

# **XXV JUBILEE POLISH-CZECH SEMINAR**

**STRUCTURAL AND FERROELECTRIC  
PHASE TRANSITIONS**

**BOOK OF ABSTRACTS**

**Lake Dymaczewskie, Poland  
May 6-10, 2024**



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**Structural and Ferroelectric Phase Transitions**

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**ORGANIZERS**

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**SYLWIA ZIĘBA**

## VENUE

The XXV Jubilee Polish-Czech Seminar will be held at a conference centre Hotel Inter Szablewski on the shore of Lake Dymaczewskie located 25 km south of Poznań - the capital of the Wielkopolska Region.

The landscape of Wielkopolska is shaped by two glaciations and presents a hilly, moraine relief with numerous lakes (about 800) occurring in the northern and central parts of the region and forming the Pomeranian, Poznań, and Gniezno Lake Districts. More than a quarter of the region's area is covered by vast forests. In terms of climate Wielkopolska is one of the warmest and driest regions in Poland.

Wielkopolska is considered the "cradle of Poland". In the 10<sup>th</sup> century it was the heart of the early Polish state, with Poznań and Gniezno as the centers of royal power. After the devastation of the region by a pagan rebellion in 1030 and the invasion of Bretislav I known as the "Bohemian Achilles" in 1038, the capital of Poland was moved by King Casimir I the Restorer to Cracow.

Today, most of the historical lands of Wielkopolska are part of the Wielkopolska Region, a province in west-central Poland located in the Wielkopolska Lake District and the South Wielkopolska Lowland, in the central Warta river basin. It ranks second in terms of area and third in terms of population (close to 3.5 million) among Polish voivodships. Poznań – the capital of the Wielkopolska Region with an agglomeration approaching 1 million inhabitants is a large industrial, transport, cultural, and scientific center (over 100000 students).

Wielkopolska Region belongs to the most developed regions in Poland. Its regional specializations include, among others, sustainable energy, renewable energy production, and alternative energy storage technologies.

## HISTORY OF THE SEMINARS

The idea of regular scientific meetings of physicists involved in ferroelectric research in Poland and Czechoslovakia was a joint initiative of Bożena Hilczer and Jan Fousek, born after the success of the first such event in Błażejewko, Poland in 1979. This first Seminar was organized by collaborating scientists from the Ferroelectric Lab of the Institute of Molecular Physics of the Polish Academy of Sciences and the Dielectric Department of the Institute of Physics of the Czechoslovak Academy of Sciences. Over the years, the Seminar evolved into a recognized international conference and a forum of presentation of recent results, unconstrained discussions and initiating joint studies. The Seminar results not only in scientific integration but also in close cooperation and friendship.

After 45 years of history, we would like to hold the Jubilee XXV Seminar at the conference centre in Hotel Inter Szablewski on the shore of Lake Dymaczewskie, not far from the place where the idea of joint conferences was born.

## PREVIOUS SEMINARS

I	Błażejewko, Poland	1979
II	Mělník, Czechoslovakia	1980
III	Kołobrzeg, Poland	1981
IV	Piesky, Czechoslovakia	1982
V	Kozubnik, Poland	1983
VI	Liberec, Czechoslovakia	1984
VII	Karpacz, Poland	1986
VIII	Senohraby, Czechoslovakia	1988
IX	Poznań-Kiekrz, Poland	1990
X	Paseky nad Jizerou, Czechoslovakia	1992
XI	Paseky nad Jizerou, Czech Republic	1994
XII	Jurata, Poland	1996
XIII	Liblice, Czech Republic	1998
XIV	Świnoujście, Poland	2000
XV	Nečtiny, Czech Republic	2002
XVI	Wierzba, Poland	2004
XVII	Znojmo, Czech Republic	2006
XVIII	Zakopane, Poland	2008
XIX	Telč, Czech Republic	2010
XX	Ustroń, Poland	2012
XXI	Sezimovo Ústí, Czech Republic	2014
XXII	Hucisko, Poland	2016
XXIII	Kouty, Czech Republic	2018
XXIV	Harrahov	2022

# **PROGRAMME**

## MONDAY MAY 6, 2024

13.00 - 18.00	REGISTRATION
18.00 - 18.15	OPENING
18.15 - 19.00	<b>MARIA POŁOMSKA</b> Memories of the earliest Polish-Czech and Czech-Polish Seminars
19.00	GET TOGETHER PARTY

## TUESDAY MAY 7, 2024

	7.30 - 9.20	BREAKFAST
CHAIR - ROLEDER	9.20 - 10.00	<b>INVITED - ANNETTE BUSSMANN-HOLDER (I-01)</b> SrTiO <sub>3</sub> : thoroughly investigated but still good for surprises
	10.00 - 10.20	<b>ANNA GAĞOR (O-01)</b> Polymorphism in organic-inorganic halo-metalates(III) based on methylhydrazine
	10.20 - 10.40	<b>DAWID DROZDOWSKI (O-02)</b> Phase transitions, optical and dielectric properties in layered hybrid perovskites of ACI and (110)-oriented type
	10.40 - 11.00	<b>LOİC MUSY (O-03)</b> Controlling ice-like surface water layers using ferroelectric polarization
	11.00 - 11.30	COFFEE
CHAIR - PARUCH	11.30 - 12.10	<b>INVITED - ELENA BUIXADERAS (I-02)</b> Recent spectroscopic advances in antiferroelectric materials
	12.10 - 12.30	<b>DARIUSZ KAJEWSKI (O-04)</b> Lattice dynamics in niobium doped PbZrO <sub>3</sub> single crystals
	12.30 - 12.50	<b>COSME MILESI-BRAULT (O-05)</b> An antiferroelectric for room temperature three-state thermal switches
	12.50 - 13.10	<b>JULITA PIECHA (O-06)</b> Electronic structure and mechanical properties of lead hafnate single crystal
	13.10 - 15.00	LUNCH
CHAIR - GAĞOR	15.00 - 15.20	<b>JACEK BOGUSŁAWSKI - MEMBER OF THE BOARD OF THE WIELKOPOLSKA REGION</b> Activities for the development of the hydrogen economy in the Wielkopolska Region
	15.20 - 16.00	<b>INVITED - MARIA GAZDA (I-03)</b> Structural phase transitions in proton-conducting oxides
	16.00 - 16.20	<b>PAWEŁ ŁAWNICZAK (O-07)</b> Low-temperature proton conductors based on cellulose - from micro to nano
	16.20 - 17.00	COFFEE
	17.00 - 19.00	POSTER SESSION
	19.00	DINNER

**WEDNESDAY MAY 8, 2024**

	<b>7.30 - 9.20</b>	<b>BREAKFAST</b>
<b>CHAIR - KAMBA</b>	<b>9.20 - 10.00</b>	<b>INVITED - PATRYCJA PARUCH (I-04)</b> Complex polarisation textures and emergent functionalities at ferroelectric twins
	<b>10.00 - 10.20</b>	<b>OLGA MAZUR (O-08)</b> Stochastic theory of domain ordering in uniaxial ferroelectrics after quenching
	<b>10.20 - 10.40</b>	<b>SEONGWOO CHO (O-09)</b> Switchable tribology of ferroelectrics
	<b>10.40 - 11.00</b>	<b>RALPH BULANADI (O-10)</b> Tracking the Nanoscale Dynamics of the Martensitic-like Phase Transition in BiFeO <sub>3</sub> via Interferometric Nanoindentation
	<b>11.00 - 11.30</b>	<b>COFFEE</b>
<b>CHAIR - KULDA</b>	<b>11.30 - 12.10</b>	<b>INVITED - LUKAS M. ENG (I-05)</b> THz Twistoptics - engineering canalized phonon polariton
	<b>12.10 - 12.30</b>	<b>NIRVANA CABALLERO (O-11)</b> From bulk descriptions to emergent interfaces
	<b>12.30 - 13.45</b>	<b>LUNCH</b>
	<b>13.45 - 19.00</b>	<b>EXCURSION</b>
	<b>19.00</b>	<b>DINNER</b>

**THURSDAY MAY 9, 2024**

	<b>7.30 - 9.20</b>	<b>BREAKFAST</b>
<b>CHAIR - BUSSMANN-HOLDER</b>	<b>9.20 - 10.00</b>	<b>INVITED - FRIEDRICH KREMER (I-06)</b> Towards an atomistic understanding of the dynamic glass transition as studied for the example of polyalcohols
	<b>10.00 - 10.20</b>	<b>NATALIA PODOLIAK (O-12)</b> Twisted domains in dimethylamino-terminated ferroelectric nematogenic liquid crystals
	<b>10.20 - 10.40</b>	<b>ANNA Z. SZEREMETA (O-13)</b> Influence of interfacial stresses on electrical properties of bismuth manganite - lead titanate - epoxy composite
	<b>10.40 - 11.00</b>	<b>NATALIA BIELEJEWSKA (O-14)</b> Preparation and characterization of LC-CNC hybrid Langmuir films
	<b>11.00 - 11.30</b>	<b>COFFEE</b>
<b>CHAIR - KREMER</b>	<b>11.30 - 12.10</b>	<b>INVITED - STANISLAV KAMBA (I-07)</b> Collinear magnetic structures induced by ferroelectric distortion in multiferroic quadruple perovskites $\text{BiMn}_3\text{Cr}_4\text{O}_{12}$ and $\text{BiMn}_7\text{O}_{12}$
	<b>12.10 - 12.30</b>	<b>SAMUEL SEDDON (O-15)</b> Coupling of multiferroic order parameters in magnetite $\text{Fe}_3\text{O}_4$
	<b>12.30 - 12.50</b>	<b>ADAM SIERADZKI (O-16)</b> Exploring the Dynamics Complexity of Ammonium-Templated Hybrid Organic-Inorganic Perovskites: Insights from Broadband Dielectric Spectroscopy
	<b>12.50 - 13.10</b>	<b>ARKADIUSZ FRĄCKOWIAK (O-17)</b> Transition from neutral to ionic phase in the charge-transfer complex $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$ , a potential ferroelectric material
	<b>13.10 - 15.00</b>	<b>LUNCH</b>
<b>CHAIR - ENG</b>	<b>15.00 - 15.40</b>	<b>INVITED - JIŘÍ KULDA (I-08)</b> From atomic scale simulations to diffuse scattering maps
	<b>15.40 - 16.00</b>	<b>JIŘÍ HLINKA (O-18)</b> Nonmagnetic antiskyrmionic medium found
	<b>16.00 - 16.20</b>	<b>VILGELMINA STEPKOVA (O-19)</b> Creation, motion and annihilation of nonmagnetic Antiskyrmions
	<b>16.20 - 17.00</b>	<b>COFFEE</b>
<b>CHAIR - GAZDA</b>	<b>17.00 - 17.20</b>	<b>SŁAWOMIR PIEPRZYK (O-20)</b> A numerical method to obtain physical properties from liquid crystal texture analysis
	<b>17.20 - 17.40</b>	<b>MAURO ANTÓNIO PEREIRA GONÇALVES (O-21)</b> $\text{BiFeO}_3$ nanoparticles using atomistic simulations
	<b>17.40 - 18.00</b>	<b>SHENG-HAN TENG (O-22)</b> Phase coexistence and complex domain structures in $\text{BaTiO}_3$ induced by $\text{SrTiO}_3$ inclusions
	<b>18.00 - 18.20</b>	<b>ANDRZEJ MUSIAŁ (O-23)</b> Magnetostructural phase transition in the pseudobinary $\text{Ce}(\text{Fe}_{0.9}\text{Co}_{0.1})_2$ compound
	<b>19.00</b>	<b>GRILL PARTY</b>

## FRIDAY MAY 10, 2024

	<b>7.30 - 9.20</b>	<b>BREAKFAST</b>
<b>CHAIR - BUIXADERAS</b>	<b>9.20 - 10.00</b>	<b>INVITED - MICHAŁ BIELEJEWSKI (I-09)</b> Supramolecular ionic conductors as an alternative for solid-state electrolytes
	<b>10.00 - 10.20</b>	<b>VALENTYN LAGUTA (O-24)</b> Spin-electric coupling in ferroelectric materials
	<b>10.20 - 10.40</b>	<b>MARTIN KEMPA (O-25)</b> Weak-field FMR near the collinear to conical ferrimagnetic phase transition in U-type hexaferrite $\text{Sr}_4\text{CoZnFe}_{36}\text{O}_{60}$ ceramics
	<b>10.40 - 11.00</b>	<b>COFFEE</b>
<b>CHAIR - HLINKA</b>	<b>11.00 - 11.20</b>	<b>JAN DEC (O-26)</b> Optical pseudo-biaxiality of relaxor strontium-barium niobate single crystals
	<b>11.20 - 11.40</b>	<b>KRYSTIAN ROLEDER (O-27)</b> What if there were no Polish-Czech Seminars?
	<b>11.40 - 12.00</b>	<b>CLOSING</b>
	<b>12.00</b>	<b>LUNCH</b>



- P-01** **BARTŁOMIEJ ANDRZEJEWSKI**  
Investigations of the key electrical parameters and structural properties of commercial ZnO ceramics used in surge arresters
- P-02** **DMYTRO BOHDANOV**  
Tailoring of Plausible Skyrmion Media in SrTiO<sub>3</sub> Perovskite
- P-03** **FEDIR BORODAVKA**  
Spectroscopic studies of magnetic and lattice excitations in van der Waals ferromagnets
- P-04** **ALEXEJ BUBNOV**  
Photo-active self-assembling materials: effect of lateral substitution far from the chiral centre
- P-05** **BOGDAN DABROWSKI**  
The Rareness of the Single Ion Perovskite Multiferroics is Caused by Complexities of the Synthesis
- P-06** **JAMIL EDUARDO FLORES GONZALES**  
Diffuse scattering of 2D ferroelectric (PbS)<sub>1.18</sub>VS<sub>2</sub>
- P-07** **JAMIL EDUARDO FLORES GONZALES**  
Short-range correlations in lead titanate close to  $T_c$
- P-08** **ANDRZEJ HILCZER**  
Low-temperature memory effect in PMN single-crystal
- P-09** **IRENA JANKOWSKA-SUMARA**  
Piezoelectric, elastic, and electrocaloric properties of a soft PZT ceramic
- P-10** **STANISLAV KAMBA**  
Unusual phase transition into frustrated antipolar phase in ferromagnetic EuAl<sub>12</sub>O<sub>19</sub>
- P-11** **ANTONÍN KLÍČ**  
The polar structure of PbTiO<sub>3</sub> studied by ab initio calculations
- P-12** **ALEKSANDRA KRUPIŃSKA**  
Structure, thermal and electrical properties of N-methylpyrrolidinium bromobismuthate(III)
- P-13** **ANIRUDH KUTTIKATTIL RAMACHANDRAN**  
Phase transition dynamics of antiferroelectric crystals with lanthanum substitution
- P-14** **IWONA LAZAR**  
Ferroelectric domain populations and high piezoelectric response
- P-15** **SERGEI MIRONOV**  
Photo-active self-assembling materials: effect of lateral substitution in the vicinity of the azo group
- P-16** **ADAM MIZERA**  
Investigation of spectroscopic and electrical properties of doped pyrrole-copoly(pyrrole-3-carboxylic) copolymers
- P-17** **DMITRY NUZHNYI**  
Search for multiferroic properties in BaCuF<sub>4</sub>
- P-18** **MAREK PAŚCIAK**  
Roles of chemical short-range order in perovskite and related dielectric materials

- P-19 ANNA PIECHA-BISIOREK**  
Structural and dielectric properties of 1,2,4-Triazolium Hexabromoantimonate(III)
- P-20 MAGDALENA ROK**  
Ferroic and nonlinear dielectric and optical properties of inorganic-organic lead-free 1D hybrid based on Bi(III)
- P-21 MAGDALENA ROWIŃSKA**  
Phase transitions, crystal structure and optical properties of 1D organic-inorganic perovskite: methylhydrazinium antimony (III) iodide
- P-22 IVAN RYCHETSKÝ**  
On the origin of the chiral phase transition in 180° domain walls of PbTiO<sub>3</sub>
- P-23 ROMAN ŚWIETLIK**  
Neutral-to-ionic transition in the complex (EDT-TTF-I<sub>2</sub>)<sub>2</sub>TCNQF - evidence of strong electron - molecular vibration coupling
- P-24 KAROL SYNORADZKI**  
Magnetic phase transitions in Eu<sub>5</sub>In<sub>2</sub>Sb<sub>6</sub>
- P-25 PRZEMYSŁAW SZKLARZ**  
Ferroic and semiconducting properties of selected hybrid iodoantimonates (III) and iodobismuthates (III)
- P-26 ALEX THEODOROU**  
Spectroscopic studies on the interface of water with hydrophilic materials
- P-27 MYKHAILO TRUBITSYN**  
EPR and optical spectroscopy of the Mn-doped LiNaGe<sub>4</sub>O<sub>9</sub> single crystals
- P-28 DZMITRY TSYHANOK**  
Broadband spectroscopy and electrical percolation of carbon coated copper nanoparticles/MWCNT/Epoxy hybrid composites
- P-29 SYLWIA ZIĘBA**  
Negative linear compressibility in the helical hydrogen bonding network of imidazolium benzoate



# **INVITED SPEAKERS**

## SrTiO<sub>3</sub>: thoroughly investigated but still good for surprises

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**A. Bussmann-Holder**<sup>1</sup>, Reinhard K. Kremer<sup>1</sup>, K. Roleder<sup>2</sup>, and Ekhard K.H. Salje<sup>3</sup>

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For decades SrTiO<sub>3</sub> is in the focus of research with seemingly never-ending new insights regarding its ground state properties, its application potentials, its surface and interface properties, the superconducting state, the twin boundaries and domain functionalities, etc. Here, we focus on the already well-investigated lattice dynamics of STO and show that four different temperature regimes can be identified which dominate the elastic properties, the thermal conductivity and the birefringence. These regimes are the low-temperature quantum fluctuation dominated one, followed by an intermediate regime, the region of the structural phase transition at ~105 K and its vicinity, and at high temperatures a regime characterized by precursor and saturation effects. They can all be elucidated by lattice dynamical aspects. The relevant temperature dependences of the soft modes are discussed and their relationship to lattice polarizability is emphasized.

## Recent spectroscopic advances in antiferroelectric materials

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The revival of antiferroelectric materials is driven mainly by their potential to store recoverable energy in small electronic devices. However, they are also of fundamental interest for understanding the behaviour of spontaneous polarisation at the microscopic or even nanoscopic scale.

Among the many experimental techniques available, far-infrared and time-domain transmission THz spectroscopy, together with Raman scattering, have proved to be a very useful combo for studying the phase transition dynamics of any dielectric material, including antiferroelectrics. Using group theory and site-group analysis, one can compare the predicted and the experimentally measured vibrational modes, for the different phases present in the material. With the aid of the far IR and THz techniques, one can also study excitations below phonons, in the sub-THz range.

We have investigated several antiferroelectric perovskite materials in the form of single crystals and ceramics, ranging from pure  $\text{PbZrO}_3$  to partially substituted samples with Ti, Hf or Sn. Each substitution perturbs the low temperature antiferroelectric state and induces intermediate phases of different nature at higher temperature: ferroelectric, incommensurate, antiferroelectric with different symmetry or even relaxor-like. The manifestation of these phases is seen by the different experimental techniques in the spectra measured at various temperatures. The dynamics of the phase transitions on cooling from the paraelectric phase is discussed in relation to the similarities and differences seen in the spectra, as well as to the thermal hysteresis, influenced by experimental conditions and the previous history of the samples [1]. The role of disorder in the A or B position of the  $\text{ABO}_3$  perovskite lattice -either static or dynamic- is well evidenced in the Raman spectra, but also in the reflectivity of the materials, where we found a high number of active modes and high damping parameters of the phonons. Some of the intermediate phases are elusive to these techniques, either because the phonons are not polar, or because of some coexistence effects.

*This work is supported by a Lead Agency Project GAČR-ARRS 24-10699K.*

### References:

[1] E. Buixaderas, C. Milesi-Brault, P. Vaněk, J. Kroupa, F. Craciun, F. Cordero, C. Galassi, Peculiar dynamics of polar states at the morphotropic phase boundary of antiferroelectric  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ , *Acta Materialia* 258 (2023) 119208.

## Structural phase transitions in proton-conducting oxides

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Many oxides, especially complex  $A_xB_yO_z$  oxides containing more than one type of cations, in which the structure is related to the length of O-A and O-B bonds, often undergo structural phase transitions. This applies also to proton-conducting oxide groups, for example, perovskites and fergusonites. Moreover, many oxides may be prepared as compositionally complex oxides (CCO), high-entropy oxides (HEO) or entropy-stabilized oxides (ESO) which also influence structural properties. Structural transitions in functional materials are fascinating phenomena to be studied by scientists, but usually, they are not welcomed by the engineers who are supposed to apply them in a device of practical use. The problems are especially severe if the structural transitions affecting such properties as the unit cell volume and thermal expansion coefficient occur at a temperature between room temperature and the operating temperature of a device.

In this work, selected properties of oxides based on well-known proton-conducting systems, namely barium zirconate perovskites and lanthanum orthoniobate fergusonites are presented. In particular, the structural transition between the monoclinic fergusonite and tetragonal scheelite phases in lanthanum orthoniobates and multi-component orthoniobates is described and discussed. Ionic radii of the A and B cations and their electronegativities are analysed in terms of their influence on the transition temperature. The relationship between structural properties and proton defect concentration, as well as proton conduction, is considered.

