

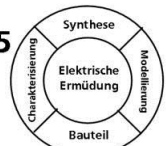
International Workshop on Relaxor Ferroelectrics

October 7th – 11th, 2012 • Schloss Edesheim • Germany



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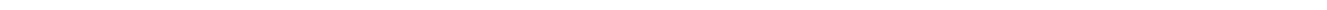
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SPP 1159
Ferroic Cooling



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General informations

Scope

The International Workshop on Ferroelectric Relaxors held from

7.10. - 11.10.2012 at Schlosshotel Edesheim

will bring together international experts on synthesis, properties, modeling and new applications of relaxor materials.

The focus of the workshop is on the fundamental understanding of structure-property relationships and on new materials including lead-free relaxors. Aspects of relaxor ferroelastic and ferromagnetic materials will also be discussed.

The workshop will present invited talks and contributed posters and will provide ample of time for scientific discussions.

Venue

The workshop will be held in Edesheim located at the “*Deutsche Weinstrasse*” in the center of the Palatinate wine-growing region, which has a long tradition extending back to the Romans and a particularly mild climate.

The “Schlosshotel” is embedded in a 5-hectare park with vineyards and fountains and provides an unique historical ambience for the Workshop. The hotel can be easily reached by car or train in about 2h from Frankfurt International Airport.

Hotel Schloss Edesheim

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Local Organizers

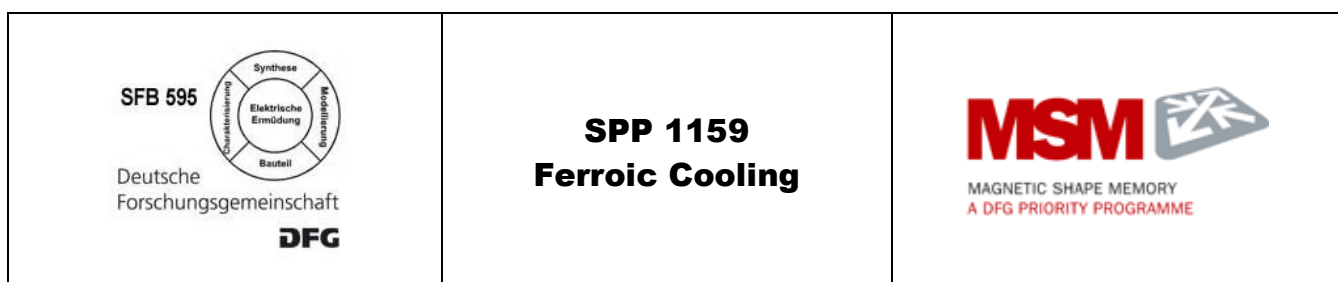
Prof. Dr. K. Albe, TU Darmstadt

Prof. Dr. J. Rödel, TU Darmstadt

Prof. Dr. W. Kleemann, U Duisburg-Essen

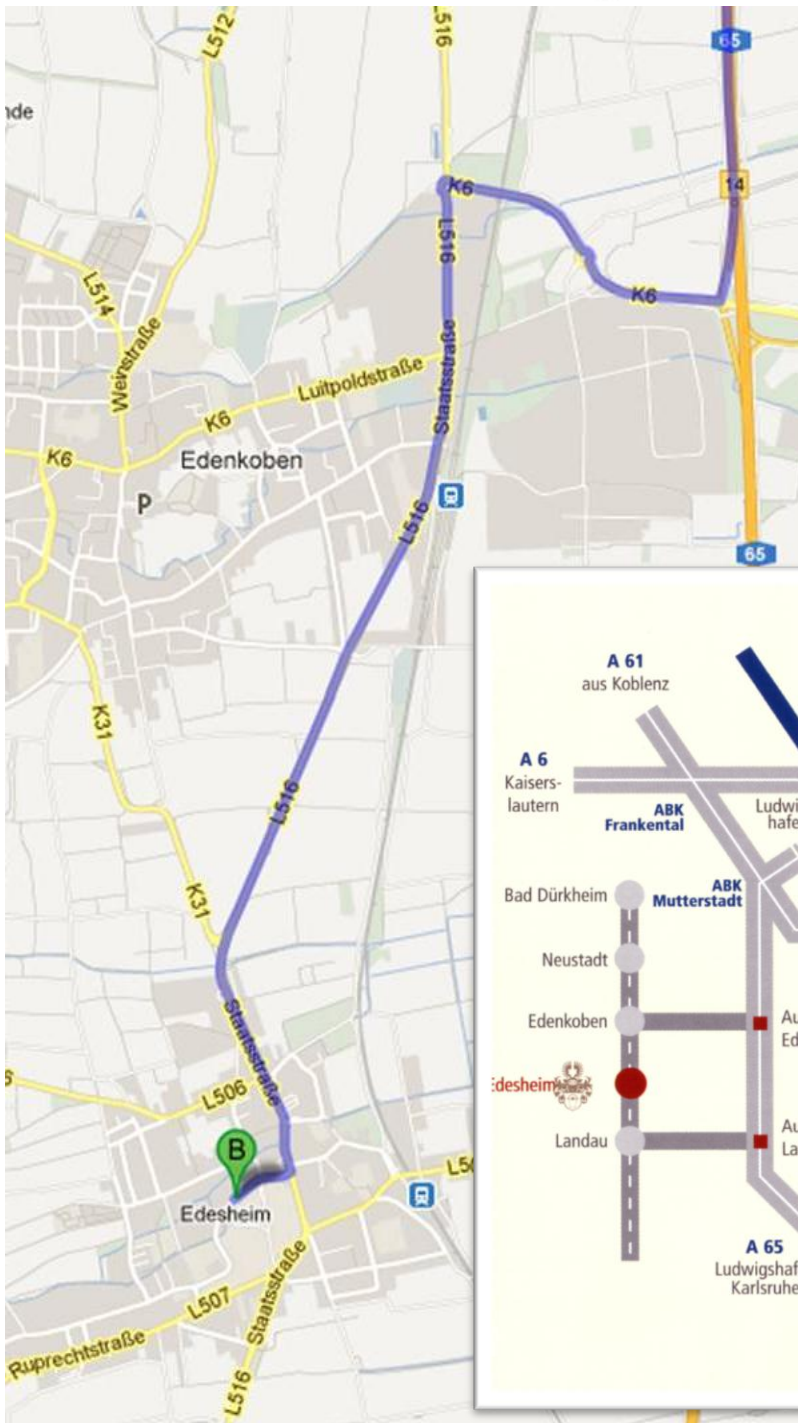
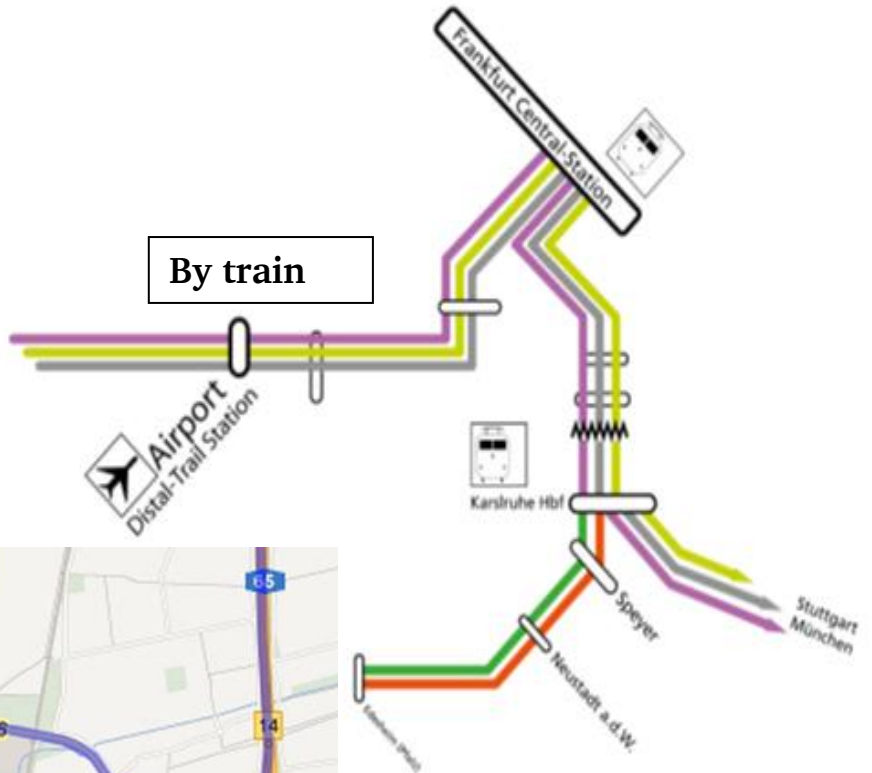
Dr. Sebastian Fähler, IFW Dresden

