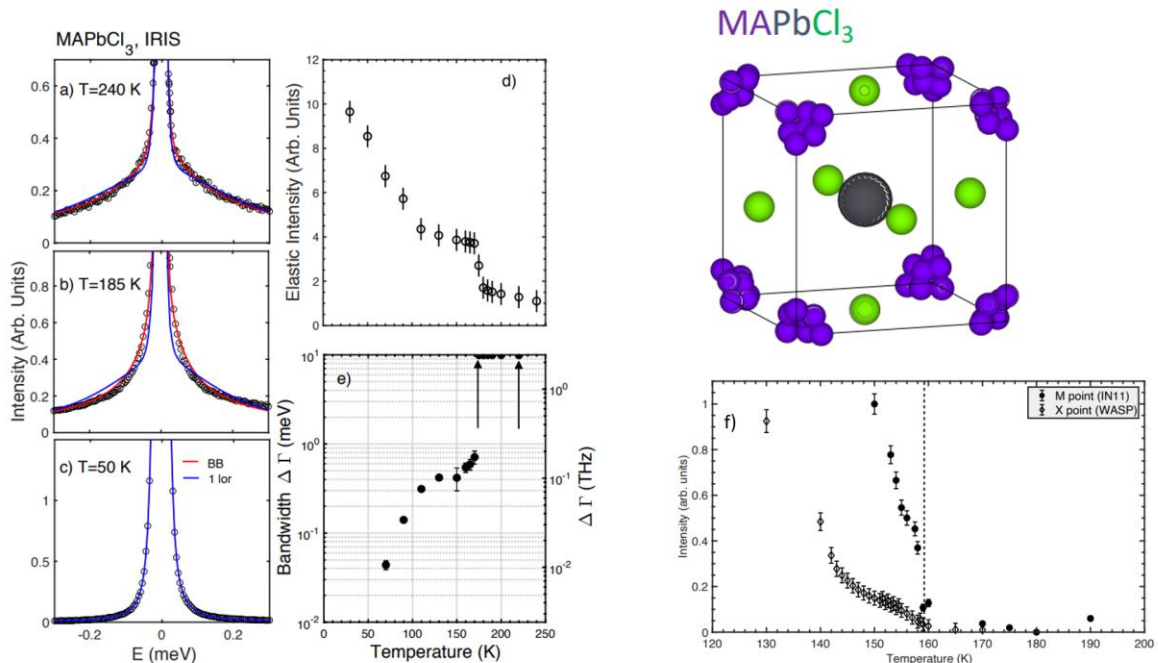


Figure 1: a-e) Backscattering data showing that a broadband of dynamics peaks drives the structural transitions in these materials. The structural transitions are characterized by the onset of resolution limited Bragg peaks (f) which do not display any measurable critical broadening in energy.

In contrast to structural transitions in perovskites where the phase transitions are driven by a single energy scale characterized by a soft transverse optical phonon, we find that the transitions in organic-inorganic perovskites is characterized by a broadband, or range, of frequencies. Applying high resolution spin-echo measurements, we observe these to drive resolution limited Bragg peaks with no measurable energy broadening, reminiscent of the “central-peak” in $SrTiO_3$ [5]. These results show that the structural transitions in the organic-inorganic perovskites are driven by a band of low energy frequencies.

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Suppression of phase transitions and glass phase signatures in mixed cation halide perovskites

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Cation engineering provides a route to control the structure and properties of hybrid halide perovskites, which has resulted in the highest performance solar cells based on mixtures of Cs, methylammonium (MA), and formamidinium (FA). Here, we present a multi-technique experimental and theoretical study of structural phase transitions, structural phases and dipolar dynamics in the mixed $\text{MA}_{1-x}\text{DMA}_x\text{PbBr}_3$ hybrid perovskites (see Fig. 1), where DMA denotes a dimethylammonium cation. Our results demonstrate a significant suppression of the structural phase transitions, enhanced MA disorder and stabilization of the cubic phase even for a small amount of DMA cations [1]. As the DMA concentration approaches the solubility limit in MAPbBr_3 , we observe the disappearance of the structural phase transitions and signatures of a glassy dipolar phase formation. We also reveal a significant tunability of the dielectric permittivity upon mixing of the molecular cations that arises from frustrated electric dipoles. We compared our findings to the related mixed cation perovskite system of $\text{MA}_{1-x}\text{FA}_x\text{PbBr}_3$ [2].

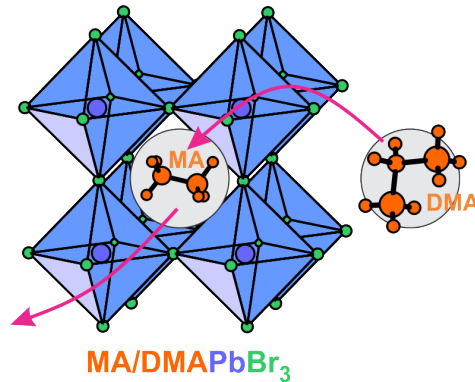


Figure 1. Cartoon representation of mixed $\text{MA}_{1-x}\text{DMA}_x\text{PbBr}_3$ hybrid perovskite.

Acknowledgements: This project has been funded by the Research Council of Lithuania (LMTLT) (agreement No. S-MIP-19-4).

References

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 [2] Šimėnas et al. Chem. Mater. 33, 5926 (2021)

On the origin of the relaxor behavior in 3D and 2D $MM'P_2S(Se)_6$ ferroics

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Layered crystals $CuInP_2S(Se)_6$ demonstrate ferrielectric and antiferroelectric ordering at thickness lowering till several structural layers [1,2,3]. The compounds of $Sn(Pb)_2P_2S(Se)_6$ system with 3D crystal lattice can reach ferroelectric or incommensurate modulated polar ordering [4] and also demonstrate double polarization switching hysteresis loops which show on the appearance of the antiferroelectric state [5]. In the mixed crystals $CuInP_2(SexS_{1-x})_6$ and in the $CuInP_2S_6$ compound the relaxor and dipole glassy states were observed at temperature lowering [6,7]. For the mixed crystals $(PbySn_{1-y})_2P_2S_6$ and $(PbySn_{1-y})_2P_2Se_6$ the relaxor-like behavior is observed near the middle of the concentration intervals, where the paraelectric state is stable till the low temperature region with dominated quantum fluctuations [8].

In this report we explain the relaxor behavior for $CuInP_2S_6$ like 2D crystals and $Sn_2P_2S_6$ type 3D crystals by similar origin, that is based within the discrete mixed Ising model [9] on $S = +1, 0, -1$ pseudospins polar fluctuations in the In^{3+} cation sublattice and $S = +1/2, -1/2$ pseudospins polar fluctuations in the Cu^+ cation sublattice of layered crystals; and on $S = +1, 0, -1$ pseudospins polar fluctuation of Sn^{2+} and Pb^{2+} cation sublattice of three – dimensional crystals. As a leading factor for the relaxor type disordering are energetically favored states with $S = 0$ for In^{3+} and Pb^{2+} cations together with the frustration of interactions between nearest and next nearest neighbors. Such frustration is described by flexoelectric coupling in continuous approximation [4,10], or in the mixed Ising Spin-1 and Spin-1/2 models [9,11] for $CuInP_2S_6$ type ferrielectrics and in the ANNNI – BC model for $Sn_2P_2S_6$ family ferroelectrics [12].