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## Complex polarisation textures and emergent functionalities at ferroelectric twins

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Ferroelectric materials can host a wide range of unusual structural features, often linked to novel functional properties, potentially useful for nanoelectronics applications. At domain walls or in regions with high strain gradients, in particular, the complex interaction between polarisation, electrostatics, and strain can lead to localised chiral polarisation textures, electrical conductivity, local mechanical responses, and charge or chemical segregation. My group uses a broad spectrum of primarily scanning probe microscopy techniques, coupled with machine learning analysis to investigate and disentangle the many complex and correlated physical phenomena in these materials.

One promising structure with strongly localised and very high strain gradients are ferroelastic twins, such as a-domains in tetragonal ferroelectric perovskites, and even more so, their intersections. In  $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$  and  $\text{PbTiO}_3$  thin films, investigated with a combination of PFM, CAFM, CRFM, transmission electron microscopy, and nonlinear optical microscopy, we find a characteristic localised piezoelectric response and evidence of a more complex rotational or closure structure in second harmonic generation polarimetry analysis. The heart of the twin domain crossing presents an extremely high susceptibility to local application of electric bias or pressure, dominating the polarisation switching dynamics in this region. We also observe distinct mechanical properties and enhanced electrical conduction at the heart of the twin crossing, and a conductive superstructure in the twins themselves, reflecting their complex polarisation textures revealed in transmission electron microscopy.



## THz Twistoptics - engineering canalized phonon polaritons

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The terahertz (THz) frequency range is key to studying collective excitations in many crystals and organic molecules. Nonetheless, due to the large wavelength of THz radiation, the local probing of these excitations in tiny (crystalline) structures or arrangements of a few molecule only, requires sophisticated methods in order to confine THz light down to the nanometer length scale, as well as to manipulate such a confined radiation [1]. For this purpose, taking advantage of hyperbolic phonon polaritons (HPhPs) in highly anisotropic van der Waals (vdW) materials [2,3] and topological insulators [3] has emerged as such a promising approach in recent years, offering a multitude of manipulation opportunities, such as control over the wavefront shape and propagation direction.

Here, we demonstrate the THz application of twist-angle-induced HPhP manipulation [4], designing the propagation of confined THz radiation between 8.39 and 8.98 THz in the vdW material  $\alpha$ -molybdenum trioxide ( $\alpha$ -MoO<sub>3</sub>) [5], hence extending twistoptics to this intriguing frequency range. Our images, recorded by near-field optical microscopy using the free-electron-laser FELBE, show the frequency- and twist-angle-dependent changes between hyperbolic and elliptic polariton propagation, revealing a polaritonic, topological transition at THz frequencies. As a result, we are able to allocate canalization (highly collimated propagation) of confined THz radiation by carefully adjusting these two parameters, i.e. frequency and twist angle. Specifically, we report polariton canalization in  $\alpha$ -MoO<sub>3</sub> at 8.67 THz for a twist angle of 50°. Our results demonstrate the precise control and manipulation of confined collective excitations at THz frequencies, particularly offering possibilities for nanophotonic applications.

### References:

- [1] M. Chen et al., Optics Express 30 (2022) 26955; <https://doi.org/10.1364/OE.454908>.
- [2] J. Matson et al., Nat. Commun. 14 (2023) 5240; <https://doi.org/10.1038/s41467-023-40789-7>.
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## Towards an atomistic understanding of the dynamic glass transition as studied for the example of polyalcohols

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Density is the key quantity for nearly all the numerous theories of the (dynamic) glass transition of supercooled liquids and melts [1-3]. As mean field quantity, it is used to describe correlations and heterogeneities between regions consisting of several molecules. In contrast, the question how density is determined by the interactions (i.e., bonds) within a molecule and to its nearest neighbors is almost unexplored. To investigate this for the example of a homologous series of polyalcohols (glycerol, threitol, xylitol, and sorbitol), Fourier-Transform InfraRed (FTIR) spectroscopy is carried [2] out in a wide range of temperatures from far above to far below the calorimetric glass transition  $T_g$ . This enables us to determine the potentials and hence the bond lengths of specific intramolecular and intermolecular interactions. While the former has an expansion coefficient of ( $\sim 0.1$  pm/100 K) with only smooth changes, the latter shows a 30 - 40 times stronger response with pronounced kinks at  $T_g$ . A comparison with the overall expansion based on mass density reveals that one has to separate between strong (OH $\cdots$ O) and weak (CH $\cdots$ O) intermolecular hydrogen (H)-bridges. Despite the fact that the latter dominates glassy dynamics, their expansivity is 5 times smaller than that of the weak H-bridges. It is to be expected that such heterogeneities on intramolecular and intermolecular scales are a general phenomenon in liquids and glassy systems demonstrating also the necessity of atomistic simulations.

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# Collinear magnetic structures induced by ferroelectric distortion in multiferroic quadruple perovskites $\text{BiMn}_3\text{Cr}_4\text{O}_{12}$ and $\text{BiMn}_7\text{O}_{12}$

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Multiferroic materials are divided into type I, where magnetic and ferroelectric ordering occurs independently at different temperatures, and type II multiferroics, where spin interactions in the magnetic phase induce weak ferroelectric polarization. In the former case (e.g.  $\text{BiFeO}_3$ ), although the ferroelectric polarization is high, the magnetoelectric coupling is weak. In the second case (e.g.  $\text{TbMnO}_3$ ) the magnetoelectric coupling is very strong, but critical temperatures and ferroelectric polarizations are usually low.

We report a new type of multiferroics where a ferroelectric phase transition from the cubic to the monoclinic phase triggers the antiferromagnetic ordering of Cr spins in  $\text{BiMn}_3\text{Cr}_4\text{O}_{12}$ . Both ferroelectric and magnetic phase transitions occur at the same temperature of 125 K. The Mn spins are further antiferromagnetically ordered at 50 K and the associated magnetoelectric coupling enhances the ferroelectric polarization [1].

In the case of  $\text{BiMn}_7\text{O}_{12}$ , a series of three structural (including two displacive ferroelectric) phase transitions above room temperature and three magnetic phase transitions below 60 K occur (see Fig. 1) [2]. Recent neutron powder diffraction studies revealed that polar distortion in the ferroelectric phase stabilizes the collinear magnetic structure due to trilinear coupling of order parameters [3].

In our talk we will show the results of magnetic and pyroelectric measurements together with lattice dynamics studied by THz, infrared and Raman spectroscopy. The temperature dependences of the soft mode frequencies and spin correlation functions were determined from the spectra.

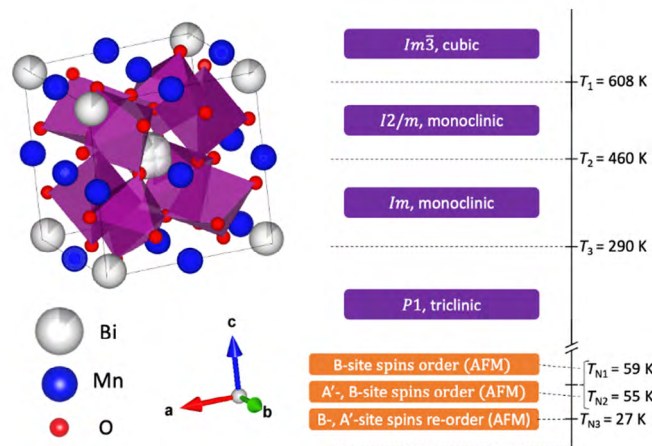


Figure 1. Crystal structure of  $\text{BiMn}_7\text{O}_{12}$  at room temperature and schematic representation of its structural (purple) and magnetic (orange) phase sequence.

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## From atomic scale simulations to diffuse scattering maps

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The structure of modern functional materials often involves a hierarchy of defects and disorder. The progress in computing techniques in last decades permits to produce realistic models of distorted crystalline lattices by a variety of approaches ranging from *ab initio* DFT methods via molecular dynamics (MD) to effective Hamiltonian and phase-field models based on the Landau formalism.

With this progress in place the bottleneck has shifted from producing supercell models to generating the corresponding diffuse scattering distributions in reciprocal space. The principal issue is due to the fact that scattering amplitudes from a distorted lattice could not be summed up using fast Fourier transform algorithms (FFT) because of the displacements giving rise to an additional  $\exp(i\mathbf{Q}\mathbf{u})$  phase factor.

As a consequence, many efforts in recent years have been restricted to simple models on small supercells [1,2] or to more involved pair distribution function (PDF) analysis [3-5], where the summation problem is reduced to a single dimension. Nevertheless, the efficiency of PDF model generation in direct space for large supercells and large correlation distances needed for good quality Fourier transforms was limited by the radial distribution function spherical shells volume diverging with  $r^2$ .

The *MP\_tools* program suite [6] addresses these issues employing innovative algorithms. In the first case, recent developments of the non-uniform fast Fourier transform [7] permit to accelerate the summation of scattering amplitudes from large supercells by orders of magnitude, bringing in the usual FFT speed and allowing for interactive work even in case of dynamic scattering functions  $S(\mathbf{Q},\omega)$  based on time sequences of thousands of frames. A similar effect in the PDF accumulation brings a Monte-Carlo algorithm with projective sampling [8], permitting to accumulate the  $g(r)$  pair-distribution function with uniform ( $r$ -independent) accuracy while bypassing the radial distribution function.

These, often spectacular, gains in computation speed open way to interactive modeling and to deeper analysis of the relationships between the applied models and the experimental reality.

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## Supramolecular ionic conductors as an alternative for solid-state electrolytes

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In recent days, secondary solid-state batteries (SSBs) have dominated the market for personal use electronics, computers, energy storage, and portable electric devices. The major advantages of these systems are lighter construction, higher safety, flexibility in forming process and wider application range. Therefore, solid-state electrolytes (SSEs) are rapidly replacing conventional liquid electrolytes. The dominating technology in SSE production is based on polymer matrices, which, however cause significant limitations concerning conductivity, high production costs, disposal, and recycling process especially in the context of growing demand for SSBs in transportation. Therefore, the search for new technologies for solid-state electrolytes gains on its importance. An alternative to polymer-based SSEs can be supramolecular systems based on low molecular weight organic gelators (LMWGs). The main difference between polymers and LMWG is the nature of forces responsible for the solidification of liquid electrolyte solutions, which in the latter case are physical forces, i.e., hydrogen bonding, Van der Waals interactions, and  $\pi$ - $\pi$  stacking. The LMWG-based systems are thermoreversible, easy to process, effective, and recyclable ionic conductors. However, the physical interaction causes some limitations concerning the mechanical strength, operation temperature range, and narrow range of usable solvents. The latest research in that field has shown that it is possible to obtain supramolecular gel electrolytes (SGEs) with technologically important solvents and ion species, improved mechanical properties, high conductivities, and easy recycling. The advanced TGA/DSC thermal analysis showed improved stability and ease of processing of the systems. Investigating molecular dynamics of the system's components with nuclear magnetic resonance and dielectric spectroscopy methods revealed the conductivity mechanisms, effectiveness, and intermolecular interactions within Li-ion SGEs.

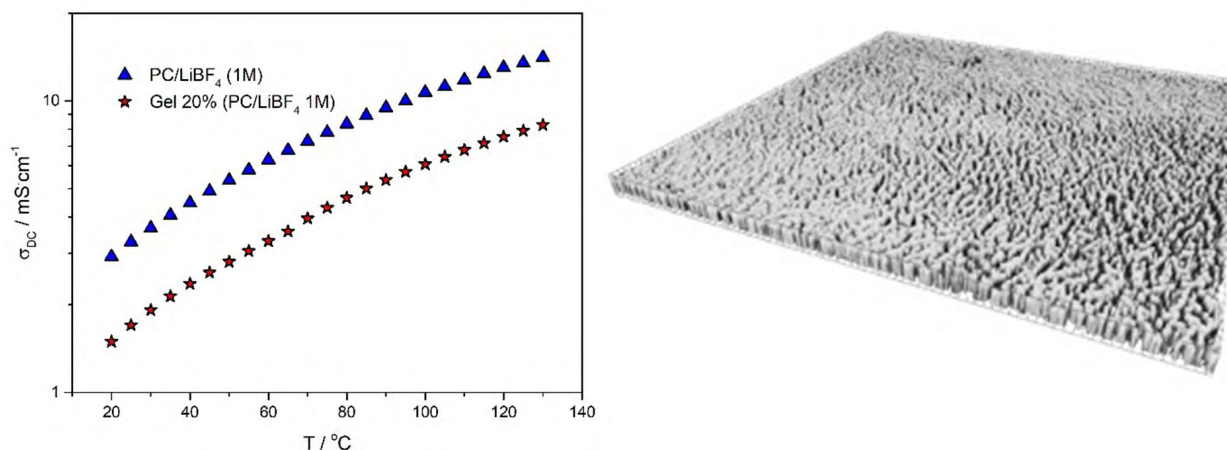


Figure 1. Temperature dependence of the  $\sigma_{DC}$  of SGE and liquid electrolyte (left) and confocal fluorescence scanning microscope image of the SGE (right).

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# **ORAL PRESENTATION**

## Polymorphism in organic-inorganic halo-metalates(III) based on methylhydrazine

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Organic-inorganic hybrids based on small polar molecules and metal-halide complex anions are typically narrow-band dielectrics or semiconductors displaying unique properties suitable for various applications, including solar cells, light-emitting diodes, photodetectors, scintillators, or nonlinear optical (NLO) devices [1]. Recent studies have shown successful synthesis of lead halide perovskites and their low-dimensional variants with protonated metal-hydrazine. MHy-based perovskites exhibit distinct properties due to the ability of MHy<sup>+</sup> to form strong hydrogen bonds with halide acceptors and N-Pb coordinate bonds, leading to structural distortions, symmetry breaking, and polar ordering. Despite their large effective ionic radii, MHy<sup>+</sup> acts as one of the four known perovskite-forming agents, molecular cations that can incorporate into 3D ABX<sub>3</sub> perovskite structures by accommodating A sites. In 2D perovskites, MHy<sup>+</sup> acts as a spacer and effectively stabilizes polar atomic arrangements, resulting, for example, in room temperature ferroelectricity [2].

Given that MHy has demonstrated its utility in the synthesis of lead halide-based perovskites, we aimed to extend studies to other MHy-inorganic compounds, as they are still not well-recognized. The presented results concern polymorphic phases in antimony(III) and bismuth(III) halides which were successfully crystallized with MHy<sup>+</sup> as the counterion. In contrast to lead halides, the inorganic substructures are one-dimensional (1D, MHy<sub>2</sub>SbI<sub>5</sub>) or zero-dimensional (0D, MHy<sub>5</sub>Sb<sub>2</sub>I<sub>11</sub>, MHy<sub>5</sub>Bi<sub>2</sub>Br<sub>11</sub>, MHy<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>). They are also less stable in air compared to other halo-antimonates(III) and bismuthates(III). Nevertheless, the ability of MHy to stabilize different polymorphs as well as non-centrosymmetric arrangements seems to be preserved, as e.g., MHy<sub>2</sub>SbI<sub>5</sub> crystallizes in two polymorphic forms (I and II) with distinct thermal behavior and structural features. Polymorph I adopts the acentric *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> chiral space group confirmed by SHG and, despite thermally activated disorder of MHy<sup>+</sup>, does not show phase transitions, while polymorph II undergoes a reversible low-temperature phase transition and high-temperature reconstructive transformation to polymorph I [3]. Both crystal structures consist of 1D perovskite zig-zag chains of corner-sharing SbI<sub>6</sub> octahedra. The structural differences between them are attributed to the spatial arrangement of [SbI<sub>5</sub>]<sup>2-</sup><sub>∞</sub> chains in the crystal structure.

*The research was funded by the National Science Centre as part of the OPUS 22 project (grant number: 2021/43/B/ST5/01172).*

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## Phase transitions, optical and dielectric properties in layered hybrid perovskites of ACI and (110)-oriented type

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Hybrid Organic-Inorganic Perovskites (HOIPs) based on lead halides have been thoroughly investigated in recent years. While the famous 3D HOIPs of  $ABX_3$  formula ( $A$  = small organic cation) offer exceptional and customizable optoelectronic characteristics, they suffer from poor stability to moisture and chemicals [1]. Thus, the focus is shifting towards more stable analogs, i.e., layered (2D) HOIPs ( $A_2BX_4$ ). Their alignment of  $PbX_6$  octahedra slabs separated by organic 'spacers' opens more possibilities for compositional engineering via A- and X-site substitution. The ACI-type 2D HOIPs (Alternating Cation in the Interlayer space) demonstrate potential for light-emitting and solar cell applications by mitigating both dielectric and electronic confinement. Another subclass, known as (110)-oriented 2D HOIPs (derivatives created by 'slicing' the 3D perovskite structure along the (110) plane), is also attractive, showcasing broad and white-colored photoluminescence (PL) emission. Both these groups are relatively new to date, and therefore, still largely unexplored.

Studies on single and multilayered ACI 2D HOIPs of  $(GUA)(MA)_n Pb_n I_{3n+1}$  ( $n = 1-3$ , GUA = guanidinium, MA = methylammonium) unveil narrower bandgaps compared to typical 2D perovskites and reduced exciton binding energy, advantageous for charge-transport related applications [2]. The (110)-oriented (N-MEDA) $PbBr_4$  (N-MEDA = N-methylethane-1,2-diammonium) demonstrates broadband and white-light PL emission upon excitation at room temperature, with the full width at half-maximum (FWHM) of the PL significantly greater (165 nm) than in similarly built (001)-oriented analog (24 nm) [3]. In our recent work on (IM)(MHy) $PbBr_4$  (IMPB) and (IM)(MHy) $PbCl_4$  (IMPC) (IM = imidazolium, MHy = methylhydrazinium), the representatives of both ACI and (110)-oriented classes, we observed a  $P2_1/c \rightarrow P2_1/c$  phase transition associated with the freezing of organic cations, resulting in structure with heavily distorted octahedra layers below 344 K (375 K) for IMPB (IMPC). Both compounds exhibit large Stokes shifts of 178 nm (IMPB) and 252 nm (IMPC) [4]. All these examples underscore the potential of 2D HOIPs with (110)-oriented and/or ACI-type structures in terms of their structural and optoelectrical characteristics.

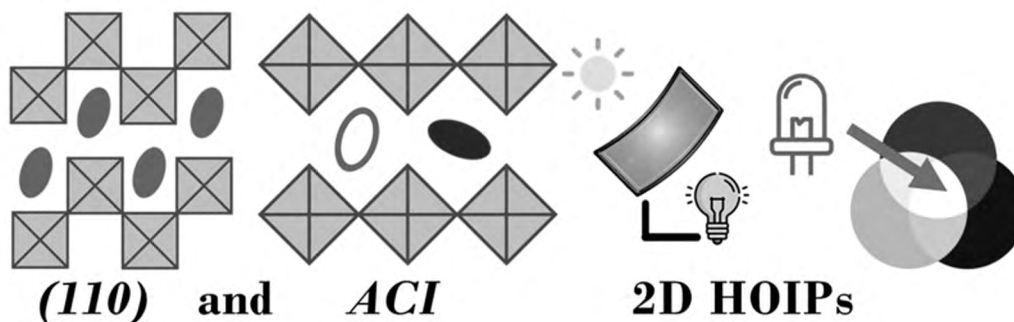


Figure 1. 2D hybrid perovskites of (110)-oriented and ACI type.

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## Controlling ice-like surface water layers using ferroelectric polarization

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Polar water molecules strongly interact with polar or charged surfaces, resulting in measurable variations of freezing temperatures [1]. On ferroelectrics, relative humidity has been observed to influence the growth dynamics and stabilization of ferroelectric domains as a result of water screening the depolarizing field [2,3]. Reciprocally, ferroelectric polarization orientation modulates the physisorption and chemisorption of water and other molecules during condensation [4]. However, previous studies have only addressed the water-ferroelectric interaction at room temperature.

In this work, we investigate the behavior of water on the surface of ferroelectric  $\text{PbTiO}_3$  thin films as a function of as-grown polarization and switching history under conditions of high humidity (95% relative humidity) and low temperature (0 °C) using Kelvin probe force microscopy, piezoelectric force microscopy, and a custom-built humidity control system [5,6].

We find that the polarization orientation, the surface morphology, and the presence of written domain structures influence the nucleation and growth of ice-like water layers. This leads, for example, to different growth rates depending on the history of both tip contact and polarization switching, with almost complete inhibition of water growth under specific switching configurations. Therefore, manipulating the local ferroelectric polarization allows a form of controlled “nanofluidics”, with the expansion of the ice-like water layers along pre-designed paths with precision down to 200 nm.

We further investigate water layer growth on periodically poled  $\text{LiNbO}_3$  single crystals to decouple the effects of tip-induced charging and polarization orientation. Here, a strong pyroelectric coefficient and higher charge retention lead to significant surface charging, inducing an unusual alternation between expansion and contraction of ice-like water layers. We propose that competition between surface tension and electrostatic forces on the water layers as a mechanism driving this unusual “breathing” behavior.

*This work was supported by Division II of the Swiss National Science Foundation under project 200021\_178782.*

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## Lattice dynamics in niobium doped $\text{PbZrO}_3$ single crystals

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Lead zirconate  $\text{PbZrO}_3$  has been of interest for dozens of years since its discovery [1]. Antiferroelectric character of the phase below  $T_c$  was not questioned and a relatively small number of papers reported on the properties of this phase. Even mechanism of transition to antiferroelectric order was not so frequently discussed as so called intermediate phase appearing directly below transition at  $T_c$  [2-7]. It was because of role of defects which could not be omitted while seeking an origin of the intermediate phase existence.