We acknowledge financial support by



Directions

By train



By car



Time schedule

Sunday, Oct. 7th

16:00-18:00			Registration
18:00-20:00			Dinner
20:00-20:15		K. Albe / J. Rödel	Welcome
Fundamentals		Chair: K. Albe	
20:15-21:00	talk 1:	W. Kleemann	Random fields in relaxor ferroelectrics
21:00-21:45	talk 2:	B. Burton	First-Principles Based Simulations of Relaxor Ferroelectrics

Monday, Oct. 8th

Polar Nanoregions		Chair: W. Kleemann	
09:00-09:45	talk 3:	J. Hlinka	On the wonderful but dangerous world of polar nanoregions
09:45-10:30	talk 4:	S. Vakrushev	Diffuse scattering in Relaxors: evidence in favor or against polar nanoregions
10:30-11:00			Coffee
11:00-11:45	talk 5:	B. Dkhil	Polar and chemical order/disorder in relaxor-based compounds
11:45-12:30	talk 6:	A. Bokov	Characteristic temperatures in relaxor ferroelectrics as evidenced by impedance spectroscopy
12:30-14:30			Lunch
Methods		Chair: H. J. Kleebe	
14:30-15:15	talk 7:	J. Petzelt	Broadband dielectric spectroscopy of relaxors and ferroelectrics with diffuse phase transitions: BZT, BZT-BCT and NBT-BT ceramics
15:15-16:00	talk 8:	V. V. Shvartsman	Piezoresponse force microscopy studies of relaxor ferroelectrics
16:00-16:30			Coffee
16:30-17:15	talk 9:	J. Daniels	High-energy x-ray scattering investigations of the structural origins of relaxor behavior in BNT-(x)BT single crystals
17:15-18:00	talk 10:	J. L. Jones	The origin of frequency dispersion and deaging of property coefficients using time-resolved X-ray and neutron scattering: The case of morphotropic phase boundary (MPB) BiScO ₃ -PbTiO ₃
19:00-20:30			Dinner
20:30-22:00			Poster

Tuesday, Oct. 9th

Lead-Free Relaxors: Principles		Chair: A. Bell	
09:00-09:45	talk 11:	D. Damjanovic	Macroscopic piezoelectricity and elastic anomalies in the paraelectric phase of BaTiO ₃ -based polycrystalline materials
09:45-10:30	talk 12:	M. Maglione	The cross-over range from ferroelectric to relaxor as an optimal piezoelectric state in Lead free ceramics
10:30-11:00			Coffee

**Lead-Free Relaxors:
Materials Development**

Chair: K. Reichmann

11:00-11:45	talk 13:	W. Jo	Phase stability of lead-free relaxor $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-BaTiO}_3$
11:45-12:30	talk 14:	J. S. Lee	Enhanced strain properties in lead-free ceramics by structuring relaxor matrix composites
12:30-14:30			Lunch

**Lead-Free:
Structural Properties**

Chair: K. Reichmann

14:30-15:00	talk 15:	L. A. Schmitt	Structural investigations of initial and fatigued morphotropic $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\text{-BaTiO}_3$ piezoceramics
15:00-15:30	talk 16:	M. Hinterstein	High pressure study of BNT-BT-KNN
15:30-16:00	talk 17:	W. Donner	Diffuse scattering and stacking faults in BNT-BT single crystals
16:00-19:00			AFTERNOON RECESS
19:00-20:30			Dinner
20:30-22:00			Poster

Wednesday, Oct. 10th

**Lead-Free:
Phase Properties**

Chair: D. Damjanovic

09:00-09:45	talk 18:	J. Kreisel	The local structure in lead-free BaTiO_3 -based (relaxor) ferroelectrics
09:45-10:30	talk 19:	P. Thomas	Parametric Study of Relaxor Sodium Bismuth Titanate $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT)– phase transitions revisited
10:30-11:00			Coffee

Phase Transitions

Chair: D. Damjanovic

11:00-11:45	talk 20:	X. Tan	Developing piezoelectricity from relaxor ferro(i)electrics
11:45-12:30	talk 21:	R. Pirc	Field-induced phase transitions in relaxor ferroelectrics: Theory and experiment
12:30-14:30			Lunch

Theory and Modelling

Chair: J. Hlinka

14:30-15:15	talk 22:	L. Bellaiche	Finite-temperature properties of $\text{Ba}(\text{Zr,Ti})\text{O}_3$ relaxors from first principles
15:15-16:00	talk 23:	I. Kornev	Gauging Relaxors
16:00-16:30			Coffee

Multiferroics

Chair: J. Rödel

16:30-17:15	talk 24:	S. Kalinin	Linking Mesoscopic and Atomic Scale Behaviors in Disordered Ferroelectrics
17:15-18:00	talk 25:	U. K. Rößler	Glassy intermediate phases and microstructures in (multi)ferroics
18:00-18:45	talk 26:	Z.-G. Ye	Multirelaxors
19:00-			BANQUET

Thursday, Oct. 11th

DEPARTURE

Random fields in relaxor ferroelectrics

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Substitutional charge disorder as in solid solutions $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3-x(\text{PbTiO}_3)$ (“PMN-PT”) [1], structural cation vacancies as in $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ [2], or isovalent substitution of off-centered cations as in $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ [3], and $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ [4] give rise to quenched electric random-fields (RFs), which we proposed to be at the origin of the peculiar behavior of relaxor ferroelectrics 20 years ago [5]. E. g., a strong frequency dispersion of the dielectric response and an apparent lack of macroscopic symmetry breaking in the low temperature phase are encountered. Both are related to mesoscopic RF-driven phase transitions, which give rise to irregularly shaped quasi-stable polar nanoregions (PNRs) at the temperature T^* [6], being “intermediate” between the Burns temperature of dynamic PNR correlations, T_d , and the global freezing temperature, T_f . Their co-existence with the paraelectric parent phase can be modeled by time-dependent field equations under the control of quenched RFs and stress-free strain (in the case of order parameter dimension $n \geq 2$) [7, 8]. Transitions into global polar order at T_c may occur in uniaxial relaxors as observed on the uniaxial relaxor ferroelectric $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ and come close to RF Ising model criticality [9]. Reentrant relaxor transitions as observed in solid solutions of $\text{Ba}_2\text{Pr}_{0.6}\text{Nd}_{0.4}(\text{FeNb}_4)\text{O}_{15}$ [10], are proposed to evidence the coexistence of distinct normal and relaxor ferroelectric phases within the framework of percolation theory.