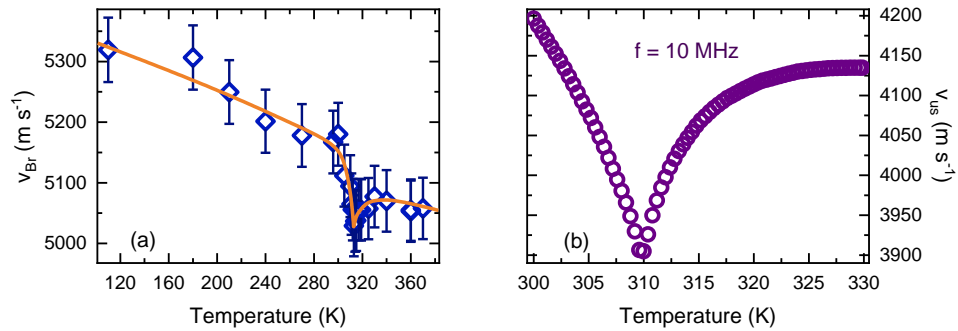


Figure 1 Temperature dependence of longitudinal hypersound velocity with the acoustic phonons propagated in the plane of the $CuInP_2S_6$ crystal layers [13] (a), and longitudinal ultrasound propagated normally to the $CuInP_2S_6$ crystal layers [14] (b).

The flexoelectric coupling was early observed by neutron scattering [10] as a linear interaction between polar soft optical and acoustic phonon branches in $Sn_2P_2S(Se)_6$ crystals. Such coupling was also clearly observed by Brillouin scattering [4,13] and at ultrasound measurements [14] as acoustic softening in the paraelectric phase at cooling to the phase transition temperature for both 3D $Sn_2P_2S(Se)_6$ crystals and 2D $CuInP_2S_6$ crystals (Figure 1).

References

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Origin of relaxor behavior in BaTiO₃-based lead-free perovskite ceramics

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Relaxor perovskites are recently the subject of intensive investigations aimed at understanding the mechanisms influencing atomic-scale polarization. These aspects, in fact, are decisive to enable tuning of the material's properties for energy storage applications, namely: how to maximize energy density and permittivity close to room temperature, at the same time minimizing leakage currents. Previous investigations suggested that compositions close to the ferroelectric-relaxor crossover are the most promising [1], however it was evidenced that different chemical substituents may impact on local polarization differently [2]. In particular, it is still debated how the long-range polarization decorrelation that is typical of relaxor can be induced on atomic scale when either homovalent or heterovalent substituents are added.

In this work, we show that in lead-free BaTiO₃ A-site or B-site heterovalent substituents greatly influence both the local strain and the electrostatic potential at the B-site through the combined effect of donor cations and B-site vacancies, and that through this mechanism they are more effective than homovalent substituents in inducing relaxor behaviour in BaTiO₃ solid solutions. We focus here on two systems, BaZr_xTi_{1-x}O₃ – BZT (homovalent substituted: Zr⁴⁺) and BaNb_xTi_{1-x}O₃ – BNT (heterovalent substituted: Nb⁵⁺). On the basis of a comprehensive integrated experimental and computational approach involving dielectric spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, Raman spectroscopy, and ab-initio calculations based on density-functional theory (DFT), we show that the extent of disorder created by substituents is higher in BNT, and evidence the presence of Ti vacancies as charge compensation scheme in BNT alone [3]. Using further molecular dynamics (MD) simulations supported by DFT, we show how long-range ferroelectric polarization can be disrupted in both BZT and BNT, and conclude that the defect arrangement present in BNT is responsible for inducing relaxor behaviour at low substituent contents. We provide also examples of A-site heterovalent substituted BaTiO₃ (with La³⁺), and B-site charge-compensated systems, which support the conclusions about the role of charge compensating defects in heterovalent-substituted BaTiO₃-based relaxors.

This study answers some open questions in the field of relaxors, and provides guidelines for tuning relaxor properties in BaTiO₃-based materials by chemical substitution.

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Polarization relaxation: about the shape, dynamics and role of coherently flipping nanoregions in Ba(ZrTi)O₃.

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Lead-free relaxor system $x\text{BaZrO}_3-(1-x)\text{BaTiO}_3$ (BZT100x) offers an interesting possibility to explore the crossover from ferroelectric BaTiO₃ to paraelectric BaZrO₃. Mixed materials show a strong and broad, frequency-dependent dielectric permittivity anomaly. Phenomenologically, the wide distribution of relaxation times can be described by introducing a proper value of the exponent in the denominator of the Cole-Cole model

$$\varepsilon^*(\omega) = \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} + \varepsilon_\infty. \quad (1)$$

but the reason for such observation calls for a microscopic insight. It is natural to postulate that the glassy character of dielectric response implies the existence of some sort of coherently fluctuating polarization nanoregions in such materials. Various possible patterns of polarization were proposed in the past, it was not clear how the shape and size of the polar nanoregions should be extracted nor how their geometry is related to

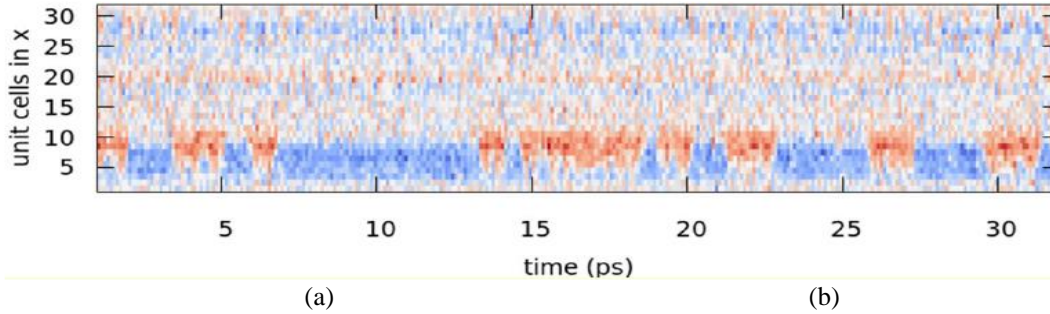


Figure 1. The color-coded temporal evolution of local polarization along B-O chain of the perovskite lattice reveals dynamics of a coherently flipping polarized nanoregion in atomistic MD simulations to be described in the contribution.

their dynamics. In this work we have thus explored spatio-temporal correlations of local polarization in BZT40 system, using 32 ps long shell-model atomistic molecular dynamics trajectories in a large simulation box containing more than 10^5 of individual atoms. In agreement with the experiments, the onset of macroscopic spontaneous polarization is not observed at any temperature. Nevertheless, the 500fs-averaged polarization field revealed multiple $\langle 100 \rangle$ -oriented, and few unit cell long chains, in which the chain-parallel polarization components were large and ordered uniformly. These polarized chains systematically occur whenever several Ti-O bonds happened to be arranged in a row. In particular, simulations conducted at $T=0.95T_{c0}$ where T_{c0} is the temperature of the ferroelectric phase transition of pure BaTiO₃ were used to reveal (i) that mutually perpendicular chains can intersect, (ii) that most of the chains are static at the 10ps scale, (iii) that some of the chains show repeated correlated 180 degree switching with few ps relaxation time, and (iv) how this switching is combined with sliding of the polarized region. Moreover, it was found that the relaxation time is slightly slowing down upon cooling and that the fraction of Ti sites with few ps relaxation time has a maximum of about 15 percent of all Ti sites near temperature of about $T=0.8T_{c0}$.

Most importantly, this work reveals the explicit geometry and dynamics of coherently flipping regions (CFRs), and it allows to relate their dynamics to the central mode, known from the ultrabroadband dielectric spectroscopy study [1]. Acknowledgement and support from the Czech-Austrian funding via GACR project LA 20-20326L and several colleagues from MCL Leoben, Austria will be included and detailed in the presentation.