Moreover introduction of heterovalent dopant could cause creation or compensation of defects leading to the changes in stability of the crystal lattice. Recently we have proved that small concentration of niobium dopant leads to the existence of new, never observed before, intermediate phase [8] of the unknown crystal structure and properties dependent on the dopant concentration.

Therefore this work will present the acoustic anomalies and precursor dynamics of high-quality niobium doped lead zirconate single crystals investigated by Brillouin light scattering in comparison with Raman light scattering measurements in the wide temperature range above and below Curie Temperature ( $T_c$ ). The acoustic anomalies were correlated with the anomalous birefringence, piezoelectric effect, and the deviation of the Curie-Weiss law.

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## An antiferroelectric for room temperature three-state thermal switches

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Antiferroelectrics have lately undergone an accrued interest, due to their high applicability as capacitors for energy storage devices or in power electronics [1,2]. The high-temperature stability of inorganic dielectric materials is a definite asset for some applications.

In particular, lead zirconate titanate (PZT), one of the most-used ferroic material in industry, is antiferroelectric at low-titanium substitution levels. PZT ceramics display a rich temperature phase diagram, composed of antiferroelectric and ferroelectric phases, which drastically changes depending on Ti-substitution and external conditions. The study of these sequences of phase transitions is hence particularly relevant to find further applications for PZT ceramics.

In this study [3], we use Raman spectroscopy to show that the heating/cooling rates and sample history of  $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$  can induce different sequences of phase transitions, as they can help to separately stabilise lattice instabilities. We also show that three-state thermal switches could be designed by cleverly exploiting these extrinsic factors.

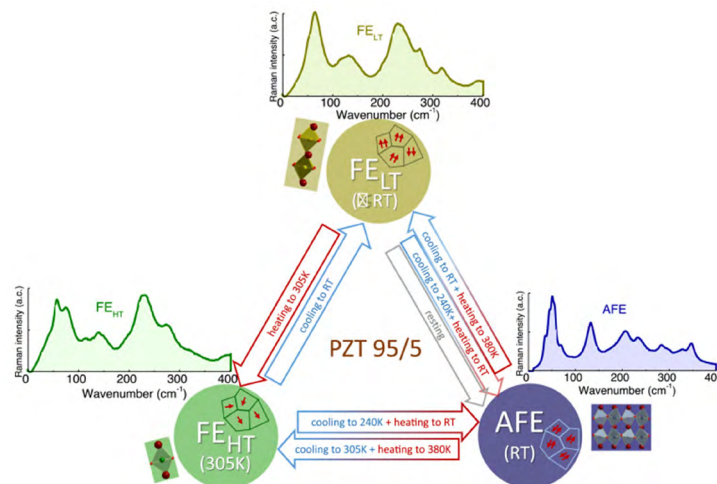


Figure 1. Scheme of thermal switching using the three near-room-temperature phases of PZT 95/5.

This work is supported by the Lead Agency Project GAČR-ARRS 24-10699K.

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## Electronic structure and mechanical properties of lead hafnate single crystal

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Lead hafnate is an anti-ferroelectric material with high application potential, e.g., as an energy capacitor for high-power applications [1,2]. The studies show the electronic structure and mechanical properties of  $\text{PbHfO}_3$  single crystals. The lead hafnate crystals were obtained by crystallization from a molten solution of  $\text{PbO-HfO}_2\text{-B}_2\text{O}_3\text{-PbF}_2$  (flux method). The crystal structure was verified by the X-ray diffraction method. The X-ray topography method was used to determine the angle of plane disorientation; the misorientation angle was equal to 0.20 degrees. The chemical composition of the crystals was checked using scanning electron microscopy, X-ray photoelectron spectroscopy, and secondary ion mass spectrometry. The crystals were investigated using dielectric spectroscopy. Both phase transitions, PE-AF2 at 473.46 K and AF2-AF1 at 430.26 K, were checked on cooling (from 623 K to 373 K) and agreed with those known in the literature [3]. The X-ray photoelectron spectroscopy tests were performed at the same temperature range to observe changes in the lead and hafnium states. The nanoindentation tests were performed to identify hardness  $H = 9.9$  GPa and reduced Young's modulus  $E_r = 125$  GPa. The obtained results were verified by nanomechanical measurements conducted by Atomic Force Microscopy, which are in good agreement with the literature [4].

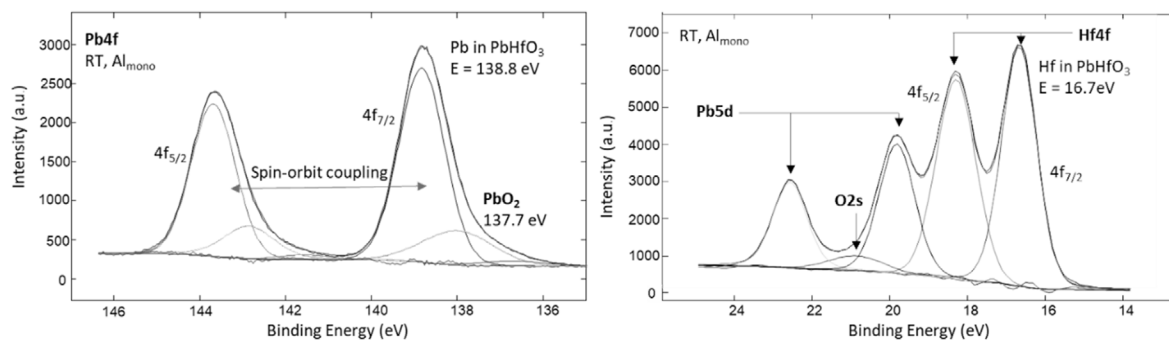


Figure 1. The XPS spectrum of lead and hafnium core lines measured at room temperature.

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## Low-temperature proton conductors based on cellulose - from micro to nano

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Low-temperature proton conductors found wide interest in modern industry due to their application potential. One of the most pressing needs that proton conductors can meet is their use in the so-called green energy, for example as an electrolyte material in PEM fuel cells or electrolyzers [1]. The most commonly used polymer, Nafion has some disadvantages caused by the thermal stability of water molecules, which are responsible for the electric properties. Due to that, Kreuer suggested using heterocyclic molecules as a potential substitute for water in proton conducting systems, as they act similarly to water and have higher boiling temperatures [2]. Moreover, the organic heterocyclic molecules are commonly combined with other organic materials, such as organic acids [3].

Another possible way to create environment-friendly proton conducting material is using cellulose, and combining it with the heterocyclic compounds. The former provides a structural backbone, while the latter is responsible for the electric conductivity. Here present the studies of different types of cellulose with imidazole: from simple microcrystalline cellulose doped with heterocyclic molecules [4] via nanocellulose and microfibers [5] to the recent studies discussing nanofibers [6]. The studies of electric conductivity show that conductivity increases with temperature, typically for protonic conductors. The strong parasitic effect of absorbed water on microcrystalline cellulose grains is thoroughly explained. The DC conductivity reaches maximum values from  $10^{-4}$  S/m at temperature  $T = 160$  °C for microcrystalline cellulose to  $10^{-1}$  S/m in the protic ionic liquid - nanofibers systems above 200 °C [7].

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## Stochastic theory of domain ordering in uniaxial ferroelectrics after quenching

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Ferroelectric materials are widely used in modern instrument making. Their unique nonlinear properties depend significantly on the state of the domain structure, which is formed stochastically under highly nonequilibrium conditions. When a sample is rapidly quenched in the region of a phase transition, both the nature of the domain ordering and the type of the formed thermodynamically stable structure are determined by the relaxation conditions. The influence of even very weak external fields (thermal, electrical, mechanical) can push the system towards the self-assembling formation of the domain structure of the different type. Understanding the mechanisms of domain formation and ordering under such conditions opens up the possibility of creating innovative methods for the production of specific ferroelectric samples.

Within the framework of the Landau-Ginzburg-Devonshire phenomenological theory, a kinetic model was developed to describe the process of the primary formation of a domain structure after rapid quenching of a sample from the paraelectric phase into the ferroelectric one [1,2]. Equations were obtained for the average polarization and its dispersion and allowed us to describe all stages of the evolution of the domain structure to a state of thermodynamic equilibrium. A phase diagram for prediction the type of observed domain states depending on the quenching temperature and external electric field was constructed. The derived analytical expressions for the correlation length, longitudinal and transverse correlation functions allowed us to describe the known experiments on quenching the TGS crystal with acceptable agreement.

In addition to the fundamental interest, further improvement of this stochastic theory will contribute to the development of practical recommendations for controlling the domain structure and optimizing the production of ferroelectric materials in demand.

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## Switchable tribology of ferroelectrics

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Switchable tribological properties of ferroelectrics offer an alternative route to visualize and control ferroelectric domains. Here, we observe the switchable friction and wear behavior of ferroelectrics using a nanoscale scanning probe-down domains have lower friction coefficient and show slower wear rate than up domains and can be used as smart masks. This asymmetry is enabled by flexoelectrically-coupled polarization in the up and down domains under a sufficiently high contact force. Moreover, we determine that this polarization-sensitive tribological asymmetry is widely applicable across various ferroelectrics with different chemical composition and crystalline symmetry. Finally, using this switchable tribology and multi-pass patterning with a domain-based dynamic smart mask, we demonstrate three-dimensional nanostructuring exploiting the asymmetric wear rates of up and down domains, which can, furthermore, be scaled up to technologically relevant (mm-cm) size. These findings demonstrate that ferroelectrics are electrically tunable tribological materials at the nanoscale for versatile applications.

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## Tracking the Nanoscale Dynamics of the Martensitic-like Phase Transition in BiFeO<sub>3</sub> via Interferometric Nanoindentation

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Bismuth ferrite (BiFeO<sub>3</sub>-BFO) is a multiferroic material that, though of rhombohedral structure in bulk, can be grown as a thin film to stabilise rhombohedral-like (R') or, at higher compressive strains, tetrahedral-like (T') monoclinic phases. This T' phase can undergo a stress-induced martensitic-like phase transition to form a localised mixture of both T' and R' phases. This local, stress-induced symmetry breaking provides a fascinating playground to investigate the effects and dynamics of these martensitic-like phase transitions at the nanoscale.

We first demonstrate how quadrature-phase differential interferometry in an atomic force microscope can be used to measure the avalanche statistics and consistent critical scaling phenomena that arise from the nanoindentation and plastic deformation of a standard lead titanate (PbTiO<sub>3</sub>-PTO) thin film. We then use a BFO film in which the T' phase is stabilised by point defects to a 70-nm thickness, and show how its scaling characteristics under nanoindentation are distinct from those of the tetragonal PTO. We here attribute this distinct scaling behaviour to the martensitic-like phase transition between T' and R' phases, and suggest this first directprobe characterisation of phase-transition dynamics can be of immense practical application for future investigation into structural phase transitions.

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## From bulk descriptions to emergent interfaces

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Controlling interfaces is highly relevant from a technological point of view. In ferroelectric materials, the energetically equivalent states of the polarization likely give rise to the existence of structures at the nanoscale in the form of interfaces (domain walls) which are widely used in sensing, actuation, nonlinear optics and information storage applications. Emergent structural and functional properties of these domain walls are widely studied for their potential integration as active nanoelectronic device components. However, their rich and complex behavior [1,2] makes them very difficult to describe theoretically and hence to predict and control. We address this problem by developing Ginzburg-Landau type models which have the advantage of allowing us to study domain properties in combination with interface characteristics [3], and that can capture features of realistic realizations of interfaces. I will show how these models can be successfully employed to probe the effects of different experimental protocols over interfaces and domains [4,5,6] and to develop new observables to characterize highly irregular interfaces [7].

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## Twisted domains in dimethylamino-terminated ferroelectric nematic liquid crystals

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Since the recent discovery of ferroelectric nematics ( $N_F$ ), these materials have become of upmost research interest due to their outstanding ferroelectric properties [1,2]. The ongoing research has been concentrated on new molecular structures promoting this type of behavior. Recently, we synthesized and characterized a new type of molecules possessing  $N_F$  phase directly on cooling from the isotropic liquid (Iso) phase in a broad temperature range and persisting till room temperatures [3]. The ferroelectric behavior of the studied series of nematogens was investigated by dielectric spectroscopy, second harmonic generation, polarization current measurements and by the analysis of the textures in polarized light. The material properties are to a great extent influenced by the geometrical conditions of the cells. In homogeneous (HG) geometry, the molecules are oriented parallel to the cell boundaries whereas in homeotropic (HT) cells the molecules are perpendicular to the surfaces.

We have investigated textural features in the  $N_F$  phase for the cells of different geometries [4]. In this work, we will describe the textures in the HG cell with antiparallel alignment. In such a cell, the molecules are mainly arranged in twisted domains with borderlines oriented preferentially perpendicular to the surface alignment (rubbing direction). We will describe these domains and present a model of  $2\pi$  disclinations, which are separating the areas of an opposite twist sense. In Figure 1, the scheme of such a disclination line is presented. We will demonstrate that the higher dipole moment and specific elastic properties of our compounds can supply remarkable topological structures. From this point of view, our data can complement the current knowledge on ferroelectric nematic phase.

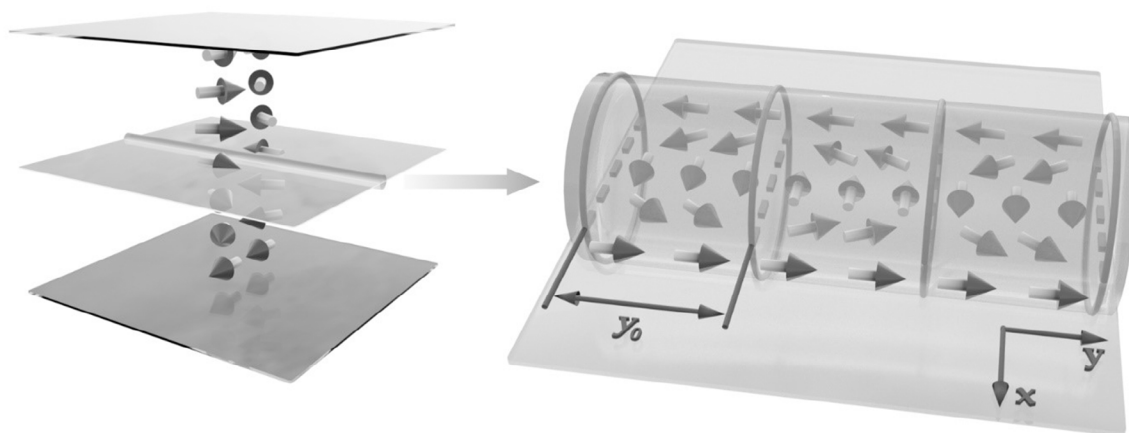


Figure 1. Scheme of the defect line, separating neighboring twisted domains.

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## Influence of interfacial stresses on electrical properties of bismuth manganite - lead titanate - epoxy composite

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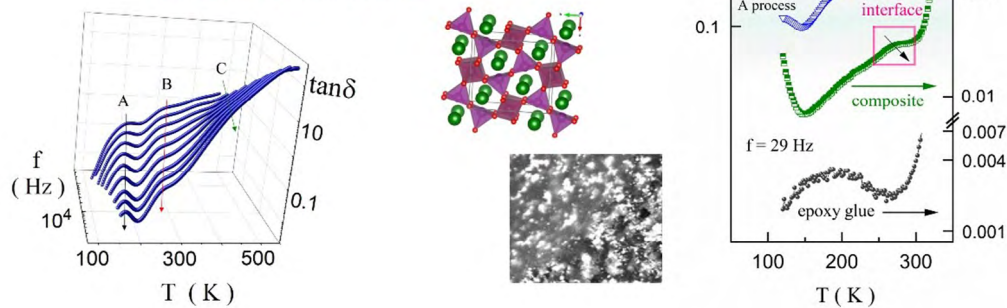
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Composite is defined as two- or multi-component material, the building blocks of which are mixed together [1]. Compared to ceramics, composites are characterized by higher electric strength and easier processing at low temperatures [2]. Hence, they help produce batteries, sensors, and electronic devices.

In our studies, we showed the electrical features of a new sintered 0.88BM-0.12PT ceramics and its organic-inorganic composite by using several interdisciplinary methods: X-ray diffraction, scanning electron microscopy, and broadband dielectric spectroscopy over wide temperature and pressure ranges. We focus on dielectric losses - an essential parameter for materials applicable in the electronics sector. In this respect, we present two paths possibilities of decrease its: application of hydrostatic pressure and preparing the composite from ceramics powder and organic matrix. We showed the high sensitivity of the studied ceramics in terms of its electrical properties to pressure changes, which makes this material attractive for application in micro-electromechanical sensors. Furthermore, we found that, surprisingly, the changes caused by embedding the inorganic material in the organic matrix and applying high hydrostatic pressure on the ceramics are similar. Hence, we show the utility of high-pressure dielectric studies of bulk inorganics to foresee their behavior in composite materials. Finally, we showed that the introduction of structural disorder in the inorganic material increases its electrical order. The interfacial stresses in the composite are proved not to destroy the electrical ordering in the crystal lattice.

### BISMUTH MANGANITE - LEAD TITANATE - EPOXY COMPOSITE



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## Preparation and characterization of LC-CNC hybrid Langmuir films

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Currently, the search for new materials often begins at the nanometric scale. The bottom-up approach in designing and synthesis of multifunctional materials or devices using nanoparticles of different size-, shape- or chemical composition- is an extreme challenge. This is especially important in the case of functional materials, also known as "intelligent" ones. In this aspect, the formation and characterization of thin layers made of materials with special properties is of great importance. In this work, the investigations of the preparation procedures and molecular stability of Langmuir films based on cellulose nanocrystals (CNC) and couple different liquid crystals are presented. The CNC-based nanocomposite Langmuir films with the 5CB, 5OCB, 5FCB, and 5PCH liquid crystals, have been obtained by the modified Langmuir technique. The liquid crystal/polymer systems will be characterized in terms of the selection of components, their concentrations and exposure time. The obtained systems were characterized using a polarizing microscope, optical spectroscopy and other auxiliary methods.

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## Coupling of multiferroic order parameters in magnetite $\text{Fe}_3\text{O}_4$

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Magnetite has long been investigated across many disciplines due to the interplay between its ferroic order parameters, namely its ferromagnetism, ferroelasticity and ferroelectricity. It is particularly of interest to the multiferroic community for this reason and is the perfect environment to investigate the coupling between its magnetism, spontaneous polarisation and crystal structure. A host of techniques have been applied to magnetite single crystals to attempt to begin untangling the interplay between these couplings, such as synchrotron X-ray diffraction, SQUID magnetometry, and various functionalised atomic force microscopies. Particular interest is taken for the material properties across magnetite's Verwey phase transitions at 120 K [1], where it becomes ferroelastic, and the lower ferroelectric phase transition, which occurs at 38 K [2].

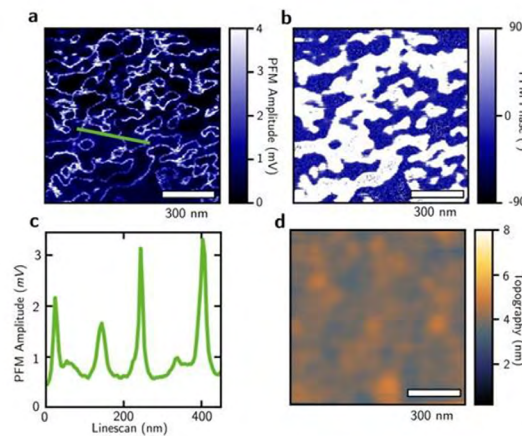


Figure 1. First real space images of ferroelectric domains. **a** Piezo force microscopy amplitude and **b** phase images of the ferroelectric phase. **c** Amplitude line scans and **d** topography.

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## Exploring the Dynamics Complexity of Ammonium-Templated Hybrid Organic-Inorganic Perovskites: Insights from Broadband Dielectric Spectroscopy

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Hybrid organic-inorganic perovskites (HOIP) constitute one of the most intensely studied classes of chemical compounds due to their diverse range of properties including optical, magnetic, dielectric, ferroelastic, ferroelectric, and multiferroic behaviors, as well as phase transitions. While numerous structures have been designed, containing predominantly small organic cations, a significant leap in complexity was achieved with the integration of elongated polyammonium molecular ions into the framework cavity. These molecular entities differently fill the cavity within the organic-inorganic framework, giving rise to a plethora of distinctive characteristics.

The investigation of general structure-property relationships within this class of compounds has emerged as a main research point, driven by the quest to unravel their distinctive characteristics. Notably, these compounds exhibit rich dielectric phenomena, including relaxation processes, which stem from dynamic disorder associated with the flexible binding of polyprotonated ions within the crystal lattice. In contrast to their monoprotonated counterparts, these ions boast multiple anchoring points, both terminal and internal, suggesting the potential activation of diverse rotor modes depending on thermodynamic conditions.

While these compounds hold promise, only limited number of HOIP with polyammonium cations have been found. This scarcity raises questions about the feasibility of segmental dynamics within the rotating part. To address this, we used broadband dielectric spectroscopy to analyze how different cationic species interact with the framework. This study aims to uncover the subtle details of molecular dynamics and drive progress in hybrid organic-inorganic materials research.