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W. Dmowski, S. B. Vakhrushev, I.-K. Jeong, M. P. Hehlen, F. Trouw, T. Egami, *Phys. Rev. Lett.* **100** (2008) 137602;
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First-Principles Based Simulations of Relaxor Ferroelectrics

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Previous applications of this effective Hamiltonian model have successfully treated variations of relaxor behavior in $\text{Pb}(\text{Sc}_{1/2}, \text{Nb}_{1/2})\text{O}_3$ and $\text{Pb}(\text{Mg}_{1/3}, \text{Nb}_{2/3})\text{O}_3$ as functions of: temperature [Burton et al. PRB 72, 064113, 2005]; pressure [Tinte et al. PRL 97, 137601, 2007]; near neighbor Pb-O divacancy pairs, [Burton et al. PRB 77, 144114, 2008]; and diffuse neutron and X-ray scattering [Ganesh et al. PRB.81.144102, 2010]; see also the review, [Burton et al. Phase Transitions, V79, 91-(1-2) 2006]. How well this model has held up will be reviewed, and new results on superlattices of ordered- and disordered-layers will be presented.

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Nature Materials 111 (12) 2001

On the wonderful but dangerous world of polar nanoregions

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We suggest to give a review on possible experimental signatures of the so-called polar nanoregions in lead-based perovskite relaxors. First of all, we propose to outline both traditional and alternative approaches to these signatures. We intend to exploit mainly the hypothesis that there are three different temperature scales in the system. Based on the accumulated results, it seems to us that the concept of polar nanoregions is useful but largely speculative. Polar nanoregions might be distinguished from and compared with ferroelectric nanodomains. In simplest approach, qualitative explanation of the principal "relaxor" properties of PMN can be narrated in both frameworks. We shall nevertheless argue that polarization as a vector is probably not well defined at any nanometric region in the relaxor state of PMN.

Diffuse scattering in Relaxors: evidence in favor or against polar nanoregions

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Existence of polar nanoregions (PNRs) is a key concept in most theories of relaxors. On the other hand there is no generally accepted point of view on “what are the PNRs?”. There are no unambiguous proof of PNRs existence and their role in the relaxor phenomena. Strong and very anisotropic diffuse scattering (DS) is usually considered as a “fingerprint” of relaxor materials and one of the strongest evidence in favor of PNRs. In the majority of papers diffuse scattering is described in terms scattering density contrast similar to that used in the case of small angle scattering, but with the contrast value being dependent on the selected Bragg point. However in our recent paper [1] we have demonstrated that such description is incompatible with carefully measured 3-D intensity distributions.

In the present we will consider the problem of the DS in relaxors in details and will demonstrate that this DS have essential common topological feature: directional minima along $\tau = \mathbf{Q} - \mathbf{q}$ [1]. To account for this feature we have to consider a model of propagating (or frozen) waves. We will consider 2 models: (i) is the originally developed in Ref.1 model of acoustic-like waves propagating through the crystal, that gives very good agreement for the describing of X-ray data were scattering intensity is mostly determined by lead, and (ii) the model including coupling of acoustic and lowest TO modes that provide satisfactory agreement for both DS shape and eigenvectors. We will also consider similarity of the DS in relaxors and simple antiferroelectric crystal PbZrO_3 .

Finally we will briefly discuss DS in PZT single crystal and will demonstrate importance of considering topology of DS for its proper interpretation

[1] Bosak, et al.

Acta Cryst. A, 117-123 (68) 2012.

Polar and chemical order/disorder in relaxor-based compounds

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Oxides with extraordinary properties like giant magnetoresistivity, superconductivity or giant piezoelectricity share more common features than previously believed. All of them display similar temperature dependence. Indeed in case of complex lead-based $\text{Pb}(\text{BB}')\text{O}_3$ relaxor ferroelectrics, in addition to the so-called Burns temperature, associated to Pb off-centering, it exists an other peculiar temperature, namely T^* , above the ordering temperature where some correlated nanoclusters appear because of quenched disorder. The chemical disorder play thus a key role for the relaxor state but can also stabilize different polar states which can in turn explain the physical and structural properties at the so-called morphotropic phase boundary (MPB). In this talk I will discuss on both polar and chemical order/disorder and I will try to bring a microscopic view for of what might be the relaxor state as well as the MPB structure.

Characteristic temperatures in relaxor ferroelectrics as evidenced by impedance spectroscopy

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Relaxor ferroelectrics are characterized not only by complicated structure and unusual properties, but also by intricate sequence of phases/states of different type observed when undergoing variable external conditions (temperature, pressure, electric field) [1-5]. The microscopic nature of these states and the phenomenological parameters capable of describing them have been discussed widely but no consensus has been achieved so far.

In this talk we present our understanding of phase transformations in relaxors based upon our previous and recent studies of the dielectric properties as a function of frequency, temperature and pressure. The complex perovskite relaxors, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{W}_{2/3}\text{Fe}_{1/3})\text{O}_3$, $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ and their solid solutions, as well as lead-free BaTiO_3 -based solid solutions, are considered as representative relaxor materials. In canonical relaxors, four well-defined (frequency-independent) characteristic temperatures are found: T_B , at which the parameters of the Curie-Weiss law and the activation energy of dc conductivity change; T^* , at which the dielectric permittivity suddenly deviates from the Curie-Weiss law upon cooling; T_A , at which the maximum of static “conventional relaxor” dielectric susceptibility is observed; and T_f , at which the dielectric spectrum freezes, i.e. the extrapolated characteristic relaxation time diverges and the extrapolated relaxation time distribution becomes infinitely wide. In those relaxors where a ferroelectric phase appears at low temperatures, frequency independent sharp or diffuse anomalies can be observed in the temperature dependences of the permittivity and relaxation time. The other often reported parameter, i.e. the Vogel-Fulcher temperature derived from the frequency dependence of the permittivity maximum temperature, is found to be frequency dependent. The physical meaning of the characteristic temperatures is discussed.

The work was supported by the U.S. Office of Naval Research (Grants No. N00014-06-1-0166 and No. N00014-11-01-0552) and the Natural Science and Engineering Research Council of Canada.

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Broadband dielectric spectroscopy of relaxors and ferroelectrics with diffuse phase transitions: BZT, BZT-BCT and NBT-BT ceramics

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The problem of broadband dielectric response of polar nanoregions (PNR) in relaxor ferroelectrics is a matter of long discussion, because, in dependence of temperature, it covers an extremely broad frequency range 0-10¹² Hz, which, being of mesoscopic nature, cannot be treated by any microscopic theory. Qualitative features are known from the example of the best known relaxors PbMg_{1/3}Nb_{2/3}O₃ (PMN) and (Pb,La)(Zr,Ti)O₃ (PLZT) [1-4]: the response of PNR emerges as a Debye relaxation from the soft phonon mode response in the THz range below Burns temperature and on further cooling it slows down and broadens, usually splitting into two broad components. The lower component follows slowing down and freezing according to the Vogel-Fulcher law, the higher-frequency component follows rather the Arrhenius law and below the freezing temperature it extremely broadens into a frequency independent (constant) loss spectrum (1/f noise) [4]. The situation is fully analogical to the response of normal (canonical) glasses with appearance of α and β relaxations, but the response is by orders of magnitude stronger. The most probable origin of the constant loss response below the freezing temperature is fluctuations (breathing) of the PNR boundaries.

In my talk I will focus mostly on our recent data on several lead-free relaxor ferroelectrics and ferroelectrics with diffuse transitions. The relaxor behavior will be best illustrated on BaZr_{0.4}Ti_{0.6}O₃, where we shall demonstrate that for correct inspection of the slowing-down law one has to follow the temperature dependent maximum in the loss spectra rather than the permittivity or loss vs. temperature maxima at different frequencies, as usually done. This maximum emerges near 10 cm⁻¹ below the lowest-frequency polar mode (~100 cm⁻¹) as an overdamped central mode and slows down without any anomaly near the permittivity maximum (~150 K) transforming into the broad Arrhenius-like dielectric relaxation mentioned above. Somewhat more complex behavior will be illustrated for the cases of Na_{1.2}Bi_{1/2}TiO₃-BaTiO₃ (NBT-BT) with 7 and 15 % of BT, where the relaxor behavior is combined with a ferroelectric transition. Here the main dispersion around the permittivity maximum (~550 K) appears in the MHz - GHz range and the THz central mode shows slow gradual softening on heating from 300 to 900 K so that it is of phononic origin rather than due to PNR dynamics.