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Advanced ab-initio approaches for the characterization of relaxor ferroelectrics

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While it is well known that relaxor behavior is only found in doped systems, the exact mechanisms of how different dopants disrupt the long-range ferroelectric order are still an active subject of investigation. A major question in this context is how doping affects the local atomic structure in terms of charge distribution and strain, and how these quantities in turn influence the macroscopic dielectric response of a material. In order to get deeper insight in the atomistic mechanisms at play in relaxor ferroelectrics, we have advanced atomistic simulations with respect to two methods: On the one hand, we have extended the ab-initio methodology for the prediction of Raman spectra towards polar ceramics, which proves to be a versatile tool for getting deep insights into the atomic structure from measured Raman spectra of ferroelectric/relaxor materials. On the other hand, we have developed an improved effective Hamiltonian approach for BaTiO₃ (BTO) based perovskites in order deliver better quantitative predictions of their macroscopic properties. In this work, we present the details of the aforementioned methodologies and show how they perform for a selection of prominent use cases. Concerning the prediction of Raman spectra for polar materials, we show the performance of this method in simple perovskite and wurtzite polycrystals [1], and apply it to unraveling the defect structure in BTO based relaxors with both heterovalent and homovalent doping [2]. Regarding our novel effective Hamiltonian approach, we have systematically extended the established effective Hamiltonian [3,4] based on soft-mode displacements, towards the incorporation of additional optical modes contributing to the local polarization [5]. First, we show how these optical modes renormalize the potential energy surface. Then we present results of large-scale molecular dynamics simulation based on our new effective Hamiltonian, which lead to a much better quantitative prediction of the phase transition temperatures and dielectric properties of BTO-based perovskites.

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Relaxing in Weird Places

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Relaxor ferroelectric materials have been widely studied due to both the scientific curiosity into their peculiar microscopic behavior and the need for temperature-stable capacitors and precision actuators. In this talk, we will discuss our new study of well-known prototype relaxor PMN-PT and recently discovered BaTiO₃ based relaxors.

Nano-scale electronic devices possess promising functionalities due to their reduced weights and power consumption. It is also well known that the physical properties of many functional materials change significantly as their sizes are reduced to nano-scale thin films. Especially, the change of relaxor behaviors with thickness and the underlying mechanism have not been thoroughly investigated. In this talk, we will take the prototype relaxor 0.68PbMg_{1/3}Nb_{2/3}O₃–0.32PbTiO₃ (PMN-PT) as an example and discuss how the surface and depolarization field effects influence its relaxor properties.

Unlike lead-based relaxors PMN and PMN-PT, bulk BTO-based relaxor (1-*x*) Ba_{0.8}Ca_{0.2}TiO₃-*x* Bi(Mg_{1/2}Ti_{1/2})O₃ (BCT-BMT) ferroelectrics are characterized by *A*-site disorder and *B*-site polarization.[1] Our study shows that the dielectric constant will be significantly flattened by doping BMT. Compared to PMN-PT which has domain size around 5 nm, we found that the domain size of 0.5BCT-0.5BMT is around 1 nm. [2] This microscopic difference in mechanism leads to smaller, temperature independent correlation lengths and ultimately the desired ultra-flat dielectric response. Looking at individual atomic response, we found that Ti displacement is considerably enhanced by the surrounding Bi. More importantly, we found that Ti relaxation time is also increased by the neighboring Bi, thus nonuniform temperature dependent response, which also contribute to flat dielectric response.

We recently found that superlattices based on ferroelectric BaTiO₃ and dielectric SrTiO₃ produce exotic dipolar textures, which dielectric studies and subsequent Vogel-Fulcher analysis associate with relaxor-like behavior. Bond-valence molecular dynamics simulations suggest that the relaxor-like behavior observed experimentally arises from shape variations of the dipolar configurations, which provides a route to tuning relaxor behavior by superlattice periodicity and reveals that relaxor behavior can emerge in structures without chemical inhomogeneity like solid solutions.[3] We also introduce the use of two-dimensional discrete wavelet transforms to capture information about spatial order in the polarization profile and its temperature dependence, which sheds light on the relationship between dipolar dynamics and superlattice structure.

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Direct Observation of Ferroelectricity in Two-Dimensional MoS₂

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Recent theoretical predictions of ferroelectricity in two-dimensional (2D) van der Waals materials reveal exciting possibilities for their use in scalable low-power electronic devices with polarization-dependent functionalities. These prospects have been further invigorated by the experimental evidence of the polarization response in some of transition metal chalcogenides (TMCs) - a group of narrow-band semiconductors and semimetals with a wealth of application potential. Among the TMCs, molybdenum disulphide (MoS₂) is known as one of the most promising and robust 2D electronic materials. However, in spite of theoretical predictions, no ferroelectricity has been experimentally detected in MoS₂, while emergence of this property could enhance its potential for electronics applications. Here, we report the experimental observation of a stable room-temperature out-of-plane polarization ordering in 2D MoS₂ layers, where polarization switching is realized by mechanical pressure induced by a tip of a scanning probe microscope. We have found an unambiguous evidence of a stable antipolar structure consisting of the monolayers with randomly alternating polarization orientation, which form stable but switchable “antipolar” head-to-head or tail-to-tail dipole configurations. The oppositely polarized layers exhibit different piezoelectric activity, second harmonic generation signal, surface potential and conductivity. Ferroelectric MoS₂ belongs to the distorted trigonal structural 1T’ phase, where a spontaneous polarization is inferred by its P3m1 space-group symmetry and corroborated by theoretical modeling. The coexistence of switchable polarization and metallic conduction makes 1T’-MoS₂ a member of a handful of materials with this unique property. Overall, the experimental demonstration of ferroelectricity in 2D molybdenum disulphide opens new perspectives for the fundamental studies of this compound and enables new functionality, which could be exploited in novel electronic applications.

What the hell is a uniaxial relaxor?

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Traditional relaxors are mainly isotropic due to its macroscopic cubic structure. The archetype of relaxor materials is $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, which possesses a cubic perovskite structure and displays the fingerprint of the relaxor behaviour, basically defined by a strong dispersion in frequency and temperature of the dielectric response. The maximum of the permittivity $\epsilon'(T)$ is broad and both temperature and frequency dependent. Nevertheless, other families show also this relaxor behaviour. The tetragonal tungsten-bronze (TTB) structure is one of the most fruitful structures producing relaxor behaviour apart from perovskites. One of the features of this family is its uniaxial character, which provides the structure with an anisotropic behaviour in most of its properties, and challenges the microscopic and atomistic interpretation of cubic relaxors. The relaxor behaviour is manifested along the main axis and, perpendicular to it, most of TTBs show a glassy behaviour at low temperatures related to the disorder created by modulated oxygen positions [1,2]. The coexistence of these two effects is still puzzling. Because of the flexibility of their dielectric properties, the unfilled TTB family has been explored more thoroughly, especially its major representative $(\text{Sr}_x\text{Ba}_{1-x})_5\text{Nb}_{10}\text{O}_{30}$ SBN-X, ($X=100x$). SBN shows a perfect tuneable relaxor-ferroelectric behaviour depending on the amount of Sr present in the lattice [1].

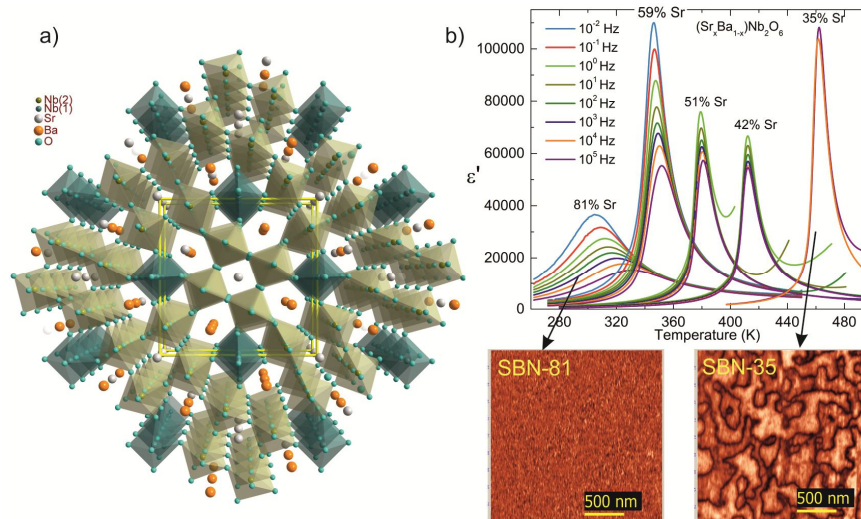


Figure 1 Structure and dielectric permittivity of tetragonal tungsten bronze SBN. (a) Structure of the paraelectric phase. (b) Permittivity for various compositions together with PFM micrographs for relaxor (SBN-81) and ferroelectric (SBN-35) compositions.