## Transition from neutral to ionic phase in the charge-transfer complex $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$ , a potential ferroelectric material

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The charge-transfer complex  $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$  ( $\text{EDT-TTF-I}_2$  = diiodinated-ethylenedithio-tetra-thiafulvalene;  $\text{TCNQF}$  = fluorinated-tetracyanoquinodimethane) belongs to crystals with mixed-stack structure, where diads of donor ( $D$ ) molecules alternate with acceptor ( $A$ ) molecules, forming stacks along  $a$ - $b$  direction. The parallel ...DDADDA... stacks interact with each other and are arranged in layers perpendicular to  $c$ -axis [1]. The  $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$  is a first complex of 2:1 stoichiometry that undergoes neutral-to-ionic transition (NIT) under external stimuli like temperature, pressure. NIT is a complex phenomenon where the change of molecular ionicity is coupled with structure distortions. In effect,  $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$  has potentially ferroelectric properties.

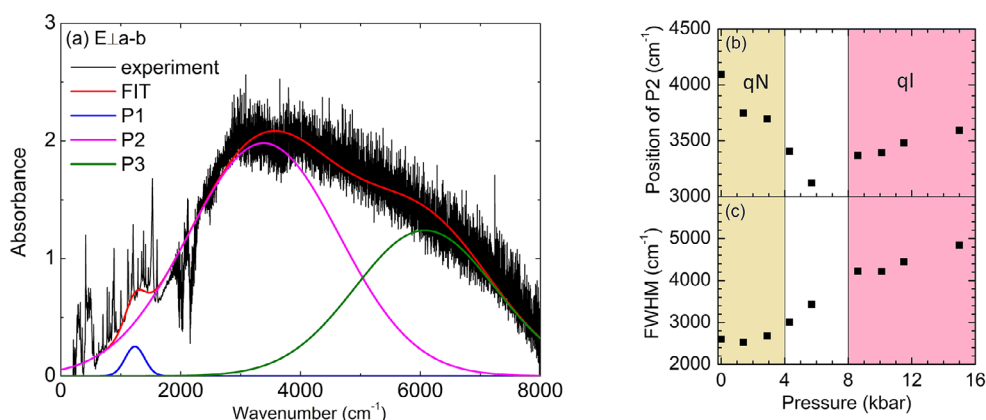


Figure 1. Pressure dependence of the absorbance spectra of  $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$  at room temperature; (a) fitted absorbance spectrum with three electronic bands; (b) position and (c) full width at half maximum ( $FWHM$ ) of  $P2$  band as a function of pressure.

Electrical transport measurements of the  $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$  crystals were performed as a function of hydrostatic pressure ( $p$ ) and temperature ( $T$ ) to provide information about  $p$ - and  $T$ -ranges of three phases: quasi-neutral ( $qN$ ), mixed, and quasi-ionic ( $qI$ ) [2]. The aim of infrared studies of  $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$  as a function of  $p$  and  $T$  was to investigate the local structure and charge distribution. The spectra were recorded in a broad frequency range to discuss electronic absorption and vibrational modes that are sensitive probe of charge distribution and structural distortions. Figure 1 shows that approaching the ionic phase, mid-infrared electrical absorption ( $P2$ ) moves towards lower frequencies with minimum frequency value at the pressure where mixed phase is formed. It is observed that the full width at half maximum ( $FWHM$ ) of  $P2$  is constant in the  $qN$  phase, whereas in the mixed phase increases abruptly and saturates in the  $qI$  phase.

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## Nonmagnetic antiskyrmionic medium found

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The prediction and experimental confirmation of magnetic skyrmions - the objects with nontrivial swirling spins patterns - revolutionized the physics of nanoscale magnetism and opened new horizons for spintronics. It seems more and more that the field of ferroelectrics may follow these fascinating physics and plausible innovation horizons.

In particular, our recent computer experiments [1] reveal that the archetype ferroelectric material, barium titanate, can actually host antiskyrmions even in its bulk form. We show that the antiskyrmion of barium titanate has just 2 - 3 nm in diameter, it has a hexagonal cross-section, and that it carries a very exotic topological charge of minus two. We argue that this beautiful and unique noncollinear polarization pattern, that has never been described before, arises due to a fortunate combination of the moderate anisotropy of the anharmonic electric susceptibility and the characteristic anisotropy of the polarization correlations in barium titanate crystals. We outline its impact of ferroelectric properties and explore the prospects of its experimental evidence.

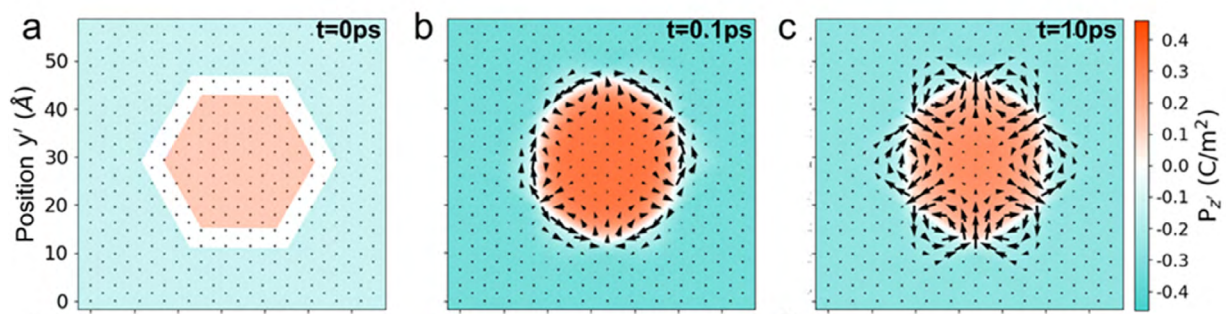


Figure 1. Results of atomistic shell-model based computational experiment with barium titanate showing spontaneous formation of the of-axis polarization pattern, responsible for the conversion of the topologically trivial ferroelectric bubble domain into a topological antiskyrmion [1].

*This work was supported by the Czech Science Foundation (project no. 19-28594X).*

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## Creation, motion and annihilation of nonmagnetic Antiskyrmions

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Inspired by the recent work by Mauro A. P. Gonçalves et al. [1] we have started to investigate the antiskyrmion structure (see Fig.1) in rhombohedral phase of  $\text{BaTiO}_3$  using the phase-field simulation method. In this contribution we shall report about our most recently obtained results describing the process of antiskyrmion creation, annihilation and the possibility of its controlled movement with electric field application.

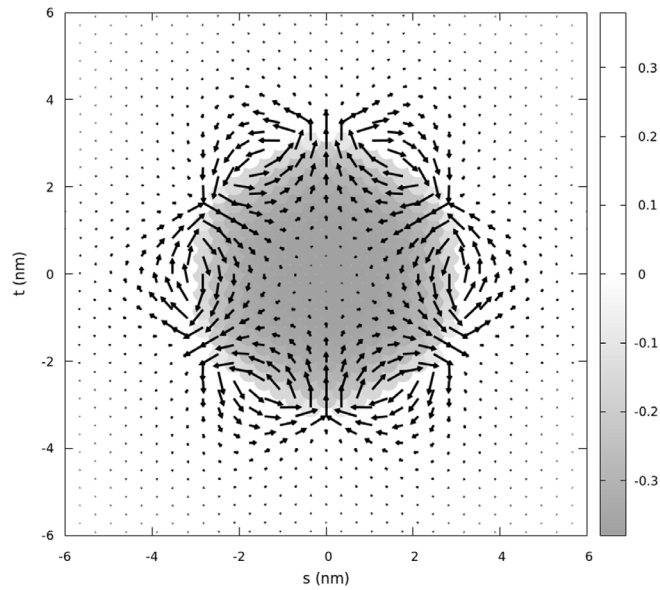


Figure 1. Antiskyrmion structure in rhombohedral  $\text{BaTiO}_3$ . The symmetry-adapted coordinate system  $(\mathbf{r}, \mathbf{s}, \mathbf{t})$  was used for this figure, where  $\mathbf{s} // [1-10]$ ,  $\mathbf{t} // [-1-12]$  and  $\mathbf{r} // [111]$  directions. Right hand palette indicates the  $P_r$  polarization component amplitude.

*This work was supported by the Czech Science Foundation (project no. 19-28594X).*

References:

[1] Mauro A.P. Gonçalves, M. Paściak, J. Hlinka, Antiskyrmionic ferroelectric medium, arXiv:2303.07389 (2023).

## A numerical method to obtain physical properties from liquid crystal texture analysis

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In many different fields of science and technology experimental results are often obtained in the form of images. An example is polarizing optical microscopy (POM), which is a basic and widely used research method in the field of soft matter, especially in the study of liquid crystals and polymers. A possible way to extract physical information from POM images is to analyse them numerically. In many cases, numerical texture analysis is based on the use of gray-level co-occurrence matrices (GLCM) with various Haralik-like characteristics. In this way, the light intensity of individual pixels is analysed without colour information. Recently, this approach has been generalized to include colour characteristics and the proposed extension will be discussed in the presentation. In this method, the mapping of the physical distribution of light wavelength is achieved by appropriate conversion of the texture image from the RGB (red-green-blue) colour space model to the HSL (hue-saturation-lightness) model [1]. This enables local colour changes caused by external factors, e.g. temperature, electric field, or stress, to be identified. In this way, it is possible to analyse some properties of the liquid crystal material.

The main goal of the presented approach is to gain some physical properties of the liquid crystal material based on the analysis of two-dimensional colour POM textures. In the presentation three examples of applications of the numerical method of texture analysis will be shown. The first one is related to the identification of the sequence of mesophases occurring in thermotropic liquid crystals by considering first and second order statistical image characteristics, in particular the possibility of locating subtle transitions between mesophases with very similar textures. The second example will show how the wavelength distribution determined from the texture analysis method changes with an increase of the external electric field applied to the liquid crystal sample. The last (third) example will concern the determination of birefringence as a function of temperature in a liquid crystal material based on the texture analysis method. In the presentation a few examples of colour POM textures of ferroelectric smectic phases and blue phases will be shown, along with the results of the numerical texture analysis method.

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## BiFeO<sub>3</sub> nanoparticles using atomistic simulations

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Ferroelectric nanoparticles exhibit intriguing arrangements of polarization, including vortex-like structures [1] and Hopfions [2]. These diverse multidomain configurations are significantly influenced by the size, shape, and termination of the nanoparticles, which impose the electrostatic boundary conditions.

In this study, we used atomistic simulations with parameters derived from first-principles calculations [3] to explore cubic-like BiFeO<sub>3</sub> nanoparticles with different terminations and sizes. Special emphasis is placed on surface effects induced by termination, where two scenarios are considered: one with opposite faces of the cuboidal nanoparticle terminated with either BiO or FeO<sub>2</sub>, and another with specially designed termination for electrostatic equivalence across all faces.

Surprisingly, our findings unveil multiple multidomain configurations and the unexpected stabilization of a different phase of BiFeO<sub>3</sub>, all separated by small energy differences. We evaluate both polarization and oxygen octahedra rotation for all the configurations obtained, taking advantage of the atomic scale details provided by the methods used in this study.

*This work was supported by the European Union and the Czech Ministry of Education, Youth and Sports (Project: MSCA Fellowship CZ FZU I - CZ.02.01.01/00/22\_010/0002906).*

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# Phase coexistence and complex domain structures in BaTiO<sub>3</sub> induced by SrTiO<sub>3</sub> inclusions

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Recently, ferroelectric-paraelectric nanocomposites have come into focus as they host complex polar topologies such as vortices and skyrmions [1,2,3]. These nanoscale polar structures can exhibit antiferroelectric-like behavior, or negative capacitance, making them promising for energy storage applications [4,5]. These exceptional properties stems from the combination of interfacial strain and the polar discontinuity at the internal interfaces. In recent years, PbTiO<sub>3</sub>/SrTiO<sub>3</sub> superlattices in particular have been extensively studied, while other morphologies and material combinations are underrepresented [6].

In this work, we study the impact of SrTiO<sub>3</sub> nanodots on phase and domain stability of a surrounding BaTiO<sub>3</sub> matrix. To screen different sizes and volume fractions of these inclusions, we use efficient molecular dynamics simulations based on ab initio derived effective Hamiltonian [7,8]. We find that once the SrTiO<sub>3</sub> inclusion size reaches a critical relative volume, strong depolarization fields induce complex domain patterns and phase coexistence over a broad temperature range, see Fig. 1.

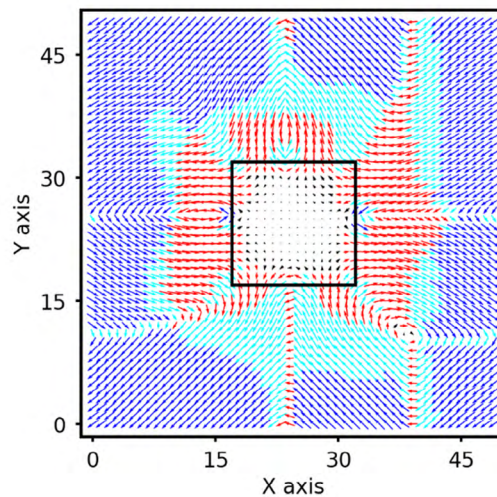


Figure 1. Local polarization profile around 6 nm SrTiO<sub>3</sub> inclusion (solid square in the middle) embedded in a BaTiO<sub>3</sub> matrix. Colors encode tetragonal (red), orthorhombic (cyan) and rhombohedral (blue) phases.

This work was supported by the German research foundation (DFG) GR 4792/2.

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## Magnetostructural phase transition in the pseudobinary $\text{Ce}(\text{Fe}_{0.9}\text{Co}_{0.1})_2$ compound

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The  $\text{CeFe}_2$  compound crystallizes in C15 Laves phase with a cubic structure. This alloy is characterized by low ferromagnetic ordering temperature and low saturation magnetization, connected with strong hybridization between Ce  $4f$  and Fe  $3d$  electrons [1]. Magnetic moments of both sublattices are coupled antiparallel.

The  $\text{Ce}(\text{Fe}_{0.9}\text{Co}_{0.1})_2$  flakes with  $\text{MgCu}_2$ -type cubic structure (C15 Laves phase) were synthesized by use of melt-spinning method. The thermomagnetic measurements exhibit phase transition from ferromagnetic to antiferromagnetic phase occurring below 90 K. Thermal hysteresis is observed indicating first-order phase transition. Magnetic transition is accompanied with distortion of cubic structure into rhombohedral one. At the lower temperatures, the simultaneous coexistence of two magnetic states (ferromagnetic and antiferromagnetic) is confirmed for such disordered  $\text{Ce}(\text{Fe}_{0.9}\text{Co}_{0.1})_2$  sample, in contrast to homogenized samples where pure antiferromagnetic phase is observed [2]. During heating, the magnetic phase transition from ferromagnetic to paramagnetic occurs at 182 K. Additionally, the influence of structural disorder introduced by plastic deformation (high pressure torsion) was investigated as utilized for  $\text{YCo}_2$  before [3]. In comparison to the as-quenched sample thermomagnetic measurements show that the vast majority of the volume fraction is ferromagnetic at lower temperatures due to highly disordered structure and significant grain refinement.

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## Spin-electric coupling in ferroelectric materials

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Control and manipulation of electron spins is presently hot topic in condensed matter physics, motivated not only by the intriguing fundamental materials physics but also by the applications in future low-power quantum information processing (QIP) and spintronics where electron spin with its two quantum states is the best candidate for quantum bit (or qubit). The main problem in designing low-power QIP instrumentation is replacing the magnetic field with an electric field in controlling of spins that can reduce the energy for one operation with a spin to attoJoules, in contrast to the rather huge energy usually used to create magnetic fields and maintain their non-zero value. Compared to magnetic fields, electric fields can be applied on a much more local length scale up to nm, thus allowing easier addressing of individual quantum bits. Electric field introduces also new functionality into quantum system. Therefore, search for new materials suitable for hosting of spins with high tunability by electric field and long spin coherence time is the main scientific and technical problem in further development and commercial realization of quantum technologies based on electron spins (spin qubits).

In this report, we demonstrate a promising perspectives in applications of ferroelectric materials in QIP, as a media for hosting spin-qubits that can be substantially more energy efficiently controlled by electric fields. For measurements, classical  $\text{PbTiO}_3$  and incipient (also called as quantum paraelectrics)  $\text{SrTiO}_3$  and  $\text{KTaO}_3$  ferroelectrics weakly doped with  $\text{Fe}^{3+}$  or  $\text{Mn}^{2+}$  spins were used. The spin-electric coupling was measured by utilizing both the continuous wave and pulse time-resolved electron spin resonance (EPR) technique at temperatures down to 3.5 K and electric fields of 0 - 50 kV/cm. High frequency rapid scan electron spin resonance spectrometer (THz-FRASCAN-ESR) operating at frequencies up to 1 THz was used as well [1]. Our measurements show a significant (up to three orders of magnitude) amplification of the spin-electric coupling in quantum paraelectrics as compared to conventional dielectrics. The effect is related to the very high dielectric permittivity (up to 25000 in  $\text{SrTiO}_3$ ) of quantum paraelectrics. Moreover, it is found that the same amplification is valid for microwave pulses used in coherent manipulation of spin ensembles at ns timescale. Applied microwave power decreases to milliwatts as compared to the tens-hundreds of watts used for spins in conventional materials [2]. The amplification of microwave magnetic field is explained by huge displacement current and that in turn creates the secondary magnetic field. We believe that a wide spectrum of ferroelectric materials, spanning inorganic oxides to polymeric systems such as polyvinilidene fluoride, presents an attractive platform to explore electric field control of magnetic properties for quantum applications.

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## Weak-field FMR near the collinear to conical ferrimagnetic phase transition in U-type hexaferrite $\text{Sr}_4\text{CoZnFe}_{36}\text{O}_{60}$ ceramics

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The natural ferromagnetic resonance (FMR) of the U-type hexaferrite  $\text{Sr}_4\text{CoZnFe}_{36}\text{O}_{60}$  ceramics, which is the dominating microwave (MW) magnon with the critical slowing-down towards the collinear to conical ferrimagnetic phase transition at  $T_{c2} = 305$  K, is analyzed in detail. Both the temperature dependence of the FMR near  $T_{c2}$  without application of the bias magnetic field and its change under application of the weak bias ( $H < 700$  Oe) at the room temperature (i.e., in the conical phase close to  $T_{c2}$ ) are under consideration. The natural FMR behavior and interference with other MW magnons at temperatures 305 - 320 K is found to correlate with the temperature evolution of the weak-field magnetization [1]: from two components in the conical phase to one component in the collinear phase.

The high sensitivity of the FMR dynamics to the weak magnetic bias field in the conical phase close to  $T_{c2}$  is shown to be caused by the gradual transformation of the mixed transversal and longitudinal conical spin magnetic moments to the predominantly longitudinal ones with the increasing bias field. Application of the weak magnetic bias field allows to adjust the MW absorption: its level of above 30 dB is achieved in the coplanar waveguide near the FMR frequency (5.7 - 7.2 GHz), which allows to consider the  $\text{Sr}_4\text{CoZnFe}_{36}\text{O}_{60}$  hexaferrite ceramics as a possible MW absorbing material [2].

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## Optical pseudo-biaxiality of relaxor strontium-barium niobate single crystals

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Solid solutions of the strontium-barium niobate  $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$  where  $0 < x < 1$  (SBN) are environmental friendly (lead free) polar materials of oxygen octahedral family. Their potential applications are based on very attractive pyroelectric, electromechanical, electro-optic, photorefractive, and nonlinear optical and dielectric properties. Strontium-barium niobate is distinguished by its open tungsten bronze structure, i.e. the compound contains five  $\text{AB}_2\text{O}_6$  formula units per tetragonal unit cell in which six  $A$  sites are occupied by five divalent metal atoms  $A$ . As a result the empty  $A$  sites give rise to quenched electric random fields even in the stoichiometric compound. Consequently, by changing the ratio between strontium and barium components one may tune the system from ferroelectric ( $x < 0.5$ ) to a generic relaxor ( $x > 0.6$ ) behavior while maintaining the structure unchanged [1].

Using the Czochralski method four single crystalline compounds with nominal  $x = 0.40, 0.50, 0.61,$  and  $0.75$ , designated hereafter as SBN40, SBN50, SBN61, and SBN75 have been grown. The crystals grown along the  $[001]$  tetragonal direction were up to 22 mm in diameter and 40 mm in length with characteristic 24 faces, free from strations and other extended defects. Density of etch pits was found to be of the order of  $10^2 - 10^3 \text{ cm}^{-2}$ .

The ferroelectric SBN crystals are tetragonal, and according to their symmetry, are optically uniaxial. On the other hand SBN75, with typical relaxor ferroelectric properties, being tetragonal, exhibits optical features characteristic for optically biaxial systems. This kind of behavior could be considered as optical pseudo-biaxiality or quasi-biaxiality.

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## What if there were no Polish-Czech Seminars?

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The Polish-Czech Seminar on Structural and Ferroelectric Phase Transitions is an exceptional form of seminar. The twenty-five editions took place over fifty years. From its beginning, the seminars always gathered experienced and young scientists, giving an extraordinary occasion to learn and discuss ferroics physics in a short time. It was a pleasure to observe how these young scientists shaped their careers and started cooperating with prestigious worldwide laboratories. This contribution aims not only to present some memories from all (except the first one) seminars I took part in, and to which I am always returning with great pleasure.