Unlike relaxor ferroelectrics, the broadband dielectric spectroscopy around the diffuse ferroelectric phase transition was so far not carefully studied and discussed. We have studied it in most details for the case of BaZr_{0.2}Ti_{0.8}O₃ and will show that on approaching the diffuse ferroelectric transition (T_c ~310 K) from 700 K, an overdamped (central) mode emerges near ~20 cm⁻¹ and softens down to the microwave range near T_c. Below T_c it merges with a (nearly) constant loss contribution, which dominates there in the whole frequency range 10-10¹¹ Hz and whose magnitude decreases exponentially on cooling down to 5 K. Analogous behavior is observed also in the case of 0.5BaZr_{0.2}Ti_{0.8}O₃-0.5Ba_{0.7}Ca_{0.3}TiO₃ (BZT-BCT) solid solution.

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Piezoresponse force microscopy studies of relaxor ferroelectrics

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Since their discovery over 50 years ago relaxor ferroelectrics have attracted continued interest due to their unusual behaviour. The physical properties of relaxors were mainly assessed by scattering and spectroscopic methods and revealed the importance of short-range polarization correlations inside so-called polarization nanometer regions. For the last ten years Piezoresponse Force Microscopy (PFM) technique has proved to be a powerful tool for the investigation of local properties of relaxors where optical techniques obviously fail because of their lack of resolution. In this presentation we overview results of PFM investigations of the spatial distribution of polarization at the nanoscale and its evolution with time, temperature, and electric field for several relaxor systems including uniaxial (Sr,Ba)Nb₂O₆ and quasi-isotropic PbMg_{1/3}Nb_{2/3}O₃-PbTiO₃. Interplay of depolarization field energy, the influence of random electric fields, and mechanical strain accommodation gives rise to a complexity of domain patterns in relaxors and even to appearance of hierarchical domain structures at different length scales. The PFM study of relaxors helps to understand mechanisms of development of polar order in relaxors and provides important information, e. g. on mesoscopic polarization patterns that were overlooked by major theories of the relaxor state. It has been shown that quasi-static nanodomains exist in relaxors above the transition/freezing temperature. The results can be interpreted as an evidence of coexisting static and dynamic polarization in a certain temperature range around the transition point.

High-energy x-ray scattering investigations of the structural origins of relaxor behavior in BNT-(x)BT single crystals

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Diffuse x-ray scattering intensities from single crystals in the solid solution of $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3) - x(\text{BaTiO}_3)$ have been collected using high-energy synchrotron x-ray scattering. This technique allows for the investigation of the breaking of long-range order in crystalline materials. Distinct features in the diffuse scattering intensities indicate structural variations at the nano-meter length scale. It is shown by *in-situ* electric field measurements that locally correlated planar-like structures on (001) type planes and octahedral tilt-domains within the room temperature phases are both electrically active and are irreversibly affected by application of an electric field. These nano-regions are not analogous to those in the relaxor ferroelectric systems of $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$ (PZN-PT) and $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$ (PMN-PT), which show diffuse streaking along $\langle 110 \rangle$ directions. The field and temperature dependence of the BNT-BT nano-scale structures is explored and correlated to the relaxor behaviour of the material.

The origin of frequency dispersion and deaging of property coefficients using time-resolved X-ray and neutron scattering: The case of morphotropic phase boundary (MPB) BiScO₃-PbTiO₃

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The solid solution between BiScO₃ (BS) and PbTiO₃ (PT) ceramics exhibits a morphotropic phase boundary at approximately 0.36BS-0.64PT. Compositions within this region exhibit both a high piezoelectric coefficient (460 pC/N) and a high Curie temperature (~450°C) [1]. Prior measurements of the piezoelectric and dielectric coefficients have suggested some degree of extrinsic contributions to this coefficient, possibly related to domain wall motion [2]. In this work, we use time-resolved X-ray and neutron diffraction to determine the contribution of extrinsic and intrinsic mechanisms to the piezoelectric coefficient at various subcoercive electric field amplitudes and frequencies.

The synthesized composition is a mixture of monoclinic and tetragonal perovskite phases, consistent with prior crystallographic refinements [3]. At low (subcoercive and sub-Rayleigh) fields, multiple cooperative electromechanical effects are observed including domain wall motion in both the monoclinic and tetragonal phases, interphase boundary motion between the two phases, and electric-field-induced lattice strains. The measurements span four orders of magnitude in frequency, facilitating the discrimination of intrinsic and extrinsic contributions to properties. In the monoclinic phase, electric-field-induced peak shifts as high as 2300 pm/V are attributed to domain wall motion in the monoclinic phase.

Domain wall motion of the tetragonal phase is very small at low fields and increases with field amplitude; this mechanism can explain the field-amplitude dependence of the piezoelectric coefficient [4]. Moreover, a deaging effect was observed during the field-amplitude measurements, or an irreversible change (within the timeframe of the experiment) due to application of small alternating fields. In the present diffraction measurements, this effect is observed as a progressive change in the average domain volume fractions during application of small alternating fields [4]. This effect contributes to the asymmetry of the polarization behavior at weak fields.

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Macroscopic piezoelectricity and elastic anomalies in the paraelectric phase of BaTiO₃-based polycrystalline materials

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Order-disorder character of the ferroelectric-paraelectric phase transition of some ferroelectrics, including BaTiO₃, is well documented.[1] The precursor order leads to local symmetry breaking and polar clusters in the paraelectric phase; they are manifested macroscopically as anomalies in birefringence and elastic constants, and in a large-field piezoelectric effect well above the ferroelectric-paraelectric phase transition temperature.[1-6] In this presentation we report on observation of the weak-field piezoelectric effect (an unequivocal sign of macroscopic polarization in polycrystalline samples) and elastic anomalies above the tetragonal-cubic phase transition temperature, T_{T-C} , in BaTiO₃, (Ba_{1-x}Sr_x)TiO₃, and (Ba,Ca)(Sr,Ti)O₃ ceramics. All properties are measured at low frequencies, from 0.5 Hz to about 100 kHz. The piezoelectric effect measured at weak fields in poled non-modified BaTiO₃ persists until at least 470 K and survives several temperature cycles over T_{T-C} (≈ 400 K). The signature of polar character is seen also in unpoled samples. The temperature dependence of the effective elastic stiffness coefficients exhibits critical behavior on approaching T_{T-C} on cooling and a maximum above T_{T-C} , as reported in other ferroelectrics.[4,7] The experimental results obtained here on ceramic samples are compared to those from the literature on single crystals and with theoretical predictions and are discussed in terms of defects and intrinsic disorder in these materials.

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The cross-over range from ferroelectric to relaxor as an optimal piezoelectric state in Lead free ceramics

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A very common feature of Lead-free ceramics is that their low temperature state continuously changes from ferroelectric to relaxor. This is not restricted to the perovskite family provided that one of the end members is a ferroelectric [1]. Such an experimental fact has been confirmed theoretically by the similarity between relaxor and ferroelectrics concerning their high temperature lattice dynamics [2].