The understanding of the anisotropy and its relation to the ferroelectric-relaxor character and to the dielectric response is fundamental. Mainly because, for practical uses, ceramics are better suited. However, in this case both responses are mixed and they are difficult to separate in order to assign a proper microscopic origin. An attempt to understand the polar dielectric response reveals one of the most complicated features of this materials: the coexistence of several relaxations related to different polarization mechanisms with various correlation lengths. All of them show dissimilar behaviours with temperature, pointing out to their distinct nature. This complex response reveals also the coexistence of displacive and order-disorder scenarios in this family [2]. In addition, SBN has been found to show two different ferroelectric subsystems within its structure related to distinct Nb atoms, which create two different polar regions of dissimilar lengths and volumes associated with the polarization mechanisms [3]. This in overall creates a totally different mechanism for the genesis of the relaxor behaviour in this uniaxial material.

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Unraveling correlated disorder in relaxor $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$

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Fundamental understanding of the origins of dielectric relaxation and ways to control the relaxor-to-ferroelectric crossover in tetragonal tungsten bronzes (TTB) continues to attract the interest of materials science and physics communities. Despite decades of research, the exact nature of structural distortions in these systems and the mechanisms of their dielectric and polar responses remain uncertain. Many studies into the structure and properties of TTBs concentrated on $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN) solid solutions ($0.33 \leq x \leq 0.82$), which exhibit electro-optic and piezoelectric properties of practical interest, with the polar response changing from ferroelectric to relaxor as the Sr/Ba ratio increases to $x > 0.5$ [1]. Like many other members of this structural class, SBN compositions exhibit an incommensurate modulation attributable to octahedral tilting. However, the pattern of octahedral rotations involved and the nature of the incommensurate periodicity are unknown. Recent studies in SBN using molecular-dynamics simulations and structural refinements from neutron total-scattering data provided some insights into the behavior of local atomic displacements [2-4]. Yet, a coherent picture of the various structural effects that co-exist in SBN and their roles in the relaxor behavior remained elusive.

Here, we aim to advance the understanding of the correlated displacive disorder in SBN by performing further in-depth analyses of its local and nanoscale structures using atomistic structural refinements via simultaneous fitting of neutron powder total-scattering data and three-dimensional distributions of X-ray diffuse-scattering intensity from single crystals. In such refinements, an instantaneous structure is described using a large-scale atomic configuration, and atomic coordinates are varied according to the reverse Monte Carlo algorithm to fit the data. We focused on $x=0.61$ as a representative relaxor composition. Ba and Sr EXAFS were also included in the fit to resolve the coordination around these species. Guided by the input from transmission electron microscopy, which points to a one-dimensional character of the incommensurate modulation, we treated our atomic configurations as assemblages of twin nanoscale domains having orthogonal directions of the modulation vector. The refinements, which were performed for a series of temperatures across the ferroelectric phase transition, revealed the types of octahedral rotations yielding the incommensurate modulation and provided new details regarding the effects of local chemistry on polar displacements and their spatial correlations. This talk will discuss our findings and their implications for interpreting a polar response in TTBs.

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Dielectric spectroscopy and piezoelectric properties of lead-free $\text{BaTiO}_3 - x\text{Bi}(\text{Zn}_{2/3}\text{Nb}_{1/3})\text{O}_3$

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Lead-based relaxors are a type of material, exhibiting high dielectric constants and slim polarization curves. For these reasons, they are widely used as capacitors, sensors, as a memory elements. Some of examples of such materials are lead magnesium niobate or lead scandium niobate. However, such materials contain lead, which, can cause damage to the ecosystem and human health. One possible alternative to replace aforementioned composites are barium titanate-based compositions, in particular novel solid solution $\text{BaTiO}_3 - x\text{Bi}(\text{Zn}_{2/3}\text{Nb}_{1/3})\text{O}_3$ (BTO-xBZN), $3.6\% < x < 7.0\%$.

It was previously reported that the composition undergoes a ferroelectric-relaxor structural phase transition in the concentration range of $4.0\% < x < 5.0\%$ [1]. However, there is still uncertainty regarding the phase composition around the boundary. Additionally, the dielectric properties were reported only for low frequency range.

The present work examines the dielectric properties in wide frequency (20 Hz – 36 GHz) and (120 – 500 K)

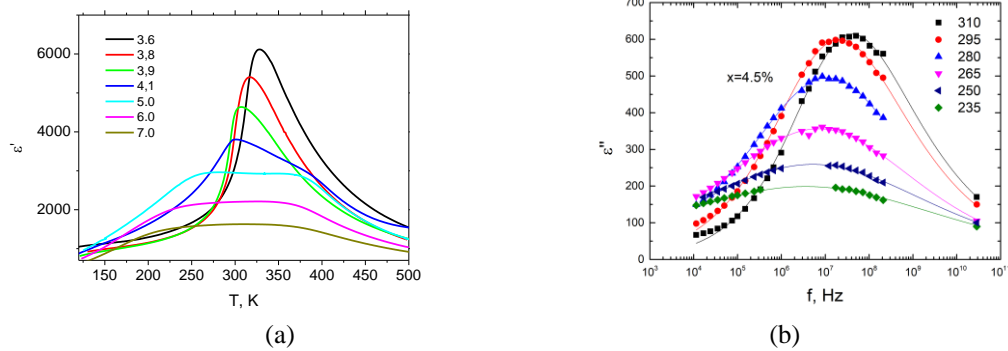


Figure 1 Dielectric permittivity of the samples with different concentrations of $\text{Bi}(\text{Zn}_{2/3}\text{Nb}_{1/3})\text{O}_3$ as a function of temperature. (a) Imaginary part of the dielectric permittivity of the BTO – 4.5BZN sample. Symbols denote measured data and solid lines are fits with Cole-Cole law (b).

temperature ranges. It was demonstrated that increase of the $\text{Bi}(\text{Zn}_{2/3}\text{Nb}_{1/3})\text{O}_3$ peak of the dielectric permittivity decreases and vanishes. The frequency dependence of the permittivity reveals the relaxation behavior. The Cole-Cole and Davidson-Cole functions were applied for the detailed analysis (see figure 1 (b)).

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²³Na Nuclear Magnetic Resonance Longitudinal and Transverse Spin Relaxation times (T_1 , T_2) Study of $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ -6mole% BaTiO_3

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Among the several models that have been proposed to explain the unusual properties of relaxors based on their microstructure, the most widely accepted model describes the coexistence of polar nanoregions (PNRs) embedded in a non-polar (cubic) matrix.[1] This model was supported by a previous Nuclear Magnetic resonance (NMR) study on relaxor $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ -6mole% BaTiO_3 at room temperature, wherein the ratio between the intensities of the two main components of the ²³Na NMR spectra: central band (CB) and spinning sidebands envelope (SSE) decreased by almost 42% for the relaxor (unpoled) state compared to the ferroelectric (poled) state.[2] However, the current study of NBT-6BT by variable temperature ²³Na NMR disproves the existence of a cubic phase and finds that the decrease of the intensity SSE/CB ratio is due to a significant intensity decrease of the SSE component without any increase or conservation of the intensity of the CB (Figure 1a). This strong decrease of SSE intensity could be related to a shortening of the transversal relaxation time (T_2). A very short time (T_2') in the unpoled state is observed as well as in the poled state but only when temperature reaches 353 K from T_2 of satellites (Figure 1b). The above reveals the existence of a low frequency motion in the relaxor state related to the rotational fluctuations of the oxygen octahedral.[3] Furthermore, temperature dependence of the longitudinal relaxation rates (T_1^{-1}) (Figure 1c) indicates that the relaxation mechanism depends on electrical history of NBT-6BT. While for the unpoled state the relaxation is caused by the coupling of fluctuating magnetic field to the nuclear spin (magnetic mechanism), in the poled state, the relaxation is mainly induced by the coupling of a fluctuating electric field gradient with the nuclear quadrupolar moment of ²³Na spin (quadrupolar mechanism). In the poled state, the change from one relaxation mechanism to the other is clear at $T_{F-R}=377$ K, but already starts around 353 K. The temperature dependency in the relaxation rate (T_1^{-1}) of unpoled NBT-6BT may be interpreted as spin-phonon interaction with interference of anharmonic dynamics. The results from temperature dependence of ²³Na NMR spin relaxation (T_1 , T_2) propose that the relaxor state in NBT-6BT is directly related to the dynamics of the lattice where the oxygen octahedral tilting may play a predominant role.