On the one hand, this contribution will answer the question posed in the title, and on the other hand, it will show some new experimental data that has not yet been published and is awaiting discussion, which always took place during these seminars. It concerns the dielectric, piezoelectric and electrostrictive properties of the  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  single crystals with the antiferroelectric and ferroelectric phase transitions. After decades, it appeared that there are doubts about pure antiferroelectric structure existence in the lead zirconate and lead hafnate, which were treated until now as classical antiferroelectrics [1]. A reason for such doubts is the observation of the piezoelectric effect at room temperature in the antiferroelectric phase of a PZT single crystal. Interestingly, while this effect cannot appear in the centrosymmetric antiferroelectric structure, it is of a stairs-like character in a specific range of frequency and electric field strength (Figure 1).

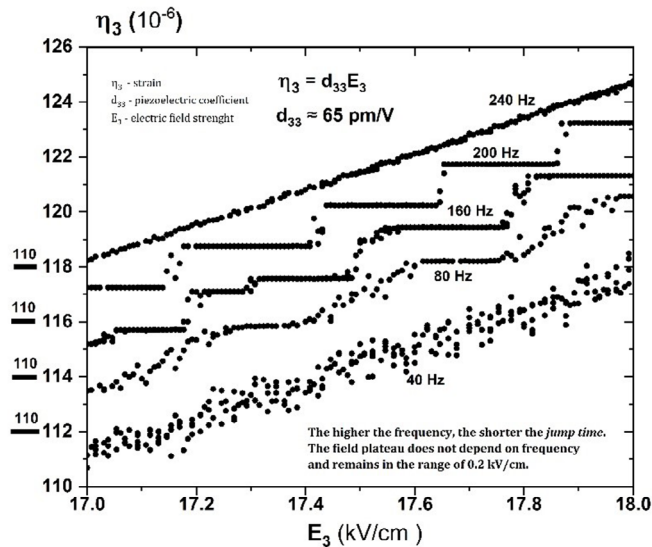


Figure 1. Stairs-like piezoelectric response in the antiferroelectric phase of  $\text{PbZr}_{0.96}\text{Ti}_{0.04}\text{O}_3$  single crystal.

This work was supported by the National Science Centre, Poland, Grant No. 2022/47/B/ST3/02778.

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## Activities for the development of the hydrogen economy in the Wielkopolska Region

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In 2021, the European Union set a new target of at least a 55% reduction in greenhouse gas emissions by 2030 and climate neutrality by 2050. Achieving these goals while maintaining the economy's competitiveness will require major structural changes, including a gradual reduction in the use of fossil fuels and energy-inefficient production processes. The general direction will be electrification, increase and accelerate the use of renewable energy, including hydrogen and its derivatives, in power generation, industry, construction, and transport.

The Wielkopolska Region was one of the first regions in Poland to recognize the use and implementation of hydrogen technology as an opportunity to improve the economic development of the region. The Wielkopolska Region Government has been in favor of developing the hydrogen economy in the Wielkopolska Region since 2018. The activities have been aimed at all stakeholders involved in the hydrogen technology development process. At the national level, Wielkopolska Region is characterized by its bottom-up approach, i.e. the Wielkopolska Region Government aims to ensure that the process of creating and implementing green solutions is based on an analysis of the use of local business and scientific potential (so-called local content), with the simultaneous support of the local government and cooperation with national and international institutions.

Therefore, we have carried out several activities aimed at supporting the energy transformation process by, among others, integrating communities, e.g. in December 2019, the Wielkopolska Hydrogen Platform was established, and in July 2021, a ceremonial signing of the Declaration of Intent to establish the Wielkopolska Hydrogen Valley took place. In April this year, the Strategy for the Development of the Wielkopolska Hydrogen Valley until 2030 with an outlook until 2040 was adopted, which also emphasizes the use of local resources in the process of building a hydrogen economy.



# **POSTER PRESENTATION**

## Investigations of the key electrical parameters and structural properties of commercial ZnO ceramics used in surge arresters

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Surge arresters are devices used to protect electrical consumers connected to power transmission or distribution lines from electrical transients caused by e.g. lightning or switching faults in high-voltage systems. Commercially available surge arresters use must comply with strict standards and demonstrate reliable and stable operation after multiple overvoltage events. Examples of surge arresters are varistors, whose resistance is highly dependent on the electrical voltage and tends to drop rapidly when the voltage exceeds a certain threshold. The active element in varistors is usually a ZnO-based ceramic doped with Bi<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub> oxides. Its quality is a key factor for proper operation of surge arresters, as it should exhibit the desired current-voltage parameters and also be resistant to ageing effects.

The aim of this study was to develop suitable tests for surge arresters and examine the effect of multiple surges on the quality of their ceramics [1]. The following key electrical parameters of commercially available surge arresters from four manufacturers were tested: voltage at the terminals of the varistor with a DC current; limiting voltage at discharge current and the resistive component of leakage current at the highest operating voltage. The ageing effects were investigated by powder X-ray diffraction (pXRD) and scanning electron microscopy after the ceramic samples were subjected to 1 and 50 electric discharges. Changes in the chemical composition of ceramics were identified using energy-dispersive spectroscopy (EDS).

Our research showed that even commercial products can be of poor quality - some of the arresters were easily damaged by current strokes, indicating a large dispersion of technical parameters and even exceeding the declared values. Paradoxically, multiple electrical strokes improved the crystallinity of some samples, as the Joule heating caused a transition in Sb<sub>2</sub>O<sub>3</sub> to a pyrochlore or spinel structure and/or to the δ-Bi<sub>2</sub>O<sub>3</sub> phase.

*This work was supported in part by Polish Energy Company ENEA.*

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## Tailoring of Plausible Skyrmion Media in SrTiO<sub>3</sub> Perovskite

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After the experimental verification of soliton solutions for the magnetization field in ferromagnetic materials, known as stable Skyrmions [1,2], researchers extended their interest to various quasiparticles arising from topological features [3,4,5]. Skyrmions, stable soliton vortices in vector fields, may exhibit different particle-like behaviors, such as a finite mass.

Stable Skyrmion phases can exist in ferromagnetics when the exchange interaction energy competes with the Dzyaloshinskii-Moria interaction (DMI). While nonmagnetic ferroelectrics lack DMI, a suitable symmetry breaking can introduce an analogous Lifshitz invariant in terms of electric polarization. Theoretical predictions suggest that phase transitions from specific parent phases to specific daughter phases should allow for Bloch skyrmion phases analogous to those of the bulk ferromagnets [6].

This work focuses on designing bulk materials where the bulk Lifshitz terms are permitted. As the prototype nonmagnetic model material, we have selected the highly polarizable SrTiO<sub>3</sub> perovskite. We try to exploit its structural anti-distortive transition from the cubic to the tetragonal phase as well as its implicit ferroelectric instabilities. Further symmetry breaking is achieved through chemical or isotopic substitutions at particular ionic sublattices. The hypothetical materials are studied in the framework of the density functional theory.

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## Spectroscopic studies of magnetic and lattice excitations in van der Waals ferromagnets

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Two-dimensional (2D) van der Waals (vdW) magnetic materials have become a target of intense basic and applied research due to the high potential for microelectronics and spintronics. Raman scattering has proven to be an effective tool for investigation of the magnetic and lattice degrees of freedom in 2D magnets [1].

In this contribution, Raman, infrared (IR) and terahertz (THz) spectroscopic techniques were used to study the magnetic and structural phase transitions in bulk  $\text{VI}_3$  single crystal at temperatures down to 4 K. Below the structural phase transition at  $T_{S1} = 79$  K, similar to the exfoliated flakes of  $\text{VI}_3$  [2], a large splitting of polar phonon modes appears, and strong ferromagnetic fluctuations are observed. Below  $T_c = 50$  K, two Raman modes appear simultaneously and show a giant softening in the narrow interval around the second structural transition temperature,  $T_{S2}$ . Below  $T_{S2}$ , a magnon comes out in the Raman spectra at low frequencies. This THz magnon, observed in bulk  $\text{VI}_3$ , indicates the application potential of 2D van der Waals ferromagnets in ultrafast THz spintronics.

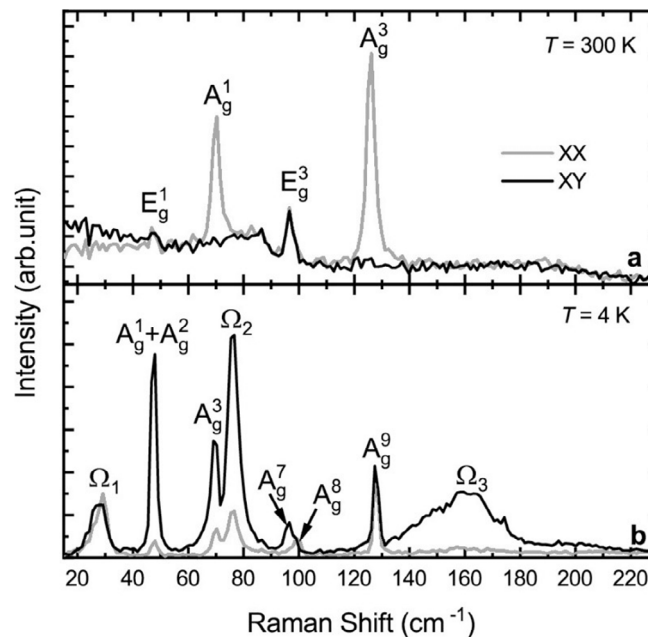


Figure 1. F Polarized Raman spectra of  $\text{VI}_3$  taken at 300 K in the rhombohedral phase and at 4 K in the FM triclinic phase [3].

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## Photo-active self-assembling materials: effect of lateral substitution far from the chiral centre

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Various photo-active materials and composites possessing self-assembling behaviour attract considerable attention due to their exciting possibility to drive, tune and control the optical properties of soft systems in a contactless way [1-7]. Lateral substitution by halogen atoms and other groups is a very effective tool to tune the mesomorphic and photo-active behaviour of an exciting class of organic self-assembling systems, specifically chiral liquid crystals [3].

To contribute to better understanding of the effect of lateral substitution (by fluorine, chlorine, bromine atoms and methyl group in R position) on the self-assembling behaviour, several new materials with lateral substituents placed on benzene ring far from the chiral centre and close to the azobenzene moiety are designed and their mesomorphic behaviour was established using POM and DSC. With exception of the bromine substituted material, all compounds possess the liquid crystalline behaviour, specifically the cholesteric phase; the TGBA\* phase was detected for the non-substituted compound only.

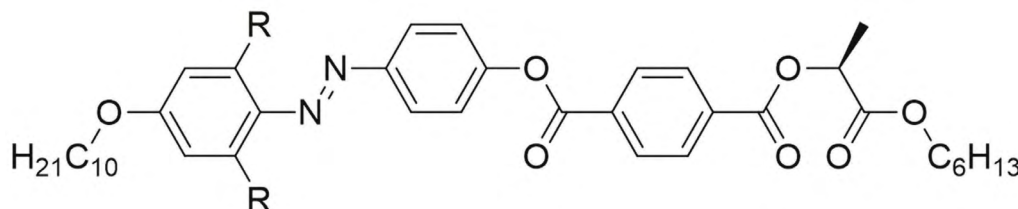


Figure 1. General chemical structure of newly designed compounds laterally substituted in R position by fluorine, chlorine, bromine atoms and methyl group

The photo-isomerization process, specifically the conversion of the *E-Z* isomers was studied in toluene solution by high performance liquid chromatography; the kinetics of the photo-isomerisation was established under illumination of the UV light (366 nm). The UV-VIS spectra show a significant difference in absorbance around 350 nm and 450 nm due to the change of *E-Z* isomer ratio for all designed azo compounds with different lateral substituents. Under irradiation by UV light at room temperature, the non-substituted compound was the fastest to reach the photostationary state (i.e. *E* and *Z* isomers are in equilibrium). In this case 93% of the material was photoisomerized to the *Z* isomer in less than 20 minutes. For other materials, the photostationary state was reached after more than 30 minutes of irradiation, and not more than 63 - 80% of the substance was the *Z* isomer. The fastest thermal relaxation time to original *E*-state was found for the non-substituted and methyl substituted compounds; it takes only ~20 - 25 hours to reach their pre-irradiation state. The chlorine substituted material was the slowest to relax back to the original *E*-state and it takes more than 140 hours.

Due to photo-active azo group, the designed chiral self-assembling materials can be used as dopants for design of functional photo-active liquid crystalline mixtures targeted for optoelectronic and photonic applications.

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## The Rareness of the Single Ion Perovskite Multiferroics is Caused by Complexities of the Synthesis

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It was believed that the single ion multiferroicity exhibiting simultaneous ferroelectric (FE) and magnetic orderings is extremely rare because it originates from the two mutually exclusive orders: the magnetism which requires partially filled  $d^n$  orbitals, and the FE distortions which occur by the hybridization of empty  $d^0$  shells. We have shown that it is possible to achieve FE distortions in a lattice of magnetic  $d^3$  system of manganate  $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_{3-d}$  perovskites when the Mn-O bonds are strongly stretched beyond the equilibrium lengths, thus demonstrating that the scarcity of multiferroic systems is not the mutual exclusion. Instead, we have shown that the reason of their rareness is the difficulty of obtaining magnetic compounds with the expected tolerance factor  $t_E(T) > 1$  above room temperature, which stretches Mn-O bonds and induces FE distortions. The difficulty of achieving  $t_E(T \sim 400 \text{ K}) > 1$  is due to the challenging demands of perovskites structural stability and their temporal properties: (1) the requirement of  $t(T) \leq 1$  for attaining them at temperatures  $T \sim 1700 \text{ K}$ , and (2) the universal temperature dependence of the measured tolerance factor  $t(T) \sim t_0 + aT^2$  that decreases on cooling.

To achieve FE distortions in a manganates  $d^3$  system we noticed that the FE with the highest  $T_C$  of 400 K has been observed in the prototypical  $d^0$  nonmagnetic titanates perovskites  $\text{A}^{2+}\text{TiO}_3$  for the largest ion  $\text{A} = \text{Ba}$ . By using the tabulated equilibrium bond lengths of [Ba-O] and [Ti-O] the  $t_E = [\text{Ba-O}]/2^{1/2}[\text{Ti-O}] > 1$ , i.e., the [Ti-O] and [B-O] bonds are respectively under tension and compression in the observed cubic perovskites with the measured  $t = 1$  at  $T > T_C$ . Similar  $t_E > 1$  is expected for the cubic antiferromagnetic ( $T_N = 234 \text{ K}$ )  $\text{SrMnO}_3$  for which the [Mn-O] bonds are also under tension, but no FE is observed. However, the tension can be increased with the substitution of the larger Ba for Sr and the FE distortion is generated for  $x \geq 0.43$ . These compounds have been achieved only by using the two-step synthesis procedure to (1) decrease  $t(T \sim 1700 \text{ K}, d = 0.5)$  below 1 by increasing the size of the  $[\text{Mn}^{3+}\text{-O}]$  bonds, thus forming the oxygen reduced perovskites at high temperatures, and (2) oxidize at lower temperatures while preserving perovskite structure to achieve  $t_E(T \sim 400 \text{ K}, d = 0) > 1$  for the shorter  $[\text{Mn}^{4+}\text{-O}]$  bonds. These new multiferroics exhibited FE distortions and the G-type magnetic structure originating exclusively from a single-ion displacement of the magnetic  $\text{Mn}^{4+}$  cations and oxygen. Typical, displacive-type tetragonal FE distortions with the estimated polarization of  $P_s \sim 14 \mu\text{C}/\text{cm}^2$  calculated from the point charge model occur when the Mn ions move out of the center of the  $\text{MnO}_6$  octahedral units below  $T_C \sim 350 \text{ K}$ . For  $t_E > 1$ , the stretched  $[\text{Mn}^{4+}\text{-O}]$  bonds split into long and short bonds along the  $c$ -axis when they are elongated by more than 1.7% above the equilibrium length. When at lower temperatures the Mn spins order magnetically below  $T_N \sim 210 \text{ K}$ , the displacive distortions decrease to  $P_s \sim 12 \mu\text{C}/\text{cm}^2$ , demonstrating that the two order parameters are strongly coupled. Thus, for these type-I multiferroics with a large electric polarization the FE and AFM orders are strongly coupled which enables the possibility for electric control of magnetism and vice versa. We have used the same design principles to increase  $T_C$  to 420 K in the Ti-substituted  $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$  multiferroics, however with the reduced  $T_N$ .

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## Diffuse scattering of 2D ferroelectric $(\text{PbS})_{1.18}\text{VS}_2$

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Ferroelectric two-dimensional materials present technologically interesting properties such as polarization switching by in-plane interlayer sliding and enhanced capacitance due to almost no structural disruption at the surface [1]. Creating 2D ferroelectrics can be done by manual stacking of exfoliated 2D monolayers with a predefined twist angle between them. The creation of manual stacked 2D heterostructures is however complex. To avoid manual stacking, we explored the misfit layer compound  $(\text{PbS})_{1.11}\text{VS}_2$ , which grows naturally with an alternated stacking of PbS and  $\text{VS}_2$  layers. The interaction between layers favors the growth of twins with a small twist angle between composite layers, resulting in the creation of a moiré lattice. For certain stacking configurations, the inversion and/or mirror symmetry is broken and thereby an in- and/or out-of-plane polarization are induced.

Efforts to elucidate the structure of  $(\text{PbS})_{1.18}\text{VS}_2$  crystals resulted in the identification of preferred twist-angles [2]. This hints the presence of a short-range correlation (twisting is between adjacent layers) that can be used for understanding better the crystal structure. X-ray diffuse scattering is well suited for the study of short-range correlated systems as it reflects the nature of such correlations. Crystals of  $(\text{PbS})_{1.18}\text{VS}_2$  were studied with synchrotron X-rays at different temperatures for tracking the changes in diffuse patterns and the dynamics between layers.

First results show that diffuse patterns have a streak-like shape along the stacking axis at low temperatures (100 K - 260 K) and room temperature (see Fig. 1), confirming the existence of short-range correlations between layers. Temperature experiments show a redistribution of diffuse scattering intensities which indicates that short-range correlations change with temperature.

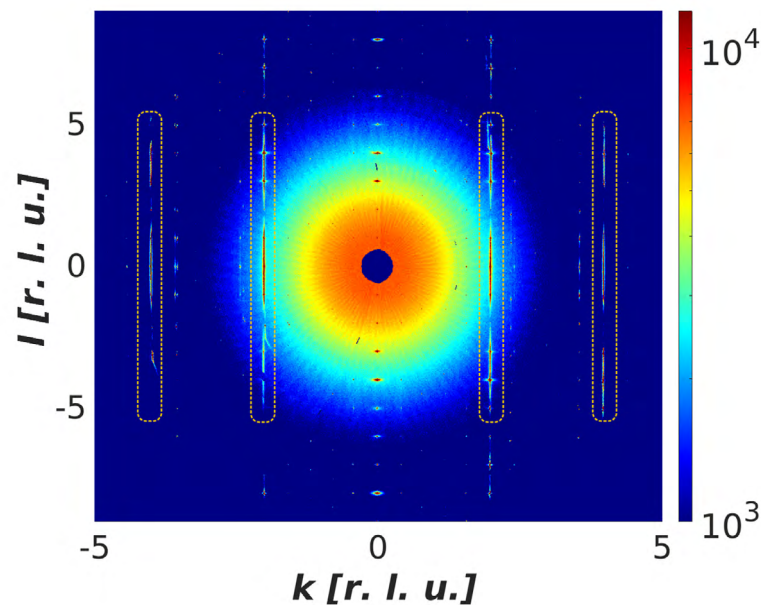


Figure 1. Reciprocal space plane  $[0kl]$  taken at room temperature. In yellow boxes, diffuse scattering streaks along  $l$ -direction showing the presence of correlated disorder in the sample.

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## Short-range correlations in lead titanate close to $T_c$

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Lead titanate ( $\text{PbTiO}_3$ , PTO) is a widely used ferroelectric material present in the exceptionally versatile  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT) and relaxors-PTO solid solution systems with a large piezoelectric coefficient and electro-mechanical coupling factor [1]. PTO undergoes a phase transition from cubic-paraelectric to tetragonal-ferroelectric phase at  $T_c \sim 753$  K; which is usually associated with a formation of domain structure. While the mechanism of the phase transition is considered to be driven by the lattice soft mode [2], the recent interpretation of the pair distribution function experiment [3] suggests that the PTO's local structure becomes disordered already at 700 K, that is  $\sim 50$  degrees below the  $T_c$ . On the other hand, in the same work nanoscale polar clusters are found to exist well above the transition temperature. For this reason a further detailed study on how short-range displacement correlations change in the vicinity of  $T_c$  is crucial. A better understanding of the changes in displacement correlations might give a new view on the mechanism of domain formation for the development of new lead titanate-based applications.

To this end we study the PTO's local structure by means of X-ray diffuse scattering in the temperature range around the phase transition. The diffuse scattering distribution and changes in intensity are used for tracking the displacement correlations in the cubic phase. The formation and the possible reorganization of the domain structure is decoded from the reciprocal-space distribution of splitted Bragg reflections. Our preliminary analysis shows that except for a very narrow temperature range the topology of the distribution is preserved and the only observed effect is the splitting increase (i.e. growing tetragonality) as temperature decreases. The diffuse scattering increases as  $T_c$  is approached from below, indicating an increasing short-range character in displacement correlations near and above  $T_c$ .