The aim of this lecture is to show that the intermediate composition range between ferroelectric and relaxor is of interest for the optimization of piezoelectric properties. Simple experimental tools will be suggested for this optimization, taking the ternary BaTiO₃-CaTiO₃-BaZrO₃ (BCTZ) solid solution as an example. This solid-solution is of interest since large piezoelectric coefficients were recently demonstrated [3] precisely at the composition range where relaxor state starts to succeed to the ferroelectric one [4]. In this composition range, we first found that the ferroelectric polarization is highly flexible both versus the electric field and the operating temperature [5]. This is consistent with the several available models using domain/polarization clusters coexistence in such materials [1, 3, 6]. We further confirmed such multistate coexistence by non-linear dielectric permittivity experiment which is an efficient probe of disorder in the paraelectric state close to the transition point. The first order non linear permittivity is sensitive to cross-correlation between misaligned dipolar moments while the linear one quantifies the mean orientation of the same dipoles.

We recall that such link between dielectric non-linearities and elastic properties were already observed in KTaO₃ based solid solution at the composition range where ferroelectricity emerges from the quantum paraelectric state.

While being far from application, some Lead-free solid solutions and quantum ferroelectrics can be understood as model systems where long range order and local disorder are balanced at the right point where the average polarization is sensitive to all external stresses.

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Phase stability of lead-free relaxor $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-BaTiO}_3$

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'Lead-free' has been one of the keywords in the piezoelectric and ferroelectric community over the last two decades.[1] Among them, the $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BNT)-based solid solution system is one of the most attended due to many scientifically intriguing issues such as antiferroelectricity with relaxor features, highly sophisticated temperature-dependent polymorphisms, the presence of morphotropic phase boundary (MPB) similar to that in the market dominating PZT ceramics, *etc.*[2] In fact, the structural complexity dates even back to the 1950s, when BNT was first introduced to the community as a normal ferroelectric material,[3] though dielectric permittivity of unpoled BNT displays a clear frequency-dependent dispersion.[4] In spite of the extensive studies over the issues so far, none of the issues have been satisfactorily clarified but became even more complicated and controversial, *e.g.*, no solid evidence for supporting antiferroelectricity has been reported, diffraction-based structural studies have turned out inconclusive, the aspect of MPB, more precisely morphotropic phase region (MPR), is fairly distinct among the known. Given this, we recently proposed that seeing BNT-based materials near MPR as a new-type of relaxor, where two different types of PNRs of competitive free energy coexist, can successfully mediate the existing controversies and unambiguity.[2,5] In this work, we will show experimental evidences supporting our new model and discuss the uniqueness of the relaxor features of BNT-based solid solution systems.

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Enhanced strain properties in lead-free ceramics by structuring relaxor matrix composites

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Increasing demand for environmentally friendly materials in electronic and automotive industries has promoted extensive studies on searching lead-free alternatives of PZT-based piezoelectrics that contain more than 60 wt% Pb. For systematic investigation of new lead-free piezoceramics with large electric field-induced strains (EFISs), the Korean government also launched a team project on July 2008, in which four Korean national research institutes based on authors' group and seven universities have participated. In the integrated project, four groups have played each role in 1) exploitation of new compositions with domain engineering, 2) preparation of nanosized lead-free ceramic powders, 3) development of multilayer ceramic actuators using lead-free ceramics, and 4) development of microelectromechanical system (MEMS) devices using lead-free thin films. This talk will give a brief introduction to the team project.

As one of various research topics, we studied the dielectric, ferroelectric, EFIS properties of BNKT modified with A- or B-site dopants or other ABO₃ compounds. As a result, we found that many modified Bi_{1/2}Na_{1/2}TiO₃ - Bi_{1/2}Na_{1/2}TiO₃ solid solution (BNKT) ceramics exhibited a large strain when there was a ferroelectric-relaxor (FE-R) crossover as the modifier content increased, which was very similar to previous works on BNT-BT-KNN [1] or BNT-BKT- Bi(Zn_{1/2}Ti_{1/2})O₃ [2]. In the case of A- or B-site impurities, the FE-R crossover was observed when the tolerance factor (*t*) of the perovskite structure was decreased by doping, whereas the FE state of unmodified BNKT remained stable when the dopant increased the *t*. Despite the fact that BNKT-based ceramics have shown large normalized strains in the range of $S_{\max}/E_{\max} = 500 - 700$ pm/V at RT near the FE-R transition region, there were several problems in applications such as large strain-field hysteresis, high electric-field to trigger large strain, and strain stability in a limited temperature range. In order to resolve such problems, we attempted to prepare ceramic-ceramic composites by embedding FE particles in a relaxor matrix. The normalized strain S_{\max}/E_{\max} was remarkably enhanced by lowering the triggering field even though the maximum strain was almost unchanged. The ceramic-ceramic composite is believed to enlighten a new road to large strain lead-free alternatives of Pb-based actuator materials.

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Structural investigations of initial and fatigued morphotropic $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ - BaTiO_3 piezoceramics

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For the last decades, lead-based piezoceramics have been the material of choice for high-performance actuator, sensor and transducer applications. Due to detrimental effect of lead on the environment, it has to be replaced by lead-free non-hazardous materials in the near future. Among the various lead-free systems, the $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ - xBaTiO_3 system is an interesting candidate for structural investigation.

For this study, lead-free piezoelectric ceramics $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ - xBaTiO_3 with $x = 0.6$ and 0.7 have been prepared by a solid state sintering method. Preliminary investigations revealed a strong degradation of macroscopic electromechanical properties within the first 100 cycles [1]. Therefore, the following structural investigation was focused on a comparative study comprising X-ray, neutron and electron diffraction of freshly prepared and cycled specimen. Transmission electron microscopy (TEM) [2] and neutron diffraction of the initial specimens revealed the presence of superstructure reflections of the type $\frac{1}{2}\{ooe\}$ and $\frac{1}{2}\{ooo\}$, where o and e denotes odd and even Miller indices, respectively. Findings can be assigned to a coexistence of a rhombohedral and a tetragonal phase with space group $R3c$ and $P4bm$, respectively. In situ electric field X-ray diffraction revealed a strong, distinct response upon application of an external electric field of 4 kV/mm, depending on composition. Moreover in situ and ex situ fatigued specimen were investigated.

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High pressure study of BNT-BT-KNN

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In $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ a new variant of the perovskite structure was published by Jones and Thomas [1]. The structure exhibits an unusual combination of in-phase ($a^0a^0c^+$) tilts and antiparallel cation displacements along the polar c axis. In the framework of the SFB 595 “Elektrische Ermüdung in Funktionswerkstoffen” we found the same structure in various compositions of the $100-x-y\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3-x\text{BaTiO}_3-y\text{K}_{1/2}\text{Na}_{1/2}\text{NbO}_3$ system (BNT-BT-KNN) [2-4]. However, the interpretation of the dielectric measurements [5] and the unusual cation displacements is still under discussion. The observed effects were explained by a non-polar phase, antiferroelectric ordering or relaxor behavior. In this contribution the characteristics of this complicated structure shall be elucidated by high pressure results. Raman spectroscopy and neutron diffraction experiments in pressure cells, that allow pressures up to 10 GPa, gave insight in an interesting sequence of phase transitions.

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Diffuse scattering and stacking faults in BNT-BT single crystals

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In our previous work we found diffuse streaks in the x-ray diffraction from the single crystal relaxor BNT-4BT [1]. These streaks connect half-order reflections associated with octahedral tilts in the sample. The diffuse streaks and diffuse half-order peaks react upon the application of an external electric field.

Similar diffuse scattering patterns had been found in electron diffraction [2] from pure BNT samples and were interpreted as arising from stacking faults in the octahedral tilt sequence. The stacking fault structure could also be viewed as a twin structure of two rhombohedral domains. Here we present results from simulations of the diffuse scattering pattern based on certain stacking faults in the R3c structure and show that the model can be applied to estimate the amount of stacking faults.

The stacking fault probability in turn can be used to estimate the size of the nanopolar regions in BNT-BT giving rise to the relaxor behavior.