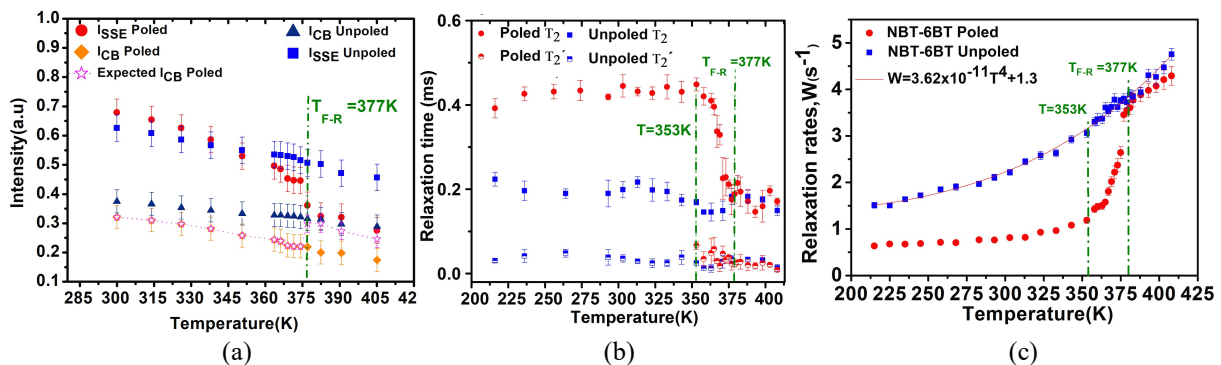


Figure 1 Relative intensity of the spectral components SSE (poled: red circles, unpoled: blue squares) and CB (poled: orange rhombuses, unpoled: navy triangles and expected CB for cubic phase: magenta stars) as a function of temperature. (a) Transversal relaxation times (T_2) of satellites in NBT-6BT unpoled and poled. (b) Longitudinal relaxation rates (T_1^{-1}) for NBT-6BT unpoled and poled. (c)

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Neutron backscattering studies of relaxor ferroelectrics

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The typical strong dielectric relaxation of relaxor ferroelectrics is supposed to be associated with correlated atomic displacements, whose presence is well documented by numerous neutron and X-ray diffuse scattering studies [1]. Particularly, inelastic neutron scattering techniques allow in principle to resolve dynamics of these correlated displacements. In total, neutron instruments cover energy range 10^{-5} – 10^3 meV (10^{-6} – 10^2 THz) which partly overlaps with typical relaxation frequencies seen by dielectric spectroscopy from Hz to sub-THz range (10^{-12} – 10^0 meV) [2]. To be able to trace and to directly link dielectric relaxations to neutron spectra, one has to combine several different inelastic neutron scattering techniques to cover multiple orders of magnitudes in neutron energy transfer [3–6].

This contribution will present the results obtained by neutron triple-axis and backscattering measurements which permit to follow the relaxor ferroelectric response down to the μ eV range (0.1–10 GHz) [4–5]. We will present a clear inelastic component in neutron backscattering spectra of two representatives of relaxor ferroelectrics with distinctly different crystallographic structures: the canonical relaxor $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN, see Figure 1) with

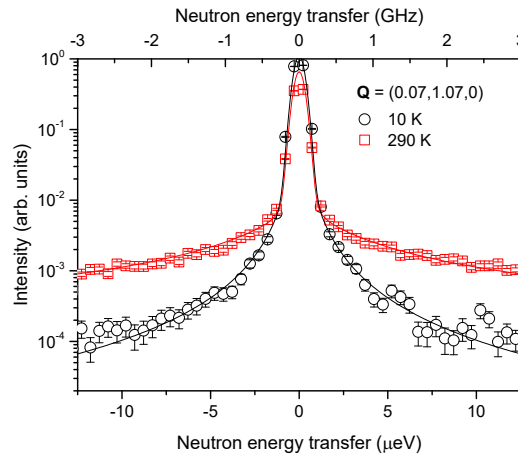


Figure 1 Neutron backscattering spectra of PMN single crystal measured at a wing of the well-known butterfly-shaped diffuse scattering using the high-resolution neutron backscattering spectrometer IN16B at ILL, Grenoble [8]. The spectrum, taken above the freezing temperature (≈ 200 K [2]), shows a clear inelastic component of the diffuse scattering. The solid lines are guides for eye.

perovskite structure and uniaxial relaxor ferroelectric $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ (SBN61) having tetragonal tungsten bronze structure [1, 6–8]. We will show that correlated atomic displacements manifested in this inelastic diffuse scattering can be directly related to the polarization fluctuations responsible for the Vogel-Fulcher-type dielectric behavior of these relaxor ferroelectrics [6, 8].

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About the origins of the large nonlinear response in relaxor ferroelectrics

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Relaxor ferroelectric perovskites are characterized by an intrinsic charge disorder that crucially affects their structure and properties at all length scales. In the $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-xPbTiO}_3$ (PMN–PT) relaxor ferroelectric system, Pb^{2+} occupies the A-site of the ABO_3 perovskite structure and mixed occupancy of cations of different ionic size and charge (i.e., Mg^{2+} , Nb^{5+} , Ti^{4+}) is on the B-site. While in tetragonal PMN–PT compositions ($x > 0.35$) Ti^{4+} is believed to increase charge ordering, leading to a long-range ferroelectric order, monoclinic compositions (up to $x \sim 0.35$ PT) are strongly influenced by the B-site positional disorder, as well as the local off-centring of the Pb^{2+} cations. This local disorder significantly impacts the domain structure of relaxor ferroelectrics, which are build-up of nanodomains separated by the so-called low-angle domain walls, in a hierarchical arrangement with the wedge-shaped micro-scale domains. These interfaces were observed to be highly mobile with an applied electric field and their unique dynamics was shown to contribute to strongly nonlinear and hysteretic weak-field responses, greatly affecting the global behaviour of lead-based relaxor ferroelectrics.

In this contribution I will present the local structural features of several PMN–PT compositions, analysed by atomic-resolution electron microscopy, in particular the Pb-positional disorder which is believed to play the key role in the relaxor behaviour of this system. The composition-dependent multiscale structure (from atoms to domains and long-range symmetry) will be further linked to the macroscopic dielectric and piezoelectric response of relaxor ferroelectrics, and compared to the ‘normal’ ferroelectric materials (namely, PZT with no charge disorder on the B-site). The revealed softening effects in these functional materials will be discussed with respect to the interface dynamics.