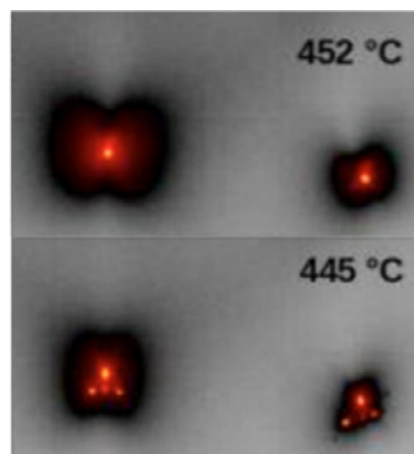


Figure 1. Reflections  $[0 -3 1]$  and  $[1 -3 1]$  at 725 K and 718 K respectively when cooling. Bragg peaks are splitted already at 718 K, indicating the presence of domains and the tetragonal phase. The increase of diffuse scattering signal with temperature is shown. The recorded  $T_c$  is shifted down due to the heating of the sample from the beam.

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## Low-temperature memory effect in PMN single-crystal

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The spontaneous aging effect, defined as a decrease of physical properties significant for application, is in ferroic materials determined by field and conjugated to the order parameter. The situation is more complex in ferroelectric relaxors in which both short- and long-range electric interaction is apparent. Our studies aim to separate the effect of long-range electric interaction on the aging process of classical  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN) relaxors. PMN crystals exhibit a strong and frequency-dependent dielectric anomaly at  $T_{\varepsilon_{\text{max}}}$  in the range 250 - 300 K. The frequency dependence is described by the Vogel-Fulcher equation ( $\tau = \tau_0 \exp[E/(T - T_{\text{VF}})]$ ) and the main contributions to the permittivity anomaly are due fluctuations of the polar cluster boundaries and polar clusters reversal [1-3]. Below  $T_{\text{VF}}$  we are dealing with the long-range electric order, whereas above  $T_{\varepsilon_{\text{max}}}$  the local polarization is apparent up to the Burns temperature ( $T_{\text{B}} = 620$  K) [4]. Above  $T_{\text{B}}$  PMN exists in the pure cubic paraelectric phase. The effect of spontaneous aging of PMN single crystals in the temperature range of about 50 K below  $T_{\varepsilon_{\text{max}}}$  was studied by Kleemann and Dec [5].

We were interested in the low-temperature dielectric behavior of PMN single crystals which have been stored for more than a dozen years at room temperature i.e.  $T > T_{\varepsilon_{\text{max}}}$ .

*The authors are obliged to Professor Kania for PMN single crystals.*

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## Piezoelectric, elastic, and electrocaloric properties of a soft PZT ceramic

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A significant number of commercial PZT ceramics exhibit marvelous piezoelectric properties, however, the commercially available piezoelectrics are characterized usually for room temperature operation. In some applications, the probes containing piezoelectrics heat up to temperatures close to 410 K. The general objective of this paper is to investigate, using the resonance technique, the thermal behavior of the piezoelectric properties of commercial ceramics sample PIC 153. We intended to show the behavior of piezoelectric properties in a wider temperature range not shown by the manufacturer and compare our results with those given by the producer. Thanks to the successive thermal cycles, the obtained results indicate that this ceramic shows elevated properties above room temperature. The secondary objective was to measure the electrocaloric effect. The investigations revealed a subtle positive electrocaloric temperature change ( $\sim 0.12$  K) near  $T_c$ .

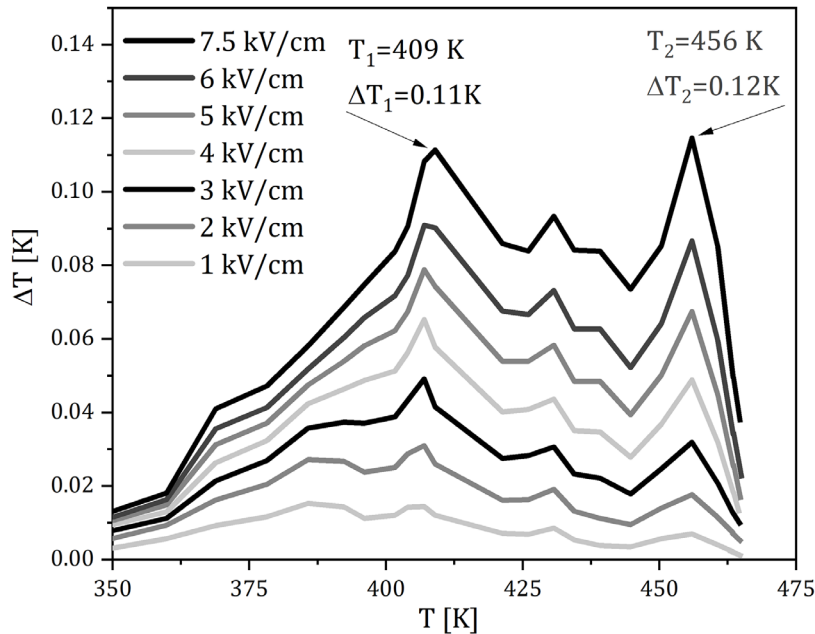


Figure 1. Temperature dependence of the electrocaloric temperature change for the soft PZT - PIC153.

# Unusual phase transition into frustrated antipolar phase in ferromagnetic $\text{EuAl}_{12}\text{O}_{19}$

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Hexagonal  $\text{EuAl}_{12}\text{O}_{19}$  is a quasi-two-dimensional ferromagnet below 1.3 K. Pyroelectric current measurements revealed a weak ferroelectric polarization below  $T_c = 49$  K. The existence of a ferroelectric phase transition is supported by an anomaly in specific heat and thermal expansion. However, the temperature dependence of permittivity does not show a peak at  $T_c$ , but only a change of slope (see Figure 1). This could argue in favor of an improper or pseudo-proper ferroelectric phase transition. However, single crystal synchrotron diffraction studies revealed no structural change at  $T_c$  and second harmonic generation measurements also showed no signal down to 5 K. This indicates that  $\text{EuAl}_{12}\text{O}_{19}$  remains macroscopically centrosymmetric (space group  $P63/mmc$ ) down to low temperatures. We propose to explain the observed behavior by frustrated antiferroelectricity or frustrated antipolar correlations below  $T_c$ . An external electric field induces a weak polarization visible in the pyrocurrent, but without the field the sample remains centrosymmetric. Dynamical frustration of antipolar order makes it impossible to see the long-range structural change in XRD and explains the observed strong relaxor ferroelectric-like dielectric dispersion below  $T_c$ . Similar frustrated antiferroelectricity was theoretically predicted in the isostructural  $\text{BaFe}_{12}\text{O}_{19}$  below 4 K [1], but it was not experimentally observed due to the occurrence of quantum paraelectricity [2]. However, the theory from [1] predicts that Al cations are much more polar than Fe and this is the reason, why the antipolar correlations begin to build in  $\text{EuAl}_{12}\text{O}_{19}$  already at 49 K.

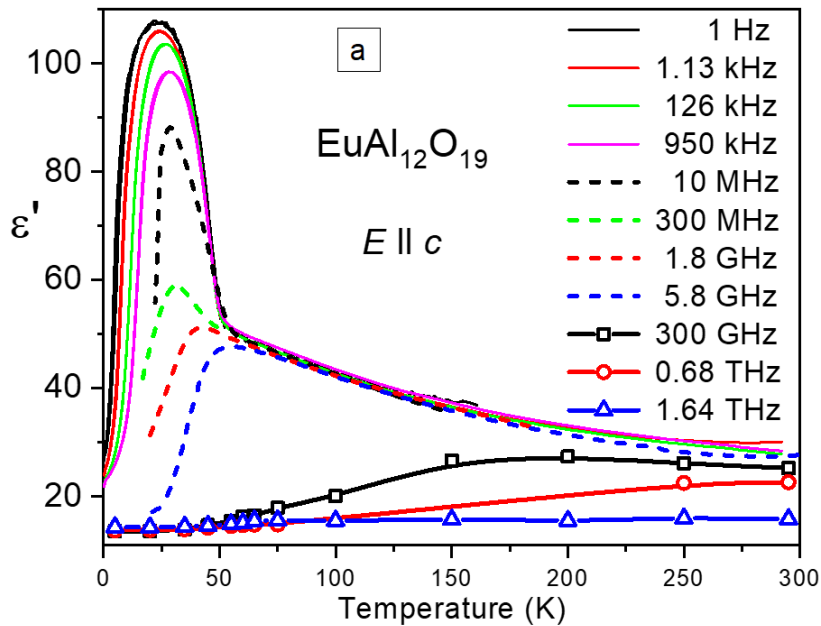


Figure 1. Temperature dependence of permittivity at various frequencies showing unusual dielectric anomaly at  $T_c = 49$  K in  $\text{EuAl}_{12}\text{O}_{19}$ .

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## The polar structure of $\text{PbTiO}_3$ studied by *ab initio* calculations

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The Landau-Ginzburg potential for a  $180^\circ$  polar domain wall (DW) in  $\text{PbTiO}_3$  (PTO) is investigated using *ab initio* density functional theory (DFT) calculations. While some authors [1] have only identified an Ising-type structure of the DW, lacking polarization within the wall, other studies [2,3] suggest the potential existence of a Néel-type component of polarization along with a Bloch-type component. Particularly noteworthy is the Bloch-type component, known for its symmetry reduction of the DW and switchability, which may arise from a new phase transition at the DW center, occurring at a temperature below the bulk critical temperature ( $T_C$ ) of PTO. Notably, standard DFT calculations do not provide insights into temperature dependences. Therefore, supplementary approaches such as Landau-Ginzburg theory [4] or molecular dynamics/Monte Carlo simulations become necessary.

The primary objective of this research is to determine the parameters of the Landau-Ginzburg functional, specifically those essential for the observed transitions, directly from *ab initio* density functional theory (DFT) calculations of the energies of appropriate configurations [5].

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## Structure, thermal and electrical properties of N-methylpyrrolidinium bromobismuthate(III)

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The synthesis and physicochemical characterization of organic-inorganic hybrids (OIH) based on metal halides (chlorides, bromides, iodides) is one of materials chemistry's more rapidly growing branches. This interest stems primarily from the possibility of obtaining materials that exhibit desirable electrical, optical, and mechanical properties. In my work, I focused on OIH containing a very promising N-methylpyrrolidinium cation in the crystal structure. The obtained material is characterized by a single reversible phase transition (313/306 K) and a unique, two-component anion sublattice (Fig. 1).

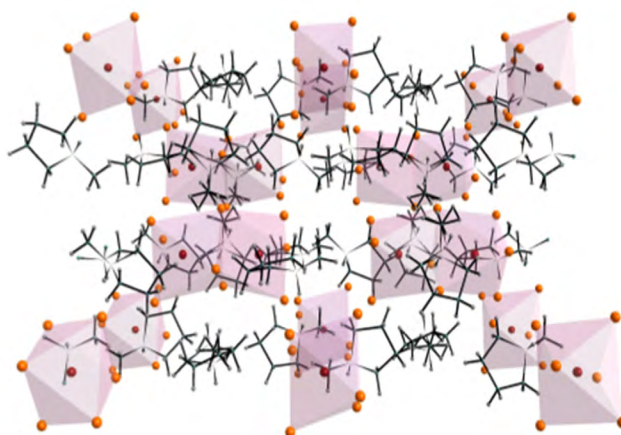


Figure 1. Crystal packing of the title compound.

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## Phase transition dynamics of antiferroelectric crystals with lanthanum substitution

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$\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (PZT) is a material extensively investigated for the past decades due to its promising dielectric, ferroelectric, and piezoelectric properties, useful for electro-optical, pyroelectric, and piezoelectric devices. Zirconium-rich PZT is special because of its remarkably big thermal hysteresis, strong antiferroelectric-ferroelectric (AFE-FE) phase transition, and wide morphotropic phase boundary, which improves its electromechanical and piezoelectric properties due to the phase coexistence and allows for fine-tuning of these properties for the development of advanced electronic devices [1]. It has been found that substitution with a small amount of La on the  $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$  (PZT 95/5) influences the stability of the long-range ferroelectric state and alters the phase sequence [2]. The antiferroelectric-paraelectric transformation was observed to shift through an incommensurate region as the La concentration increased [3].

We used Raman scattering and Differential Scanning Calorimetry (DSC) to investigate the phase transition mechanism of PZT 95/5 under the influence of 2% La substitution on the Pb site (PLZT 2/95/5). We found by DSC that between the paraelectric and incommensurate AFE states of PLZT 2/95/5, the slim FE state (relaxor-like [2]) exhibits a diffused phase transition. However, Raman scattering does not straightforwardly show this phase transition. The presence of La alters the phase diagram compared to PZT 95/5, and the differences between the incommensurate AFE phase in PLZT 2/95/5 and the FE phase in PZT 95/5 at similar temperatures, are obvious in the Raman spectra. The low-temperature AFE phase is macroscopically similar in both compounds, therefore the influence of La is mainly seen in the dynamics of the phase transitions at higher temperatures, between the paraelectric and the AFE phases.

*This work is supported by the Lead Agency Project GAČR-ARRS 24-10699K.*

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## Ferroelectric domain populations and high piezoelectric response

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Currently, the most effective and commonly used piezoelectric materials are those with a perovskite structure. The polarization rotation model [1] describes how the spontaneous polarization vector rotates and produces high piezoelectricity in single-crystal materials, such as  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$  (abbreviated as PZT),  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$  (PZN-PT), and  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{PbTiO}_3$  (PMN-PT). This theoretical model could not be verified on PZT single crystals until recently because of these crystals growth difficulties.

We observed a high piezoelectric response in PZT single crystals (Figure 1) somewhat unusual composition and temperature range because it is far away from the Morphotropic Phase Boundary [2-3]. The optical studies performed have proved a significant influence of the domain dynamics on such high-efficiency piezoelectric response. The origin of the strong piezoelectric phenomenon in perovskites concerns the intrinsic and extrinsic mechanisms [4].

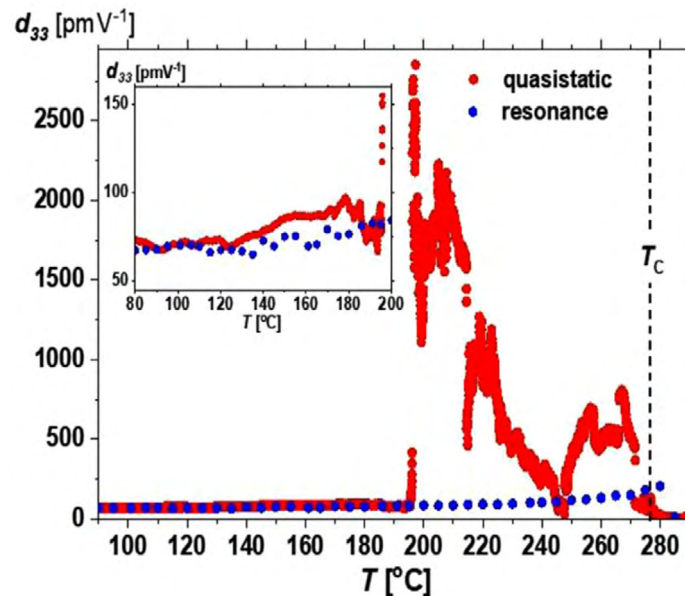


Figure 1. Piezoelectric coefficient  $d_{33}$  in a function of temperature, for a PZT crystal in a weak (in blue) and strong (in red) electric field. The inset concerns the temperature range in which  $d_{33}(T)$  runs are similar [2].

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## Photo-active self-assembling materials: effect of lateral substitution in the vicinity of the azo group

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Photo-active liquid crystalline materials, i.e. those possessing self-assembling behaviour, attract considerable attention due to their exciting possibility to drive, tune and control the optical response of soft systems in a contactless way [1-7]. Lateral substitution by halogen atoms and other groups is a very effective tool to tune the mesomorphic and photo-active behaviour [1,2,6,7].

To contribute to better understanding of the effect of lateral substitution by fluorine, chlorine, bromine atoms and methyl group in R1 and R2 positions in various combination on the liquid crystalline and photo-active behaviour, several new materials with lateral substituents placed on benzene rings in the vicinity to the azobenzene moiety are designed and their mesomorphic behaviour was established using Polarising Optical Microscopy and Differential Scanning Calorimetry. All compounds possess the liquid crystalline behaviour, specifically the chiral nematic (cholesteric) phase; the twist grain boundary orthogonal smectic A\* phase was detected for the non-substituted compound only. In most cases, lateral substitution allows to considerably decrease the clearing point of all the substituted materials compare with the non-substituted analogue. However, the presence of the fluorine atom, as lateral substituent in R2 position, considerably increases the clearing point with respect to any other tested combination of the substituents.

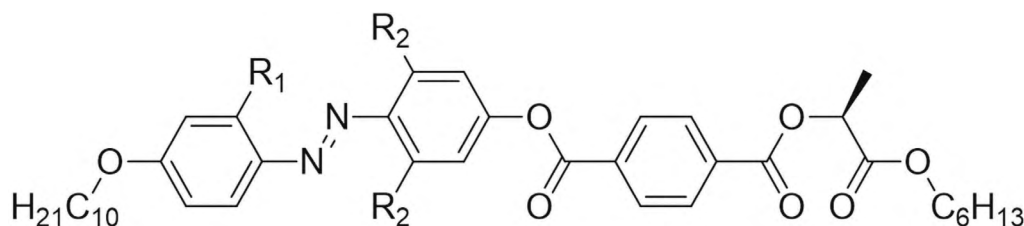


Figure 1. General chemical structure of newly designed compounds laterally substituted in R1 and R2 positions by fluorine, chlorine, bromine atoms and methyl group in various combination

The photoisomerisation process, specifically the conversion of the *E-Z* isomers was studied in toluene solution by high performance liquid chromatography; the kinetics of the photo-isomerisation was established under illumination of the UV light (366 nm). The rate of photoisomerisation process in halogenated series decreased with the size/drop of electronegativity and the thermal *Z-E* isomerization process showed similar trend, with fluorinated material having the most stable *Z* isomer. Materials with non-polar substituents possess excellent photoisomerisation rate and stability of *Z* isomers.

Due to photo-active azo group, the designed chiral self-assembling materials can be used as dopants for design of functional photo-active liquid crystalline mixtures with light controlled properties targeted for advanced opto-electronic and photonic applications.

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## Investigation of spectroscopic and electrical properties of doped pyrrole-co-poly(pyrrole-3-carboxylic) copolymers

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In recent years, there has been a significant interest in semiconductor polymers as a category of materials that have the potential to facilitate the advancement of flexible and biocompatible electronic devices. Many studies are now being conducted to find new applications for semiconducting organic polymers, including polypyrrole derivatives. Researchers are particularly interested in analyzing molecules' optical and conductive properties created from polypyrrole and its derivatives [1-3].

The research object of investigation is a conductive polypyrrole-co-poly(pyrrole-3-carboxylic acid) copolymer formed based on pyrrole and pyrrole-3-carboxylic acid. This polymer is doped with sodium p-toluene sulfonate TBA-p-TSA (p-TSA) and sodium anthraquinone-2-sulfonate (AQS). Optical and electrical properties were analyzed using infrared, Raman, and impedance spectroscopy. The optical conductivity spectra were acquired by Kramers-Krönig analysis of the reflectance spectra measured from the surface of a compacted pellet of a polycrystalline material.

The investigations showed that the conduction mechanism in the studied copolymer is related to the jumps of charge carriers, such as polarons and bipolarons. The investigated copolymers exhibit 3D conductivity and less than 0.35 eV energy gaps. The nature of the change in electrical conductivity as a function of temperature suggests that the systems exhibit electrical properties typical for semiconductors.

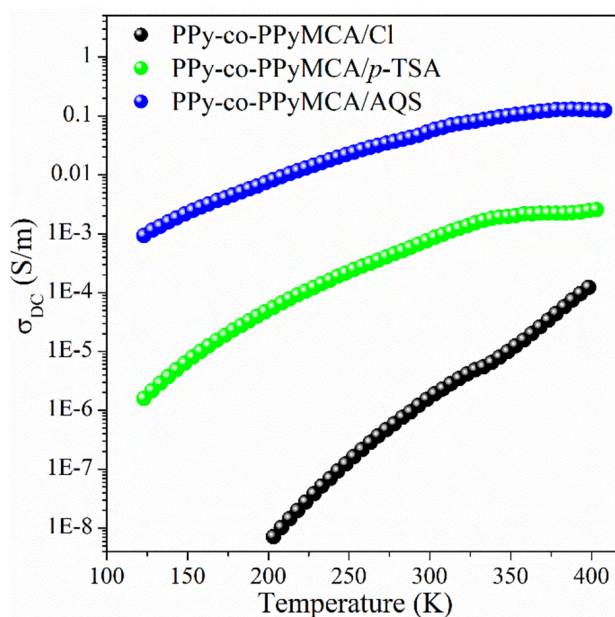


Figure 1. Plots of the DC conductivity of the investigated copolymers as a function of temperature.

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## Search for multiferroic properties in $\text{BaCuF}_4$

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The search for single phase magnetodielectric materials pushes the scientific community to pay attention to a broader class of inorganic compounds, not just perovskite oxides. Fluorides are very good candidates for exploiting their multiferroic properties in applications based on polarization switching by a magnetic field due to coupling between polarization and magnetization. In this sense, especially  $\text{BaCuF}_4$ , one of the members of the broader family of  $\text{BaMF}_4$  ( $M = \text{Zn, Mn, Mg, Fe, Co, Ni}$ ) materials [1], is the most promising candidate.