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The local structure in lead-free BaTiO₃-based (relaxor) ferroelectrics

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BaTiO₃-based relaxors such as BaTi_{1-x}Zr_xO₃ (BTZ) present a homovalent Zr⁴⁺/Ti⁴⁺ substitution and the origin of its relaxor properties has attracted a significant interest [1], more recently namely in the light of reports on large piezoelectric effects in Ca-doped BTZ [2]. As to the relaxor properties, it has been proposed that the finite correlation length of the local dipole moment orientations is related to chemically-induced random local strains due to the difference in size of Zr⁴⁺ and Ti⁴⁺ cations ($r_{\text{Zr}^{4+}} / r_{\text{Ti}^{4+}} = 1.18$) [3]. Such fields could affect the displacement of the ferroelectrically active Ti⁴⁺ ions in their oxygen octahedra; yet it is not known how, and on which scale such random elastic fields build up and how they act on the perovskite-characteristic structural instabilities such octahedra tilts and cation displacements.

We will first recall our experimental results from X-ray absorption [4-5] and neutron pair distribution functions (PDFs) [6] before putting emphasis on insight that can be gained from ab-initio calculations [7]. Our experimental studies of the local structure in BTZ show that the O₆ octahedral cages around a Zr atom have a significantly larger size (4.20 Å) than those around a Ti atom (4.05 Å), as expected from the different Ti⁴⁺ /Zr⁴⁺ cation sizes. In order to know if a Zr atom further affects its surrounding structure, including the position of its Ti neighbors, one has to analyze the oxygen cage distortions and the Ti displacement changes as a function of the local Ti/Zr distribution. This information is very difficult to access by experiments since the atomic positions are averaged out on all the Zr and/or Ti octahedral sites, even when using local probes such as x-ray absorption spectroscopy XAS or neutron PDFs. On the other hand, supercell first-principles calculations offer a promising theoretical route to study the local interplay between the Zr and Ti atoms [7].

From first-principles calculations on the $x = 0.26$ composition, we present evidence for four types of local Ti-atom polar displacements: along the $\langle 111 \rangle$, $\langle 110 \rangle$, or $\langle 100 \rangle$ directions of the cubic unit cell, or almost cancelled [5, 8]. The type of a Ti displacement is entirely determined by the Ti/Zr distribution in the adjacent unit cells. We show that the underlying mechanism involves local strain effects that ensue from the difference in size between the Ti⁴⁺ and Zr⁴⁺ cations. Interestingly, the local strain effects induce distortion of the octahedra but not their rotation (tilting). Our results shed light on the structural mechanisms that lead to disordered Ti displacements in BTZ, and probably in other BaTiO₃-based relaxors with homovalent substitution. Finally, we will put our observations and calculations in the light of the recent report of a large piezoelectric effect in Ca-doped BTZ [2] and discuss possible origins why such a large response is observed in BCTZ but not in BTZ.

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Parametric Study of Relaxor Sodium Bismuth Titanate $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT)–phase transitions revisited

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Sodium bismuth titanate, $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) and its derivatives are of possible interest as alternative lead-free piezoelectric materials particularly as the end-member in solid-solutions with BaTiO_3 and $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ *inter alia*. In an earlier comprehensive study of NBT, we determined from powder neutron diffraction from instrument D2B at Institut Laue-Langevin (ILL), Grenoble, an unusual sequence of average symmetries with increasing temperature of $R3c$ to $P4bm$ to $Pm-3m$ (Jones and Thomas 2000 and 2002) although later studies have suggested that the rhombohedral phase is in-fact monoclinic (space group Cc) but strongly pseudo-rhombohedral (Aksell 2011, Gorfman and Thomas 2010). The transformation from $R3c$ (or Cc) to $P4bm$ has always been a source of controversy together with the optical observation of a so-called “isotropisation point” (hereafter, the I-point), where the crystal looks cubic, at temperatures that have been variously reported in the interval 530-600K. This phenomenon has been ascribed to a rhombohedral (R) and tetragonal (T) phase coexistence in which the size of R and T domains is smaller than the wavelength of light and fits with the view of NBT as an inherently relaxor system. Alternatively, extensive electron microscopy studies (*eg* Trolliard and Dorcet, 2008) of ceramics of NBT have suggested the existence of an orthorhombic modulated phase sandwiched between the R and T phases, although this has not apparently been seen as a long-range ordered phase by diffraction methods to date.

This paper presents the analysis of previously-unseen neutron diffraction data collected from 293-943K on the High Resolution Powder Diffractometer (HRPD) at ISIS in steps of (a) 2K in the vicinities of the optical isotropisation point at 573K and the tetragonal-cubic phase transformation at 873K; (b) 10K throughout the rest of the temperature range. The data from the high-resolution back-scattering detector bank ($2\theta=168^\circ$) are refined using GSAS to obtain the lattice parameters in each phase and to make detailed plots of the tetragonal strain between 573K and 973K. These provide compelling evidence that as the temperature decreases to the I-point at 573K, the unit cell becomes increasingly metrically cubic and the tetragonal strain tends to zero (Figure 1). Seen from the other side ie from the R phase, a similar reduction of the rhombohedral strain to zero as the I-point is approached from below is observed.

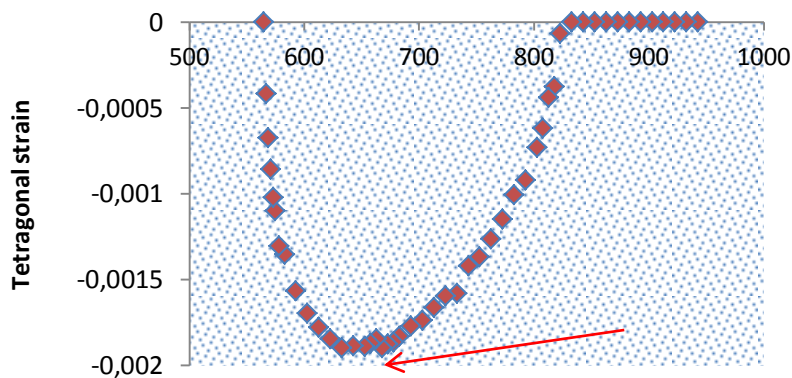


Figure 1: Tetragonal strain ($1-c/a$) vs temperature in or the cubic (zero strain) and tetragonal phases of NBT.

The findings from this parametric study are discussed in the context of (a) a re-entrant cubic phase model; (b) an entrant tetragonal phase model, for the phase transition sequence in NBT. Taken together with new optical (SHG) measurements and using group-theory testing with the programme ISODISTORT, the phase transition behaviour of this peculiar compound is rationalised anew and its relaxor credentials re-examined.

Developing piezoelectricity from relaxor ferro(i)electrics

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Relaxor ferroelectrics exhibit a strong frequency dispersion in their high relative permittivity around T_m where a broad dielectric peak is observed. The origin of the relaxor ferroelectric behavior can be traced back to the existence of polar nanoregions. In the prototype relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, the structure of the polar regions is slightly distorted along the $\langle 111 \rangle$ direction, yet the long-range structure preserves cubic symmetry. According to the superparaelectric model, the polar vectors in these nanodomains are constantly fluctuating among the eight equivalent $\langle 111 \rangle$ directions. As a result, relaxor ferroelectrics typically do not display a piezoelectric behavior. On the other hand, it has been known that fine domains usually enhance piezoelectricity in normal ferroelectrics. For example, a d_{33} value as high as 460 pC/N was reported in fine-grained BaTiO_3 ceramics with nanometer-sized ferroelectric domains [1].