Phase Evolution and Ferroelectric Properties of BiFeO₃-BaTiO₃ Ceramics around Morphotropic Phase Boundary

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BiFeO₃-BaTiO₃ (BF-BT) ceramics have attracted attention as a candidate lead-free piezoelectric ceramic because of its excellent piezoelectric properties [1,2]. The phase has been reported to change from a ferroelectric rhombohedral (R3c) to relaxor pseudo-cubic at approximately 0.3BT when the BT content increases in a BF-BT solid solution, and the highest piezoelectric properties have been reported around the morphotropic phase boundary (MPB). Many studies have reported piezoelectric properties and crystal structure evolution in samples with chemical compositions around the MPB. Discrepancies, however, exist in the crystal structures at the MPB and piezoelectric properties around the MPB. The rhombohedral phase and a pseudo-cubic phase have been reported to coexist around the MPB [3]. Some researchers, however, claimed that a tetragonal phase (P4mm) or a monoclinic (Cm) phase coexisted with the rhombohedral phase around the MPB [2,4]. The piezoelectric properties and the crystal structure are quite sensitive to the fabrication process conditions such as the sintering temperatures and the cooling rate.

In this work, (1-x)BF-xBT ceramics ($x = 0.2 - 0.4$) were prepared with nano-sized BT powder to enhance chemical homogeneity. Crystal structures and phase boundary were analyzed by Rietveld refinements with X-ray diffraction data. Domain structures were observed using SEM and TEM. Temperature-dependent dielectric permittivity was measured to investigate phase transition behavior. Ferroelectric P-E hysteresis and piezoelectric properties were measured. The crystal structure evolutions, phase transition behaviors and ferroelectric properties were investigated in quenched and slowly-cooled BF-BT ceramics around MPB.

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Relaxor terpolymers P(VDF-TrFE-CFE) for electrical energy storage

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Ferroelectric polymers, such as polyvinylidene fluoride P(VDF) and its copolymers with trifluoroethylene (TrFE), hexafluoropropylene (HFP), chlorofluoroethylene (CFE), and chlorotrifluoroethylene (CTFE), exhibit high polarizability, which makes them promising materials for electrical energy storage applications [1]. Ideally, all the stored energy should be recoverable, which entails that the remanent contribution to polarization should be small. In ferroelectric polymers, saturation and remanent polarization often do not differ much, which is unfavorable for the recoverable energy storage density, which is defined by the area between the discharging part of the polarization hysteresis loop and the polarization axis. Therefore, materials with high polarizability and a slim hysteresis loop are more suitable for energy storage applications. Such a combination of properties is typical for relaxors. The relaxor behavior in P(VDF-TrFE) copolymers can be achieved by incorporation of a bulky monomer such as chlorofluoroethylene (CFE), hexafluoropropylene (HFP), or chlorotrifluoroethylene (CTFE) into P(VDF-TrFE) chains.

In this presentation we report the dielectric and polarization properties of some new P(VDF-TrFE-CFE) compositions. The relaxor behavior was confirmed for all the studied samples. Increasing the CFE content shifts the freezing temperature down and stabilizes the ergodic relaxor state at room temperature. The application of a sufficiently strong electric field induces a transition to a ferroelectric state, as manifested in double hysteresis loops. The critical field corresponding to this transition depends on the composition and temperature. It becomes larger at temperatures far from the freezing temperature [2].

Energy storage performance is evaluated based on the analysis of unipolar polarization hysteresis loops. P(VDF-TrFE-CFE) 59.8/40.2/7.3 has an energy density of about $5 \text{ J}\cdot\text{cm}^{-3}$ (at the field of 200 MV/m) and a charge-discharge efficiency of 63%, which is comparable to the best literature data for the terpolymers.

A further improvement in energy storage characteristics was achieved by adding $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ inorganic relaxor nanoparticles. In the studied electric field range (below 125 MV/m), the discharge energy density for the obtained composites significantly exceeds the values reported in the literature [3].

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Relaxor to Ferroelectric Crossover in the Lead-Strontium Zirconate-Titanate Perovskite Solid Solution System

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To explore lead-reduced dielectric materials in the SrTiO₃-PbTiO₃-PbZrO₃ ternary system, a novel solid solution between relaxor ferroelectric (Pb_{0.5}Sr_{0.5})(Zr_{0.5}Ti_{0.5})O₃ and ferroelectric PbTiO₃, namely (1 - x)(Pb_{0.5}Sr_{0.5})(Zr_{0.5}Ti_{0.5})O₃-xPbTiO₃ (lead-strontium-zirconate-titanate [PSZT]-PT), has been synthesized in the perovskite structure by high-temperature solid-state reaction method in the form of ceramics. The ternary phase diagram is shown in the Figure 1. The crystal structure and phase symmetry of the materials synthesized were analyzed and resolved based on X-ray powder diffraction (XRD) data through both the Pawley and Rietveld refinements. The results of the structural refinements indicate that at low PT-concentration end of the solid solution system, for example, x = 0.05, the PSZT-PT solid solution exhibits a cubic structural symmetry (with the space group *Pm-3m*). As the PT concentration (x) increases, the structure of (1 - x)PSZT-xPT gradually transforms from the cubic to a tetragonal (*P4mm*) phase. In the composition range of x = 0.10 - 0.25, a mixture of the cubic and tetragonal phases was identified. As the concentration of PT increases, the proportion of the tetragonal phase increases at the expense of the cubic phase. For a composition of x > 0.25, a pure tetragonal phase is observed. The dielectric properties of the materials were studied by measuring the permittivity as a function of temperature at various frequencies. For the composition of x = 0.05, the temperature dependence of dielectric constant shows a relaxor behaviour with a broad and frequency dependent dielectric anomaly. For the compositions of x = 0.10 ~ 0.25, a crossover from the relaxor behaviour to normal ferroelectricity was observed, accompanied by double peaks on the dielectric permittivity. For x ≥ 0.275, the dielectric peaks become sharper and show no frequency dispersion, indicating a normal ferroelectric phase. In addition, the Curie temperature (T_C) of the PSZT-PT samples shifts towards higher temperatures as x increases. Interestingly, the room-temperature dielectric constant of PSZT is greatly increased by the substitution of PT, reaching 3,032 for x = 0.20 (at 1 kHz), making this material a new candidate for multilayered ceramic capacitors.

The dielectric data of the PSZT-PT solid solution samples were fitted with various formalisms and equations to obtain critical parameters, such as the freezing temperature, the Burns temperature, etc., to characterize the relaxor behaviour. Moreover, the polarization - electric field relation transforms from a narrow nonlinear shape to a wide-open hysteresis loop with increasing remanent polarization and coercive field, confirming the crossover from the relaxor state to ferroelectric phase with increasing PT concentration in the PSZT-PT binary system. Finally, the domains of nanometer size were revealed by transmission electron microscopy (TEM) in the relaxor phase, which are assigned as the polar nanoregions. These domains grow into macroscopic domains in the ferroelectric domain. In general, the macroscopic crossover from relaxor ferroelectric behaviour to normal ferroelectric properties can be attributed to the effects of the substitution of the ferroelectrically active Pb²⁺ and Ti⁴⁺ ions for the non-ferroelectrically active Sr²⁺ and Zr⁴⁺ ions, which causes a series of intriguing transformations on multiple scales, from nano-domains to macro-domains, from non-polar cubic structure to polar tetragonal structure. Thus, the analysis of the crystal structure, dielectric, ferroelectric and domain properties provides a general picture of an interesting relaxor to ferroelectric crossover phenomenon in the PSZT-PT solid solution and allows us to construct overall phase diagrams.

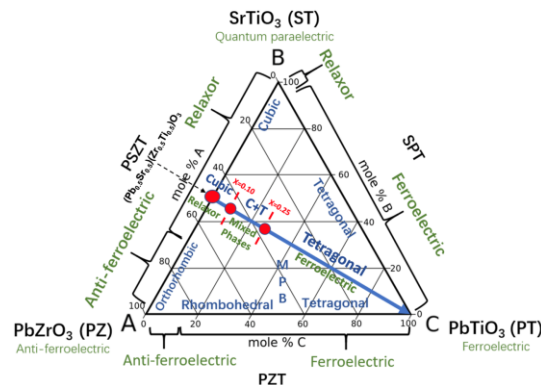


Figure 1. The ternary phase diagram of the SrTiO₃-PbTiO₃-PbZrO₃ system with the composition series of (1-x)(Pb_{0.5}Sr_{0.5})(Zr_{0.5}Ti_{0.5})O₃-xPbTiO₃ shown as the blue line. Different phases and structural symmetries and various properties are illustrated in blue and green characters, respectively.