The crystal structure of  $\text{BaCuF}_4$  was determined as an orthorhombic with polar  $Cmc2_1$  space group [2]. The first magnetic susceptibility measurements showed the paramagnetic behavior with a Curie-Weiss deviation below 212 K and non-measurable due to very low values below 77 K [3]. Later, the evidence of one-dimensional (1-D) antiferromagnetic behavior at high temperatures and weak ferromagnetic behavior at temperatures below 20 K was found in magnetic susceptibility and electron paramagnetic resonance measurements [4]. The existence of direct coupling between polarization and magnetization, as well as the high Néel temperature of 275 K, were predicted employing density functional theory calculations [5]. In contrast, first-principles calculations have recently confirmed 1-D magnetic topology, but with a Néel temperature below 1 K, if exists [6]. Although the structural and magnetic properties of  $\text{BaCuF}_4$  have been studied since the 1970s, its ferroelectric and magnetoelectric properties still require experimental clarification.

$\text{BaCuF}_4$  powder is prepared by solid state synthesis [4]. The ceramic samples are formed by uniaxial pressing (600 MPa / 2 min) and sintering at 700 °C for 24 hours in an argon atmosphere with heating rate of 10 °C/min. The ceramics were characterized by x-ray diffraction and differential scanning calorimetry. To infer the existence of magnetoelectric coupling, we study dielectric properties, including Raman and infrared spectroscopy, piezoresponse force microscopy (PFM), and magnetic properties in a broad temperature range (2 - 300 K). The results of these experiments will be presented and discussed in the light of the theoretical prediction of a direct coupling between polarization and magnetization [5] and our search for magnetoelectric coupling. Our preliminary results show no anomaly in magnetization down to 2 K, and polarization switching is complicated by conductivity in  $\text{BaCuF}_4$ . PFM study reveals a certain domain structure in particular grains of the sample. Infrared and Raman spectra reveal a phonon near 70  $\text{cm}^{-1}$ , which hardened on cooling. Unfortunately, we could not measure its possible softening above room temperature because the surface of the sample quickly decomposed above room temperature. Low-frequency dielectric measurements performed up to 550 K reveal Maxwell-Wagner relaxation above 300 K and no hint of the ferroelectric phase transition.

In conclusion, although  $\text{BaCuF}_4$  crystallizes in a polar  $Cmc2_1$  structure, based on our measurements it is unclear whether it is a ferroelectric or just a pyroelectric system. The magnetic data reveal only paramagnetic behavior on cooling down to 2 K, so the system is not multiferroic as theoretically predicted.

*This work has been supported by the Czech Science Foundation (project No. 24-10791S).*

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## Roles of chemical short-range order in perovskite and related dielectric materials

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Substantial effort aiming at optimizing technologically important properties of perovskite materials has been undertaken by harnessing various forms of chemical short-range order (CSRO). Solid solutions featuring a homovalent substitution on cation positions, as exemplified by the famous  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ , often have composition regions where macroscopic phases compete [1,2] and can produce enhanced electromechanical or piezoelectric properties [3]. In other cases, as in  $\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ , the substitution involves the only ferroactive cation and a diluted correlation medium is created [4] leading to a relaxor-like or glass-like dielectric behaviour [5]. Yet a different CSRO type involves a heterovalent occupational disorder, as observed in lead-based relaxor materials  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  or  $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ . There, depending on the engaged cations, degree of NaCl-like ordering of the B-site cations can be altered at synthesis effectively driving shifts in dielectric response [6].

In this contribution we concentrate on microscopic-scale displacive distortions brought about by these different forms of CSRO in various materials (predominantly perovskites). Atomistic calculations (both *ab-initio* and classical) are used to this end, providing means for studying various chemical arrangements. We pay attention to ionic size effects, local polarization disruption, octahedral tilt triggering and electrostatic multipole effects. We pinpoint some general trends and link the microscopic behaviour to macroscopic properties.

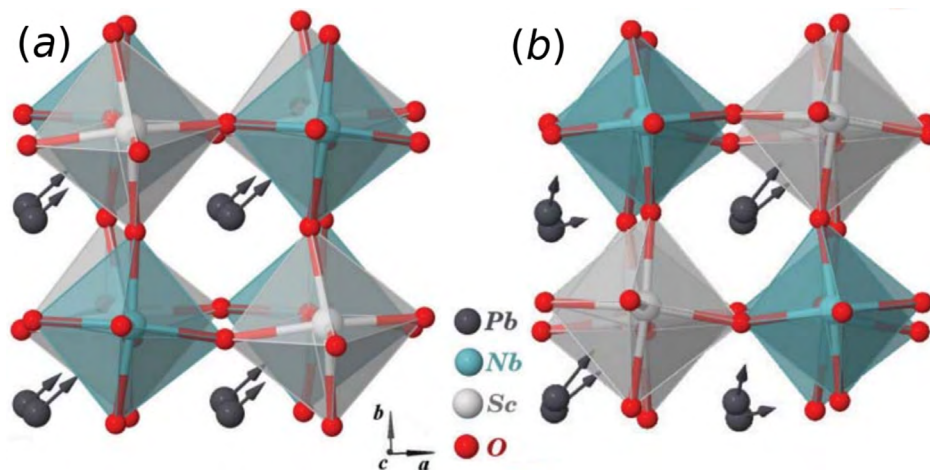


Figure 1. Dependence of local Pb displacement on distribution of Sc and Nb atoms as obtained in *ab-initio* calculations [7].

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## Structural and dielectric properties of 1,2,4-Triazolium Hexabromoantimonate(III)

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Hybrid organic-inorganic perovskites based on Sn<sup>II</sup>, Ge<sup>II</sup>, and Pb<sup>II</sup> have emerged as novel functional materials that arouse particular interest in light-emission applications, energy storage and energy conversion [1]. An undesirable feature of these materials is chemical instability and environmental toxicity, both of which prevent widespread adoption and commercialization. Organic-inorganic hybrids (OIH) based on Bi<sup>III</sup>, Sb<sup>III</sup> are expected to exhibit semiconducting properties and very similar band structures to those of divalent Sn- and Pb-based compounds. Bismuth(III)/antimony(III) derivatives can be an alternative of sorts to lead-based systems due to their low toxicity, production costs, and resistance to high temperatures. Moreover, the higher durability of the OIHs results in an increased lifetime of the devices. It should be stressed that the halide perovskites with remarkable semiconducting properties have the potential of being ferroelectric, yet the evidence of ferroelectricity in the typical 3D Pb-based hybrid halides has been elusive. In contrast, ferroelectricity/piezoelectricity in bismuth(III) or antimony(III) derivatives are well-known and characterized [2].

In particular, underexplored groups of haloantimonates(III) and halobismuthates(III) with the  $R_aM_bX_{3b+a}$  general formula (where R is an organic cation, M = Sb<sup>III</sup>/Bi<sup>III</sup>, and X = Cl, Br, or I) have become the focus of interest because they feature easy synthesis and processing, are inexpensive, and exhibit relevant electrical and optical properties, such as ferroelectricity and light emission. These molecular-ionic materials are characterized by a significant diversity of anionic networks (from zero- (0D) to one- (1D), two- (2D), or even three-dimensional (3D) architectures) [2]. Interestingly, the ferroelectric properties are found for a limited number of stoichiometric types and selected anionic forms such as  $R_5M_2X_{11}$  (0D),  $R_3M_2X_9$  (0D and 2D),  $RMX_4$  (1D),  $R_2MX_5$  (1D), and  $R_3MX_6$  (0D).

Lately, we have successfully synthesized and characterized the first ferroelectric of the halobismuthate(III) family with an  $R_3MX_6$  stoichiometry, that is, tris(acetamidinium) hexabromobismuthate(III),  $(CH_3C(NH_2)_2)_3[BiBr_6]$  (ABB), having a one-component organic network [3]. Rich polymorphism in the solid state of ABB occurs between tetragonal (paraelastic) and triclinic (ferroelastic) crystal phases. The ferroelectric phase was confirmed for phase IV, whereas the antiferroelectric arrangement is suggested to appear in phase III. The ferroelectric transition should be considered as “displacive” for both cationic and anionic substructures.

Stimulated by the literature, we employed a simple, small aromatic heterocyclic building block (1,2,4-triazolium), which is practically unexplored in assemblies with halometals(III), and managed to obtain a new representative of the family of  $R_3MX_6$  haloantimonates(III), namely,  $(C_2N_3H_4)_3[SbBr_6]$  (TBA). In our poster, we present the synthesis, X-ray single crystal structures, and dielectric properties of TBA, the second example of ferroelectric material, crystallizing with the stoichiometry  $R_3MX_6$  [4].

*This research was funded by the National Science Centre, Poland, grant number 2022/47/B/ST8/02199 (A. Piecha-Bisiorek).*

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## Ferroic and nonlinear dielectric and optical properties of inorganic-organic lead-free 1D hybrid based on Bi(III)

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The presented project will focus on the correlation between the structural change resulting from phase transition in solid-state and the electrical/optical properties. Two examples of new organic-inorganic hybrids based on Bi(III) halides will be discussed. Recording the ferroelectric hysteresis loop and the temperature-resolved second harmonic generation (TR-SHG) measurements will provide spectroscopic evidence for one of the (non)centrosymmetric phases. NMR measurements will illustrate the molecular dynamics of the organic cation in the solid. In addition, the results of quasi-elastic neutron scattering (QENS), which is complementary to the other methods used in the project, will be discussed.

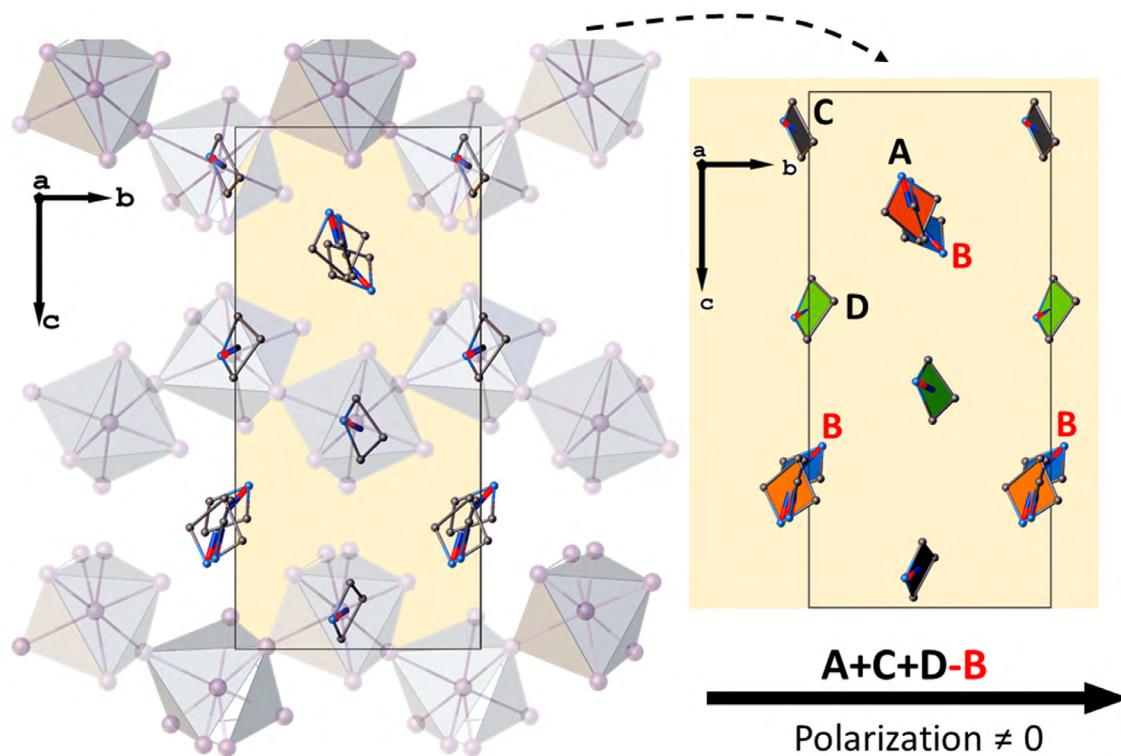


Figure 1. Example of structure and mutual orientation of the dipole moments contributing to  $P_s$  within the cationic network.

This research was funded by the National Science Centre, Poland, grant number 2022/47/B/ST8/02199 (prof. A. Piecha-Bisiorek).



## Phase transitions, crystal structure and optical properties of 1D organic-inorganic perovskite: methylhydrazinium antimony (III) iodide

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Organic-inorganic halo-metalates often crystallize in polar space groups and demonstrate nonlinear optical, piezoelectric, and ferroelectric properties. Their narrow energy bandgaps and broad absorption spectra render them suitable for applications in solar cells. Particularly, perovskite solar cell technology based on methylammonium lead iodide semiconductor has resulted in a notable 25% enhancement in efficiency in a very short time [1]. Beyond their utility in photovoltaics, organic-inorganic perovskites or perovskitoids have found applications in diverse optoelectronic devices, including light-emitting diodes, [2], photodetectors [3], and dielectric switchers [4].

The latest research has demonstrated that lead halide perovskites can be synthesized with methylhydrazinium cation, offering potential applications as spacers in layered perovskites[5]. However, despite their promising features, materials with lead in their structure exhibit chemical instability under moderate humidity and light exposure, motivating ongoing investigations into alternative organic-inorganic hybrids with different amines and metal centers [6].

In this study, we focus on hybrid compounds incorporating methylhydrazine and antimony iodide, with a stoichiometry of  $(\text{MHy})_2[\text{SbI}_5]$ , synthesized using a direct method. This specific stoichiometry has been identified as capable of exhibiting ferroelectric behavior [7]. Our investigation delves into the crystal structure and luminescent properties of a new 1D organic-inorganic hybrid,  $\text{MHy}_2\text{SbI}_5$ , based on methylhydrazine. The compound is characterized by the red photoluminescence (PL) coming from the  $5s^2$  electron pairs of Sb (III) as well as complex structural behavior. The studied  $\text{MHy}_2\text{SbI}_5$  exhibits two room-temperature polymorphs (**I** and **II**) with separate thermal properties and structural characteristics. In both polymorphs, the crystal structure consists of one-dimensional (1D) zig-zag anionic  $[\text{SbI}_5]_{\infty}^{2-}$  chains built of  $\text{SbI}_6$  corner-sharing octahedra. The MHy cations, which are dynamically disordered and located within the crystal voids, interact with the chains through weak hydrogen bonds.

Polymorph **I** adopts the acentric  $P2_12_12_1$  chiral space group confirmed by SHG and does not show any phase transitions even with disordered methylhydrazinium cation. Conversely, polymorph **II** undergoes a reversible low-temperature phase transition and high-temperature reconstructive transformation to polymorph **I**, driven by the unstable arrangement of the  $[\text{SbI}_5]_{\infty}^{2-}$  chains in the structure. The energy band gap ( $E_g$ ) values were estimated based on the UV-Vis absorption spectra, indicating band gaps of 2.01 eV for polymorph **I** and 2.12 eV for polymorph **II**.

*The research was funded by the National Science Centre as part of the OPUS 22 project (grant number: 2021/43/B/ST5/01172).*

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## On the origin of the chiral phase transition in $180^\circ$ domain walls of $\text{PbTiO}_3$

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A new mechanism leading to a switchable Bloch-type polarization in a domain wall separating two ferroelectric domain states is proposed. A biquadratic coupling of the primary order parameter and its gradient originating from inhomogeneous electrostriction triggers the chiral phase transition (Ising-to-Bloch) in the domain walls (DW) with softening of the local polar mode and anomalous increase of the dielectric susceptibility at the phase transition temperature  $T_{\text{DW}} < T_c$ . This mechanism describes the origin and properties of the polar Bloch component  $P_2$  that emerges below  $T_{\text{DW}}$  additionally to the antipolar Néel component  $P_1$  within the  $180^\circ$  DW between bulk domains with opposite polarizations ( $-P_3$  and  $+P_3$ ) in  $\text{PbTiO}_3$ .

The tensile strain of the DW plane promotes the development of the Bloch polarization.

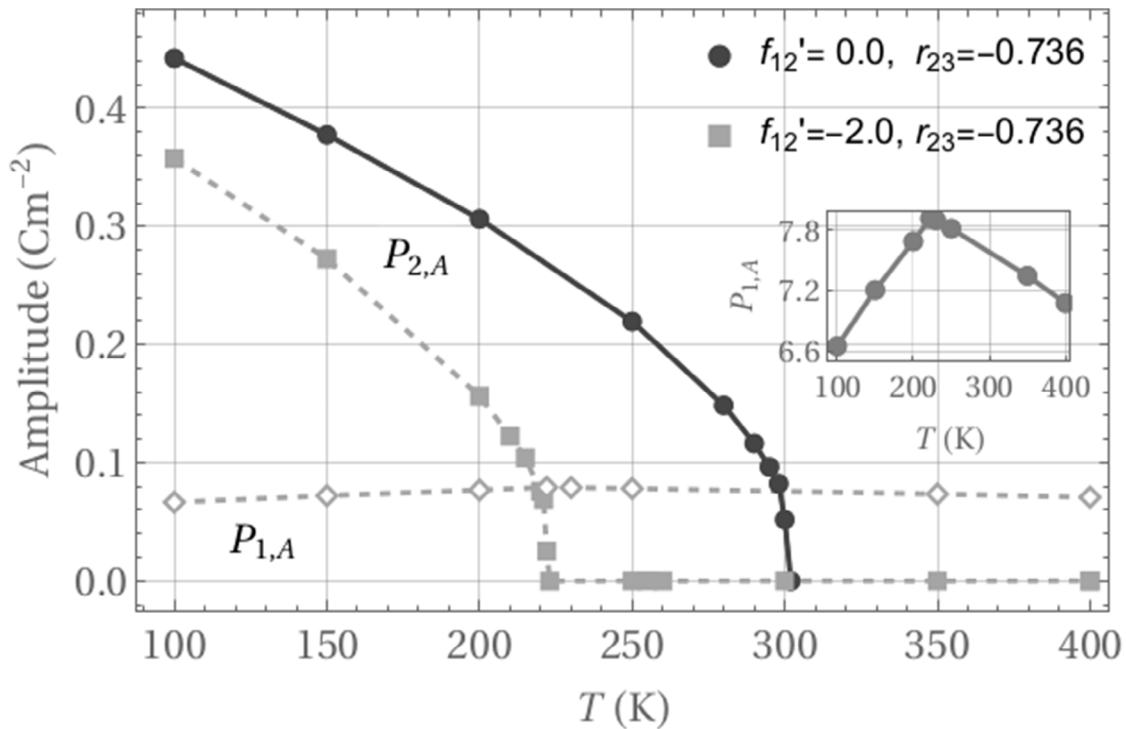


Figure 1. Temperature dependence of amplitudes of the Bloch  $P_2$  and Néel  $P_1$  components.

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# Neutral-to-ionic transition in the complex $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$ - evidence of strong electron - molecular vibration coupling

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The 2:1 charge-transfer (CT) complex  $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$  (where: donor (D) EDT-TTF = ethylenedithio-tetrathiafulvalene and acceptor (A) TCNQ = tetracyanoquinodimethane) undergoes a rare temperature-induced neutral-to-ionic (N-I) transition at about  $T = 100$  K. In crystal the planar molecules are arranged in mixed-stacks composed of centro-symmetric DAD trimeric units. The X-ray crystal structure shows that the degree of CT between D and A changes from about  $0e$  at room temperature to about  $1e$  at 8 K [1]. Subsequently, the N-I transition was confirmed by IR and Raman spectroscopic studies [1, 2]. The N-I transition depends on the relative electron affinity of A and ionization potential of D, inter-molecular hopping integrals, electrostatic interactions and interactions of electrons with intramolecular vibrations (EMV coupling) and with lattice phonons. Here, we report on spectroscopic evidence of a strong EMV coupling in  $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$ , observed both in IR and Raman spectra.

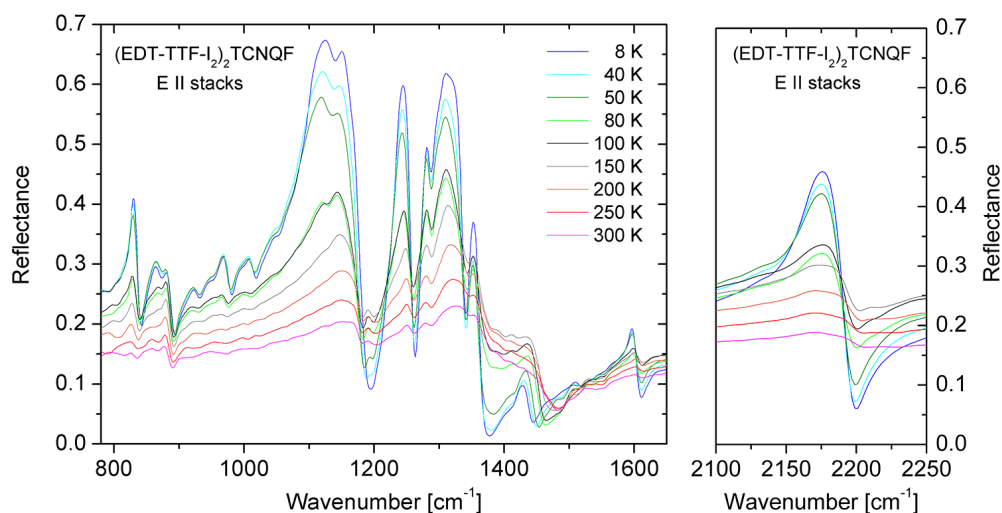


Figure 1. Temperature dependence of IR reflectance of  $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$  single crystal.