In this work, experimental results will be presented to demonstrate that through composition optimization in the $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$, $\text{Pb}_{1-3x/2}\text{La}_x(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$, and $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{O}_3-x\text{BaTiO}_3$ systems, the nonergodic states can be utilized for piezoelectricity. Specifically, the dynamic fluctuations of polar vectors can be significantly slowed down and the nanodomains can then be poled with a large remanent polarization. As a result, very high values of the piezoelectric coefficient d_{33} are observed in all three systems after proper poling. Furthermore, the coalescence of ferrielectric nanodomains during poling is directly visualized with the *in situ* transmission electron microscopy technique in a ceramic in the $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{O}_3-x\text{BaTiO}_3$ binary system.

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Field-induced phase transitions in relaxor ferroelectrics: Theory and experiment

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Relaxor ferroelectrics represent a class of disordered ferroelectrics, which are characterized by the absence of long range ferroelectric order in zero applied field at any temperature. In contrast to incipient ferroelectrics, however, relaxors undergo a freezing transition into a nonergodic state at low temperatures. It had been shown some time ago that by cooling a relaxor in a static electric field E larger than some threshold value E_c , a sharp first-order phase transition into a ferroelectric state occurs [1]. The line of first order transitions in the E - T plane terminates at a liquid-vapor type critical point beyond which the system is in a supercritical phase [2]. In normal ferroelectrics, this phenomenon can be described in terms of a standard Landau free energy expansion [3]. It has recently been shown [4] that an analogous Landau expansion is also applicable to relaxors, however, the first Landau coefficient $a(T)$ must always be positive because the zero-field transition is suppressed. In a quasi-static description, $a(T)$ is proportional to the inverse zero-field cooled static dielectric susceptibility, which can be derived from a suitable mesoscopic model [5], while the remaining coefficients $b < 0$ and $c > 0$ can be chosen, as usual, to be constant. In this manner, the temperature and field dependence of the electrocaloric effect in organic and inorganic relaxor materials has been calculated and compared with experiments [6]. It has been shown that the electrocaloric effect reaches a maximum value close to the field-induced critical point CP. The critical exponents for various physical quantities at CP have also been calculated.

In order to investigate in more detail the mechanism of the field-induced phase transition in relaxors, we have applied the above model to the problem of thermal properties such as the heat capacity and the latent heat at the first order field-induced transition. At fields and temperatures below CP the heat capacity shows a sharp peak and diverges at CP, whereas the latent heat is nonzero below the critical point and vanishes on approaching CP. The results of high-resolution calorimetric experiments [7] performed on PMN crystals oriented along [110] are in agreement with these predictions. In particular, the calorimetric study has shown that in zero applied field there are no thermal anomalies and consequently no phase transition in PMN [110] at any temperature.

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Finite-temperature properties of Ba(Zr,Ti)O₃ relaxors from first principles

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Relaxor ferroelectrics are characterized by some striking anomalous properties (see, e.g., Refs [1-21] and references therein). For instance, they adopt a peak in their *ac* dielectric response-versus-temperature function while they remain macroscopically paraelectric and cubic down to the lowest temperatures [1]. Furthermore, this dielectric response deviates from the "traditional" Curie-Weiss law [22] for temperatures lower than the so-called Burns temperature [2]. Other examples of anomalous properties include the plateau observed in their static, *dc* dielectric response at low temperature [23, 24], and the unusual temperature behavior [16] of the Edwards-Anderson parameter [25]. Determining the origin of these intriguing effects has been a challenge to scientists for more than half a century. Moreover, many other questions remain opened for discussion. Examples of such questions are: what do the different critical temperatures usually found in relaxors correspond to? Do polar nanoregions really exist in relaxors? If yes, do they only form inside chemically-ordered regions? Is it necessary that antiferroelectricity develops in order for the relaxor behavior to occur? Are random fields and random strains really the mechanisms responsible for relaxor behavior? If not, what are these mechanisms?

Motivated to resolve such important questions and to better understand relaxors, we decided to study disordered Ba(Zr_{0.5}Ti_{0.5})O₃ (BZT) solid solutions, via the development and use of a first-principles-based effective Hamiltonian. Note that BZT is also fascinating because, in addition to be a relaxor within some compositional range, its parent compounds are rather different, namely BaZrO₃ is paraelectric while BaTiO₃ is a typical ferroelectric.

Interestingly, our *ab-initio*-based calculations not only reproduce the anomalous features of relaxors but also offer a deep microscopic insight into BZT. Such insight allows to successfully answer the aforementioned questions, and will be discussed in detail during this talk.

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Gauging Relaxors

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We develop a new theoretical framework for describing and analyzing relaxor ferroelectric materials. Starting with the first-principles-based effective Hamiltonian approach [1] that can capture much of the essential physics of ferroelectrics with perovskite structure, we formulate our model in a manifestly gauge-invariant manner, based upon continuous symmetry and lattice gauge theory.

In this talk, a first-principles-based scheme that incorporates ferroelectric and elastic degrees of freedom, as well as gauge fields taking values in a Lie group allowing the computation of finite-temperature properties of relaxor ferroelectrics with perovskite structure will be presented. We illustrate the efficiency of this computational method in providing understanding of the fundamental physics of relaxor properties.

Even though our primary motivation is the relaxors, we expect the formalism to be of significance to other disordered systems. Furthermore, the lattice gauge approach to relaxor ferroelectrics can be generalized to describe a variety of systems with defects. Finally, some of these generalizations, challenges, and opportunities towards the long-sought goal of materials-by-design will also be discussed in this talk.

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Linking Mesoscopic and Atomic Scale Behaviors in Disordered Ferroelectrics

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Disordered ferroelectric (FE) systems including relaxors, morphotropic FE-FE-boundaries and FE-antiferroelectric remain Terra Incognitae of modern physics. While macroscopic behaviors are well explored and in fact utilized in multiple applications, it is the mechanisms underpinning unique properties of these materials and their emergence from atomic to mesoscopic scales that presents a challenge. In this presentation, I will summarize the results of our recent studies of structure and functionality of disordered ferroelectric systems using the synergy of piezoresponse force microscopy (PFM) and spectroscopy and atomic-level order parameter imaging by scanning transmission electron microscopy (STEM).

On the mesoscopic scale, previous PFM studies of relaxor systems suggest the presence of at least two components of order parameter identifiable based on time and voltage responses. Both ergodic and non-ergodic relaxors possess dynamic polarization component superimposed on the static polarization distribution with characteristic length scale of the order of 100 nm. To get insight in the structural and electronic factors controlling these systems, we have explored the atomic structures of model BiFeO₃ based ferroelectrics in the bulk in the vicinity of FE-AFE boundary, and in the proximity of symmetry-mismatched interface. We demonstrate direct atomically-resolved mapping of polarization and structure order parameter fields in Sm-doped BiFeO₃ system and their evolution with composition as the system approaches MPB. The experimental phase diagram and the phase evolution observed by STEM can be explained by taking into account flexoelectric interaction, which renders the effective domain wall energy negative, thus stabilizing modulated phases in the vicinity of the MPB. The interfaces between BFO and materials with different tilt system demonstrate emergence of interface-stabilized AFE phase, providing further insight into interaction between structural and polarization order parameters. Interestingly, PFM studies for all these systems illustrate FE-like responses, indicative of the proximity of AFE and FE states and large relaxation times.