Optimization of Piezoelectric Properties of Relaxor-based Crystals via Domain Engineering

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A versatile strategy for the design of ferroelectric materials includes the selection of an appropriate chemical composition followed by the development of fabrication conditions. In relaxor-based solid solutions, $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ (PMNT), $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ (PZNT) and related relaxor single crystals, the compositions corresponding to the morphotropic phase boundary (MPB) are known to be unique in terms of the properties they possess. In fact, PMNT, PZNT and related relaxor single crystals may exhibit record high piezoelectric characteristics in MPB composition range. To achieve such excellent performance the domain engineering is used, that is, preparation of crystals with the optimal domain structure. The direction and configuration of domains may greatly influence the piezoelectric coefficients, since the properties of relaxor-based crystals are highly anisotropic. Besides, it has been widely believed that the domain boundaries significantly increase the piezoelectric coefficients. However, our piezoresponse force microscopy investigations of local piezoeffect in domain engineered PMNT crystals demonstrated that d_{33} piezoelectric coefficient is significantly (almost twice) *reduced* within the distance of $\sim 1 \mu\text{m}$ from the domain wall inclined to the surface of the crystal. This allowed us to suggest that to increase macroscopic d_{33} it would be useful to fabricate the crystals oriented and poled along a nonpolar direction, but free from domain walls [1]. However, this suggestion has not been realized until recently because of the difficulties in the preparation of wall-free domain engineered relaxor-PT crystals. It is only in 2020 that a simple method was found for the fabrication of [001]-oriented rhombohedral PMNT crystals not containing inclined domain walls [2]. In this method an AC voltage is applied to pole the crystals instead of the commonly used DC voltage. It was found that elimination of domain walls leads not only to higher d_{33} , but also makes the crystal transparent, providing a route to applications in novel hybrid electromechano(ultrasound)-optical devices.

In this talk, we report our investigations of the influence of poling conditions on piezoelectric and dielectric properties of PMNT single crystals with a composition close to the MPB and also the relation between the properties and the crystal domain structures of AC and DC poled crystals.

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Broadband dielectric properties of the $\text{BaTiO}_3\text{--BaZrO}_3$ solid solutions

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Broadband dielectric spectra (from Hz up to THz and infrared frequencies) of the $x\text{BaZrO}_3\text{--}(1-x)\text{BaTiO}_3$ (BZT) ceramic solid solutions will be presented. We studied the BZT system in a broad (almost complete) concentration range and in a broad temperature range from 10 to 700 K.

BZT is a model lead-free system which, depending on the concentration x , behaves as incipient, relaxor, diffuse or classical ferroelectric material. The behaviour is compared to that of pure BaTiO_3 and BaZrO_3 end members. Based on the results of the broadband fits of the spectra, we will discuss different processes and their origin that play role in the dynamics, such as (soft) phonons and relaxations. The spectra are characterized by an overdamped central mode in the microwave range which weakens on cooling. Except for BaTiO_3 , the soft mode and central mode do not soften appreciably and do not contribute substantially to the low-frequency permittivity maximum. The most important dielectric contribution is brought by Cole–Cole relaxation assigned to hopping of Ti ions in the BaTiO_3 clusters, which obeys the Arrhenius law.

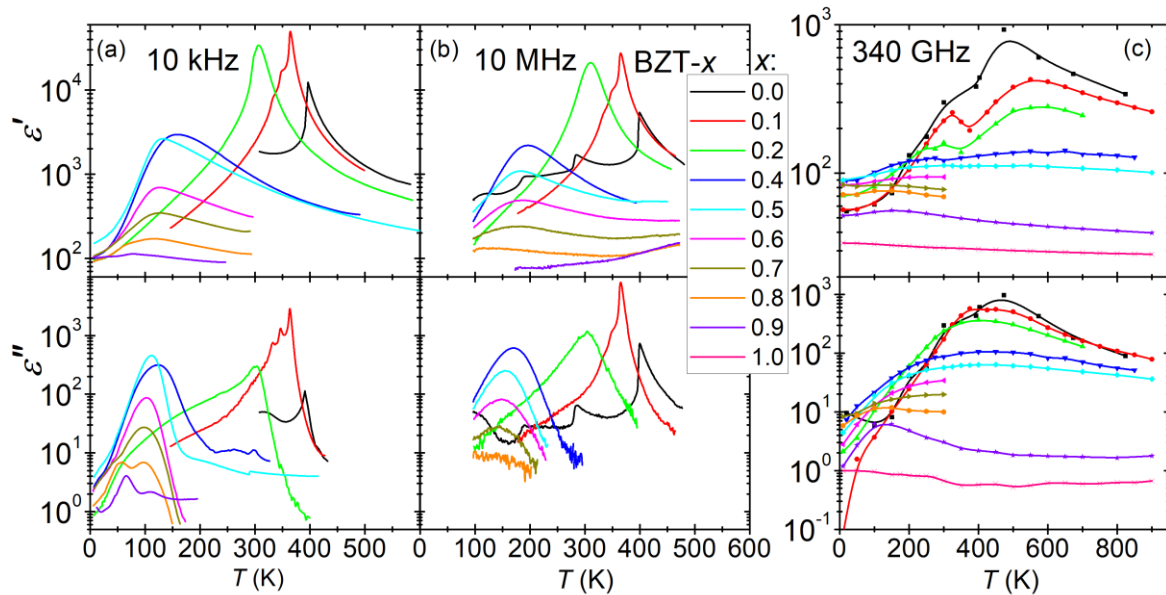


Figure 1 : Temperature dependences of the complex dielectric permittivity of BZT- x for three selected frequencies up to the THz range: a) 10 kHz, b) 10 MHz, and c) 340 GHz [1].

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Influence of dopant ions on mechanical and dielectric properties of $K_{0.5}Bi_{0.5}TiO_3$ ceramics

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One of the main requirements of the European Union is to search for safe and ecological materials that can replace compounds containing toxic elements such as: lead - Pb, cadmium - Cd, mercury - Hg and hexavalent chromium - Cr⁶⁺. These expectations were described in the Directives of the European Union such as: RoHS (The Restriction of Hazardous Substances in Electrical and Electronic Equipment) and WEEE (Waste of Electrical and Electronic Equipment). The RoHS directive specifies the value of the maximum weight concentration of elements in a homogeneous element, which should be 0.1% (0.01% for cadmium) [1, 2].

Such materials should represent properties similar to PbZrO₃-PbTiO₃ (PZT) or better [3, 4]. One of the most promising compounds in recent years has become bismuth-potassium titanate $K_{0.5}Bi_{0.5}TiO_3$ (KBT) [5].

This study attempts to answer how selected doped ions: cerium - Ce, strontium - Sr, calcium - Ca and manganese - Mn influence the technology and selected properties of KBT. First of all, the basic parameters, i.e. the apparent density of the obtained materials, were evaluated. The microstructure of the obtained materials was assessed by means of scanning electron microscopy (SEM). A study with use of X-ray diffraction was taken, it will allow to answer the key question - whether the obtained materials are single-phase or multiphase. The influence of dopant ions on mechanical and dielectric properties was assessed.