In middle IR spectra of  $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$  we observe two strongly overlapping electronic bands centered at about  $3160$  and  $4600$   $\text{cm}^{-1}$ , attributed to CT transitions  $\text{D} \rightarrow \text{A}$  and  $\text{D} \rightarrow \text{D}$  in mixed stacks, respectively. The vibrational spectra are dominated by strong bands related to EMV coupling of A molecules with  $\text{D} \rightarrow \text{A}$  transition (Fig. 1). The most important bands are as follows:  $\text{C} \equiv \text{N}$  stretching at about  $2190$   $\text{cm}^{-1}$ ,  $\text{C}=\text{C}$  stretching at about  $1356$  and  $1336$   $\text{cm}^{-1}$ , and  $\text{C-H}$  bending at about  $1256$  and  $1173$   $\text{cm}^{-1}$  (at  $300$  K). The doublet structure of  $\text{C}=\text{C}$  and  $\text{C-H}$  modes is a consequence of existence of neutral  $\text{A}^0$  and ionized  $\text{A}^-$  molecules in stacks (at lower and higher wavenumbers, respectively). On temperature decreasing, the degree of ionization grows and the intensity of EMV bands strongly increases. Additionally, we see also a weaker vibrational feature at  $1431$   $\text{cm}^{-1}$  attributed to coupling of the donor  $\text{C}=\text{C}$  stretching modes with  $\text{D} \rightarrow \text{D}$  electronic transition. Similarly, the EMV effects are observed in Raman spectra. Our studies give evidence of important role of the EMV coupling for the N-I transition in  $(\text{EDT-TTF-I}_2)_2\text{TCNQF}$ , which is the first clear case of such transition in 2:1 complex at ambient pressure. Most probably, the low temperature quasi-ionic phase should be considered as an electronic ferroelectric.

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## Magnetic phase transitions in $\text{Eu}_5\text{In}_2\text{Sb}_6$

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Europium-based intermetallic compounds represent an intriguing realm of materials wherein various distinct physical phenomena emerge. Among these, the Zintl phase  $\text{Eu}_5\text{In}_2\text{Sb}_6$  crystallizes in the orthorhombic  $\text{Ca}_5\text{Ga}_2\text{As}_6$ -type structure (space group  $Pbam$ , no. 55). This unique structure exhibits nonsymmorphic symmetry, that gives rise to a plethora of captivating physical effects. The compound exhibits insulator-like electrical transport properties, and displays negative colossal magnetoresistance (CMR) which reaches a value as large as  $-10^6\%$  at 9 T and 15 K [1]. Additionally, the compound exhibits giant anisotropic piezoresistance, namely the resistivity is reduced by over 99.95% upon application of uniaxial pressure along the [001] direction over 99.95% [2].  $\text{Eu}_5\text{In}_2\text{Sb}_6$  has also promising thermoelectric properties. Due to its low thermal conductivity, samples with proper chemical composition exhibit an enhanced thermoelectric figure of merit of 0.5 at 700 K. The compound orders antiferromagnetically (AFM) at  $T_{N1} \approx 14.0$  K and undergoes another AFM phase transition at  $T_{N2} \approx 7.1$  K [3]. In the present study, we investigated the crystal structure, magnetic properties, and magnetocaloric performance of  $\text{Eu}_5\text{In}_2\text{Sb}_6$  single crystals grown from In-flux. Our research confirmed that both AFM transitions are of the second-order type (Figure 1(a)). In addition, at low temperatures, we observed a magnetic field-induced transition of the first-order type, associated with reorientation of the Eu magnetic moments in the  $ab$ -plane (Figure 1(b)). We found that  $\text{Eu}_5\text{In}_2\text{Sb}_6$  exhibits both normal and inverse magnetocaloric effects, along with a rotational magnetocaloric effect, the latter being a result of sizable magnetocrystalline anisotropy of the compound investigated (Figure 1(c)).

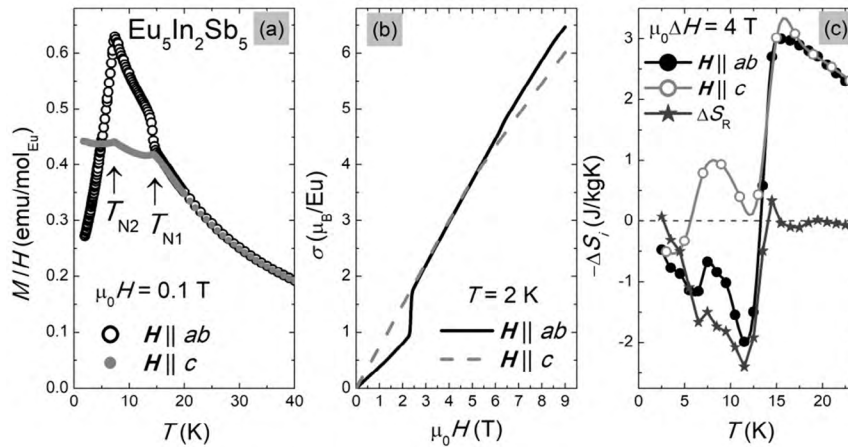


Figure 1. Magnetic properties of  $\text{Eu}_5\text{In}_2\text{Sb}_6$ . (a) Low temperature part of the magnetic susceptibility for the  $ab$ -plane and along the  $c$ -axis. (b) Magnetization curves for both magnetic field orientations at  $T = 2$  K. (c) Isothermal entropy change  $\Delta S_i$  as functions of temperature for  $\mu_0 \Delta H = 4$  T evaluated for the  $H \parallel ab$  and  $H \parallel c$  orientations together with rotating magnetocaloric effect ( $\Delta S_R$ ).

This study was supported by the National Science Centre (Poland) under grant 2021/41/B/ST3/01141.

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**Ferroic and semiconducting properties of selected hybrid iodoantimonates (III) and iodobismuthates (III)**

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Halobismuthate(III) and halo antimonate (iii) compounds have generated significant interest in inorganic-organic hybrid materials due to their potential applications as nonlinear dielectric, optical, and solar cell lead-free materials. Extensive research is now being carried out on many lead-free compounds with a perovskite or equivalent structure, in which the B-place in the ABX<sub>3</sub> formula would be occupied by a different, less toxic metal. Bi(III) and Sb(III) based materials represent a new line of research as they exhibit less toxicity and better air stability. Moreover, many of these compounds crystallize in the polar space groups exhibiting nonlinear optical, piezoelectric, and ferroic (ferroelastic/ferroelectric) properties. It should be underlined that ferroelasticity within organic-inorganic hybrid materials has recently evoked much interest due to the unique mechanical properties of these materials, such as spontaneous strain, strain-stress hysteresis, and domain conversion. Thus, these materials have potential applications in piezoelectric sensors, mechanical switches, and multiple-state memories.

In this contribution, we report a novel Sb/Bi-based formamidinium (NH<sub>2</sub>CHNH<sub>2</sub><sup>+</sup>), guanidinium (C(NH<sub>2</sub>)<sub>3</sub><sup>+</sup>), pyrazoline (C<sub>3</sub>N<sub>2</sub>H<sub>5</sub><sup>+</sup>), trimethyl sulfonium ((S(CH<sub>3</sub>)<sub>3</sub>)<sup>+</sup>) materials, which exhibit ferroic and semiconducting properties at wide temperature ranges (Tab 1.).

Table 1. Crucial ferroic and semiconducting properties of presented materials.

	Ferroelectric	Ferroelastic	Band gap [eV]	Ref.
(C(NH <sub>2</sub> ) <sub>3</sub> ) <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> <b>Guanidinium Sb</b>	No	Yes	2.17	[1,2]
(C(NH <sub>2</sub> ) <sub>3</sub> ) <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> <b>Guanidinium Bi</b>	No	Yes	2.05	[1,2]
(NH <sub>2</sub> CHNH <sub>2</sub> ) <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> <b>Formamidinium Sb</b>	Yes	Yes	2.10	[3]
(NH <sub>2</sub> CHNH <sub>2</sub> ) <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> <b>Formamidinium Bi</b>	Yes	Yes	1.85	[4]
(C <sub>3</sub> N <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> <b>Pyrazolium Sb</b>	No	Yes	2.10	[5]
(C <sub>3</sub> N <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> <b>Pyrazolium Bi</b>	No	Yes	1.97	[5]
(S(CH <sub>3</sub> ) <sub>3</sub> ) <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> <b>TriMethylSulfonium Sb</b>	No	?	2.27	[6,7]
(S(CH <sub>3</sub> ) <sub>3</sub> ) <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> <b>TriMethylSulfonium Bi</b>	No	Yes	2.10	[6,7]

This research was funded by the National Science Centre, Poland, grant number 2022/47/B/ST8/02199.

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## Spectroscopic studies on the interface of water with hydrophilic materials

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Water/solid interfaces abound in nature and understanding their atomic-level structure is crucial for unraveling various phenomena in fields such as chemistry, physics, and materials science. The complicated nature of water and its fluctuating hydrogen bonds network results in many anomalies of physical properties not yet fully understood, including its interaction with solid materials. Recent studies, both theoretical [1,2] and experimental [3,4], suggest that interfacial water formed on different synthetic materials tends to display long-range order with unique physicochemical properties such as the exclusion of solutes (Exclusion Zone water), higher refractive index and viscosity as well as charge separation. Herein, we investigated the structural profile of nano-pure water in the vicinity of hydrophilic materials like Nafion-117 and quartz by employing Raman spectroscopy. Our results depict two characteristic aspects of interfacial water which are differentiated from bulk water. The difference resides in the increased intensity of the low-frequency modes of water (below  $300\text{ cm}^{-1}$ ) as well as the presence of a fluorescent background both having a maximum intensity at a distance of 20 to  $50\text{ }\mu\text{m}$  from the surface of the material. These findings might provide preliminary evidence of the existence of micro-scale coherent water structures.

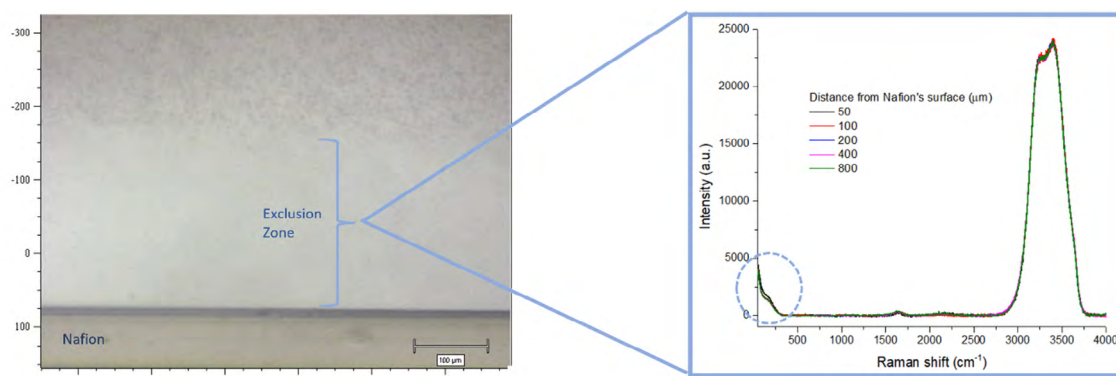


Figure 1. Exclusion zone water (left) and Raman spectra of water (right) in respect to the distance from the Nafion's surface.

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## EPR and optical spectroscopy of the Mn-doped $\text{LiNaGe}_4\text{O}_9$ single crystals

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Doping of dielectrics with transition metal ions is widely used to design new functional materials for quantum optoelectronics, spintronics, solid state ionics and other applications. Reasonable choice of the dopants is necessary prerequisite to design the materials with targeted optical and electric characteristics.

Lithium-sodium tetragermanate  $\text{LiNaGe}_4\text{O}_9$  (LNGO) belongs to the group of Ge-germanate crystals which are intensively studied as the prospect matrixes to design new optoelectronic materials and solid electrolytes. The structural framework of LNGO crystals is formed by  $\text{GeO}_6$  octahedra and  $\text{GeO}_4$  tetrahedra. Alkali metals Li and Na ions occupy the sites within structural cavities and on heating demonstrate high mobility along the channels formed by the Ge-O lattice framework. At room temperature,  $\text{LiNaGe}_4\text{O}_9$  crystal has the orthorhombic structure ( $D_{2h}^8$  space symmetry group) and on cooling below  $T_c \approx 113$  K undergoes the phase transition (PT) to the ferroelectric ( $C_{2v}^5$  group) phase with dipole moment directed along [100] axis [1,2]. Structural changes at the PT are attributed to the sublattices formed by  $\text{Li}^+$ ,  $\text{Na}^+$  ions, which are ordered in the off-center sites below  $T_c$  [2].

As shown in [3-5] the doping of Ge-germanates crystals with transition metals ions allow to modify optical properties and to control ionic conductivity. Here we report the data on studying EPR and optical absorption spectra in para- and ferroelectric phases of  $\text{LiNaGe}_4\text{O}_9$  crystals doped with Mn ions. The crystals studied were grown from the melt by the Czochralski method. EPR spectra were recorded at the microwave frequencies of 8.9 and 320 GHz. The optical absorption spectra were measured in the wave number range 45000 - 11000  $\text{cm}^{-1}$ . All the experiments were done in the temperature interval 85 - 300 K including the ferroelectric PT point  $T_c \approx 113$  K.

Study of EPR spectra revealed the tetravalent state of the manganese dopant and showed existence of two structurally inequivalent centers Mn1 and Mn2 in the lattice. The components of  $g$ -factor and hyperfine tensor  $A$ , the parameters of axial  $D$  and rhombic  $E$  crystal fields have been calculated for the both Mn1,2 centers using angular variations of the EPR spectra. EPR spectra testify that Mn1,2 paramagnetic ions occupy the positions of monoclinic point symmetry with the  $C_2$  symmetry group. Measurements of the optical absorption spectra show that  $\text{Mn}^{4+}$  ions occupy lattice sites with the coordination number  $\text{CN} = 6$  and give evidence for strong electron-phonon interaction. Joint analysis of EPR and optical absorption spectra allows to suppose that Mn1,2 ions are substituted for  $\text{Ge}^{4+}$  hosts within oxygen octahedra. Appearance of two structurally inequivalent manganese centers is attributed to perturbation at least, one of the centers, by a structural defect in the next coordination sphere.

EPR and optical absorption spectra were also measured on cooling through the ferroelectric phase transition. The spectral changes below  $T_c$  are analyzed on the basis of lowering the symmetry of Mn positions at PT.

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## Broadband spectroscopy and electrical percolation of carbon coated copper nanoparticles/MWCNT/Epoxy hybrid composites

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In order to obtain material that possess low transmission and reflection and absorption as primary Electromagnetic Interference (EMI) shielding regime, series of epoxy composites containing carbon-coated copper nanoparticles (Cu@C, 99.8%, 25 nm, USNano) at volume fraction A (A equals 5%), and MWCNT (>95%, OD: 10 - 20 nm, USNano) at volume fractions B (B equals 0.05%, 0.10%, 0.25%, 0.50%, 0.75%, 1.00%), were prepared.

The dielectric properties were investigated with an LCR-meter HP4284 in the frequency range 20 Hz - 1 MHz and with scalar network analyzer Elmika R2400 in 25 - 39 GHz frequency range. Conductivity temperature dependency measurements were performed in the 40 - 500 K temperature region in the 20 Hz - 1 MHz frequency range. The properties of investigated materials were calculated using standard techniques [1].

The electrical percolation threshold lies around 0.25 - 0.30 vol% for MWCNT/Epoxy composites and around 1.8 - 2 vol % for Cu@C/Epoxy composites.

Cu@C/MWCNT/Epoxy hybrid composites conductivity temperature dependencies at 0.573 kHz are presented in the Figure 1.

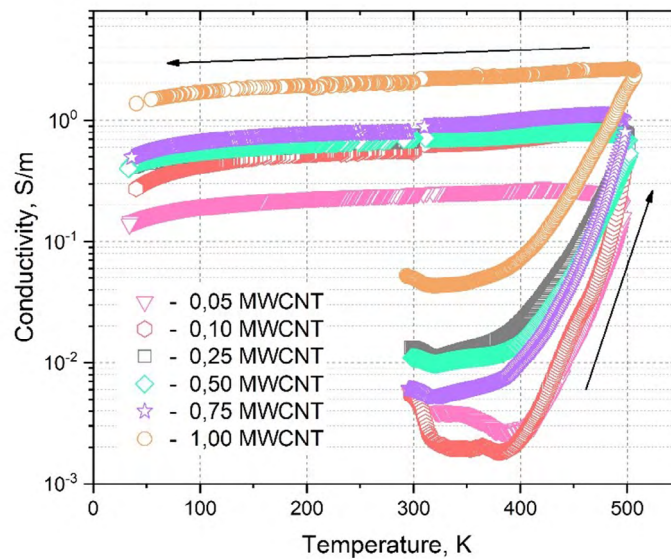


Figure 1. Conductivity temperature dependencies of Cu@C/MWCNT/Epoxy composites with fixed (5 vol%) Cu@C concentrations and varying MWCNT concentrations.

In the Figure 1 one can clearly see conductivity value increase with increasing MWCNT volume fraction, also when heated, conductivity value increases up to 2.5 S/m (5 vol% Cu@C, 1 vol% MWCNT sample) followed by a slight decrease in its value during cooling (1.5 S/m). For 100 - 200 K temperature range our data follows well with fluctuation induced tunneling model [2] and Arrhenius law at 420 - 480 K. The absorption peak value also increases with increasing MWCNT concentration and this peak shifts to lower frequencies at higher MWCNT concentrations i. e. 0.58 at 39.5 GHz for 0.05 vol% MWCNT samples and 0.62 reached at 31.5 GHz for 1.0 vol% MWCNT samples (2 mm thickness).

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## Negative linear compressibility in the helical hydrogen bonding network of imidazolium benzoate

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Negative linear compressibility (NLC) and negative area compressibility (NAC) are rare types of crystal strain in which one or two dimensions expand with increasing hydrostatic pressure [1]. In general, NLC has significantly lower positive compressibility than conventional materials [2]. Materials that exhibit negative linear compressibility can be used to build, for example, pressure sensors, artificial muscles, or actuators [2]. Cairns and Goodwin [2] classified materials exhibiting NLC into four groups depending on the microscopic mechanism responsible for NLC: (a) compounds in which NLC is a consequence of ferroelectric phase transitions, (b) network solids for which correlated polyhedral tilts drive NLC, (c) helical systems, and (d) framework materials with wine-rack, honeycomb, or related topologies, where NLC arises from framework hinging. A negative linear compressibility was observed for imidazolium benzoate salt [3]. X-ray diffraction and vibrational spectroscopy were used to analyze interactions in the crystal. The Quantum Theory of Atoms in Molecules (QTAIM) approach was applied to analyze the hydrogen bonds and other interactions.

In the crystal lattice, ions interact by conventional  $N^+ \cdots H \cdots O^-$  (within helices; medium strength) and unconventional  $C-H \cdots O$  (between helices; weak strength) hydrogen bonds. The interactions within the helix are stronger than interactions between helices. Imidazolium benzoate (formula moiety:  $C_7H_5O_2^-$ ,  $C_3H_5N_2^+$ ), crystallizes as a monoclinic system with space group  $P2_1/n$ . The asymmetric part of the unit cell is composed of one anion and one cation molecule. As the pressure increases, the values of the parameters  $a$ ,  $c$ , and  $V$  for imidazolium benzoate get smaller while the parameter  $b$  increases. We study the dynamics of hydrogen bond networks using absorption spectra and Raman scattering methods. Bands below  $200\text{ cm}^{-1}$  are associated with the studied salt's translational and librational network modes. As the pressure increases, the bands observed at about  $160$  and  $100\text{ cm}^{-1}$  shift toward higher wavenumbers, indicating a shortening of hydrogen bond lengths.

As the pressure increases, the semi-major axis value decreases while the helix pitch and semi-minor axis increase. The decrease in the value of the semi-minor axis and the increase in the helix pitch with increasing pressure result from changes in the structure of the  $N^+ \cdots H \cdots O^-$  hydrogen bond network and the libration motion of imidazolium ions. Imidazole ions rotate around an axis, passing through C2-C3 carbon atoms. In addition to changes in helix parameters, the angle between the carboxylate group and the phenyl ring also changes. It shows that the system moving to a lower energy structure "makes changes" not only in the dimensions of the helix itself but also in its internal structure.

We have proposed a helical model to explain the negative linear compression of imidazolium benzoate crystals. The mechanism of the negative linear behavior can be correlated with the structural distortions of helices. As the pressure increases, the semi-major axis value decreases while the helix pitch and semi-minor axis increase. The decrease in the value of the semi-minor axis and the increase in the helix pitch with increasing pressure result from changes in the structure of the  $N^+ \cdots H \cdots O^-$  hydrogen bond network and the libration motion of imidazolium ions.

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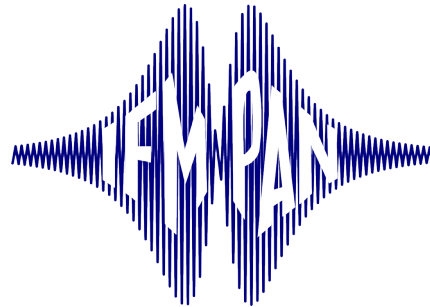
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