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Dielectric and NMR studies of $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ solid solutions

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Dielectric properties of barium titanate-based relaxor ferroelectrics has been the subject of debates for several years. Relaxor behaviour occurs substituting titanium ions with ferro-inactive isovalent substitutions like Zr^{4+} , Ce^{4+} or Sn^{4+} . However, charge disorder was considered to be the cornerstone for the relaxor behaviour. Unlike in Pb-based relaxors, it is absent in BTO-based relaxors. Such different behaviour motivated research which showed that lead displacements in PMN-based relaxors cannot be neglected and contributes to the appearance of relaxor behaviour together with the charge disorder at the B site [1,2].

BTO-based relaxors were considered as simpler systems which are very useful for understanding relaxor phenomenon, but many disputes whether to call it relaxor or dipolar glass can be found in the literature [3–7]. Thus, the necessity to proceed the investigation further is necessary to finalize the picture of the relaxor/glass-like behaviour in BTO-based solid solutions.

In this contribution we will focus on the Sn^{4+} substituted barium titanate ($\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$) in the crossover region (i. e. $0.15 \leq x \leq 0.3$) between ferroelectric and relaxor behavior. The dynamics of the crossover will be studied by broadband dielectric spectroscopy methods from milihertz to terahertz range. The dielectric relaxation of these compounds will be compared to BZrT and BCeT.

The NMR studies will reveal insights about the local environment of ferroelectrically active Ti^{4+} ions. For that matter, ^{119}Sn , ^{137}Ba , $^{47,49}\text{Ti}$ were probed by conventional Hahn-echo experiments in 200–350 K temperature interval.

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Relaxors for neuromorphic computing

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An artificial neural network is basically an ensemble of neurons connected by weighted synaptic connections allowing superior computing performances over classical von Neumann-based systems in processing cognitive and data intensive tasks, such as such as real-time image recognition, data classification or natural language processing, to cite a few. Typically, the information represented by a weight for each synapse is transmitted from the pre-synaptic neuron to the post-synaptic neuron. The network is then trained by updating its synaptic weights to perform a specific task. In the race for efficient materials to emulate neuronal and synaptic functions, classical ferroelectrics (oxides and PVDF-based polymers) are good candidate materials.

Here, we take advantage of the polar instabilities and the flat energy landscape characteristic of relaxors to exploit this special class of ferroelectrics for mimicking neuromorphic elements. We show that field-induced transitions are useful for tuning the capacitance and polar responses along multiple states and in a non-volatile manner to reproduce memristor and memcapcitor behaviors. We use such component to emulate some fundamental learning rules including short-term and long-term memory, spike-timing- and spike-rate-dependent-plasticity, etc. Furthermore, we also use ultrafast THz electric field excitations to generate both neuron and synaptic behaviors, via the creation of out-of-equilibrium hidden states of polarization, resulting from the ultrafast response of polar nanoregions. These findings may open a new field of research dedicated to employ relaxors for the design of neuromorphic architecture and computing.

Domains populations and piezoelectric properties in PZT single crystals

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The origin of the strong piezoelectric phenomenon in PZT perovskites still suffers from a lack of complete understanding. It concerns the distinction between the intrinsic and extrinsic mechanisms that govern PZT's piezo-activity. These two mechanisms have been investigated in PZT single crystals. After poling in a DC electric field, the piezoelectric properties were examined on the same crystal by observing piezoelectric resonances and measuring quasistatic deformation to determine the coefficients d_{31} and d_{33} . The domain populations were investigated during and after poling in a DC electric field. These populations were also investigated as a function of DC fields for strengths similar to those used to measure quasistatic piezoelectric properties for a poled crystal. By combining the investigations of optical properties and quasistatic and dynamic piezoelectric properties of a poled single crystal, it was found that the main extrinsic origin of enhancement of the piezoelectric properties is connected with a change in the population of domains with monoclinic symmetries [1]. The results presented in Figure 1 are compared with the piezoelectric properties of relaxors.

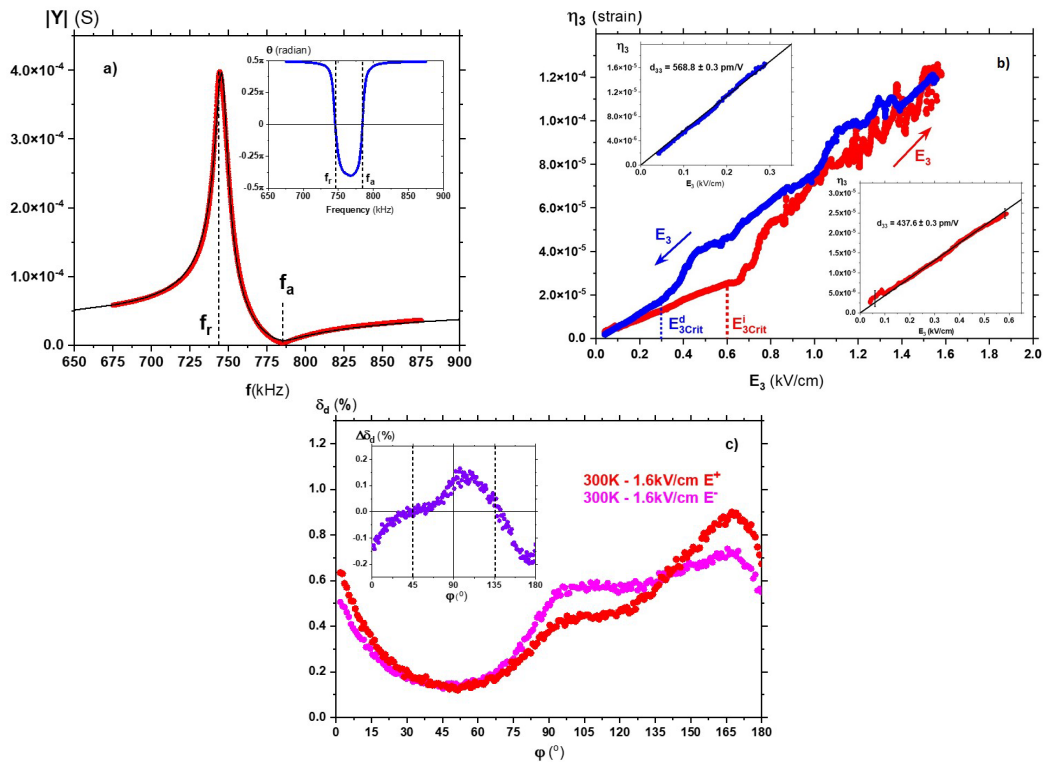


Figure 1. **a)** Piezoelectric resonances in a poled PZT single crystal from morphotropic phase boundary, **b)** for the same crystal, quasistatic field-dependent strain η_3 on field-increasing (red) and field decreasing (blue), **c)** distribution of the domains for two opposite DC fields denoted E^+ and E^- . Inset shows the difference in domain populations $\Delta\delta_d$ under the action of such fields. Interestingly, these fields do not affect the population of the rhombohedral 45° and 135° domains.

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Complex symmetry of phases and magnetic properties of the oxide perovskite EuTiO_3

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Some novel puzzling and unexplained observations regarding the cubic to “tetragonal” phase transition at $T_S=282\text{K}$ in the almost multiferroic perovskite EuTiO_3 have been reanalyzed in order to obtain deeper insight into the true structure and magnetic activity evolving below T_S . For this purpose earlier and new birefringence [1] and high resolution XRD data [2] have been used where zero magnetic field data are compared to data under the influence of a direction dependent magnetic field. The XRD structural data have been taken as input to derive the magnetic exchange constants, the related Néel temperatures T_N and the energies of the possible magnetic ground states. Taken both results together we conclude that below T_S the symmetry cannot be tetragonal but only monoclinic followed by another symmetry lowering transition around $T^*\approx 210\text{K}$. Furthermore, the exchange interactions, T_N , and the energies evidence that any kind of magnetism stems from a competition of the various ground state energies and must be a consequence of frustration.

References

1. Bussmann-Holder, A. et al. Transparent EuTiO_3 films: A possible two-dimensional magneto-optical device. *Sci. Rep.* **7**, 40621 (2017).
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