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Glassy intermediate phases and microstructures in (multi)ferroics

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Structural glass states are abundant and often easily produced in ordinary condensed matter composed of molecular units. No quenched disorder is required to stabilize such solid-like amorphous states from the liquid as metastable phases. But, in equilibrium, self-generated glass states in a clean system seem elusive. For a ferroic order, as in a ferroelectric material, the notion of a glassy state even seems inconsistent with the requirement of homogeneity within (macroscopically large) domains in the symmetry-broken state. However, glass-like equilibrium mesophases are known to exist in chiral nematics in the form of the greyish “blue phase III” and indications for similar states have been found in precursor phases of chiral helimagnets [1]. Using phenomenological theory of such states as a guide [2], it is shown how similar complex textures can occur in multiferroics. The ingredients are coexisting or competing order parameters, closeness to a bicritical point, and particular “twisting” gradient couplings, known as Lifshitz-type interactions, between these ordering modes. The molecular units of such glassy textures are static multidimensional solitons that are stabilized by the twisting mechanism [3] frustrating a homogenous space-filling with the ferroic ordered state [4], as the skyrmion strings in chiral magnets [2,5]. In a flexoelectric texture localized dielectric polarization and strains can stabilize each other in a twisted way over a restricted region in space by forming small domains with the shape of a ball or tubular string and with a physical diameter fixed by the intrinsic couplings. Similar textures may exist in magnetoelectric materials with high symmetry of the parent phase. Extended mesophases then can be composed of such localized units. These glassy mesophases or precursor states may become frozen or pinned as (metastable) microstructures by the effect of quenched disorder. The phenomenological theory formulates an intrinsic mechanism for the generation of lumps of ferroic order with a fixed physical size in clean systems. The possible relation of this mechanism to phenomena like relaxor ferroelectricity, strain-glasses, or martensitic precursor states is an open problem at present.

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Multirelaxors

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Multiferroic materials which exhibit both magnetic and ferroelectric orders and effects of coupling between magnetization and electric polarization have been widely studied in the last decade and considered to be extremely attractive for a number of advanced applications such as spintronics and data storage. On the other hand, it is known that quenched disorder in crystal structure can often lead to the breaking of ferroic (magnetic and electric) long-range order, resulting in development of ferroic glassy phases below a certain freezing temperature, T_g (magnetic spin glasses, electric dipolar glasses, relaxor ferroelectrics etc.). However, the situation where both magnetically and electrically glassy states are observed simultaneously in the same material is quite rare and the microscopic mechanism and consequences of such coexistence are poorly understood.

In this talk we report our investigations of multiferroic crystals and ceramics with perovskite structure, in which, besides long-range magnetic order existing at comparatively high temperatures, the effects of nonergodicity are observed at low temperatures pointing to the possibility of the development of re-entrant spin-glasslike phase. We study the $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ crystals and the $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ - PbTiO_3 and BiFeO_3 - PbTiO_3 solid solutions in which compositional disorder in the arrangement of different ions on equivalent crystallographic sites is observed, and compare the behaviour with pure BiFeO_3 in which compositional disorder is absent.

The measurements of field-cooled and zero-field-cooled magnetization, frequency-dependent ac magnetic and electric susceptibilities and magnetic and electric hysteresis loops allow us to find the compositions in which both magnetic and electric relaxor states coexist, which entitles them to be true multirelaxors.

We reveal and analyze the effects of magnetic and dielectric relaxations as well as magnetoelectric effects and show that the magnetic relaxor behaviour can be explained in the framework of a model implying the development of static and dynamic antiferromagnetic clusters upon cooling from $T > T_N$, the Neel temperature, the appearance at $T=T_N$ of infinite antiferromagnetic cluster consisting of antiphase domains whose boundaries give rise to magnetic relaxation due to frustrated interactions among the Fe^{3+} ions, and finally, the freezing of the relaxation spectrum at $T=T_g$.

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Influence of heat treatment on thermal behavior of polar nanoregions in relaxor ferroelectrics

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Although relaxor ferroelectrics have been studied for decades, the physical mechanism of their dielectric properties and the origin of the dielectric anomalies are still unclear. Thermal evolution of polar nanoregions (PNRs) in the relaxor ferroelectric material BNT-6BT has been proposed by Jo et al. as a physical model to disentangle these issues [1]. To obtain experimental evidence of the thermal evolution of PNRs, influence of heat treatment such as quenching and annealing have been investigated on both lead-containing PLZT and lead-free BNT-6BT materials. The change in permittivity has been observed for both systems, which suggests the mechanism of the thermal evolution of PNRs in relaxor materials. The difference as well as the similarity of PLZT and BNT-6BT is discussed based on permittivity data and structural analysis. Thermal behavior of PNRs over the temperature range up to 500 °C is proposed for both materials.

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Modelling of PNR dielectric response in lead-free piezoelectrics and relaxor dielectrics

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The search for lead-free piezoelectrics has uncovered a number of systems with unusual dielectric and electromechanical behaviour of which the origin has caused some debate. This behaviour includes: (i) relaxation peaks in the temperature dependence of permittivity that do not coincide with the Curie temperature, (ii) large, non-remanent, field-induced strain and (iii) unusual frequency or time dependence of polarization hysteresis loops and field-induced phase transitions.

It has been suggested that the dielectric relaxation below the Curie temperature should be characterized as relaxor behaviour and that the observed characteristics are due to significant contributions from polar nano-regions (PNRs). [1]

To explore this hypothesis, a simple model first developed in the context of “conventional” relaxor dielectrics [2] has been used to model the low field complex permittivity and dielectric hysteresis of ensembles of PNRs. The model applies statistical mechanics to determine the influence of thermal fluctuations on both the magnitude and direction of the polarization vector in PNRs. The model has been tested using experimental data from the $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - $(\text{K}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ system (NBT-KBT). [3]

It can be concluded that the flattened Curie peak and the lower temperature relaxation peak are both intrinsic properties of PNRs. The dielectric characteristic observed in NBT-based systems can be interpreted as being part of a spectrum of behaviours that encompass the conventional single relaxation peak of conventional $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -like relaxors and the double peaks seen in other systems such as $(\text{Pb}, \text{Ba})(\text{Zr}, \text{Ti})\text{O}_3$. [4]

This range of behaviour, particularly its dependence on PNR size and dipole moment, is explored by examining the data for both NBT-KBT and La-doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. [5] It is suggested that the simplicity of the model can provide significant insights into the underlying origins of the dielectric behaviour of these materials.

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Nonlinear dielectric response: an effective tool for investigation of polar states in ferroelectrics, relaxors and dipolar glasses

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"No phase transition can take place without nonlinearity, and therefore it is absolutely necessary to disclose the nonlinearity aspects in order to understand the mechanism of phase transitions." This statement of Ishibashi [1] is still very timely. Despite its obvious importance different aspects of phase transformations are still mainly investigated via some linear responses, which manifest their anomalies at the phase transition point. In the particular case of the dielectric response this unsatisfactory situation is due to the lack of commercially available devices for measuring the nonlinear electric *ac* susceptibility. Only a few methods have been developed to this end [2-5]. With materials featuring nonlinear dielectric properties many advanced devices can be constructed, where the electric susceptibility can be controlled by electric fields.

Using our susceptometer [4] we have obtained very reliable data on the nonlinear dielectric responses of barium titanate, BTO (discontinuous phase transition, PT), triglicine sulphate, TGS, and lead germanate, PGO (continuous PTs), as well as the prototypical relaxor lead magnoniobate, PMN, the uniaxial relaxor strontium-barium niobate, SBN, and the doped quantum paraelectrics $K_{0.995}Li_{0.005}TaO_3$, KLT, and $Sr_{0.98}Mn_{0.02}TiO_3$, SMnT. The classic ferroelectrics BTO, TGS and PGO display all features of the third order dielectric susceptibility, χ_3 , where $P = \epsilon_0(\chi_1 E + \chi_2 E^2 + \chi_3 E^3 + \dots)$, as predicted by mean-field theory (including the change in sign of χ_3 at the continuous PT). On the other hand, the positive sign of χ_3 measured in relaxors is due to the presence of polar nanoregions. The 3rd order susceptibility of diluted KLT discloses features of a weakly interacting dipolar system, while it hints at a divergence at the dipolar glass temperature in SMnT.

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Nanoscale Insight into Lead-Free Relaxor Ferroelectrics

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In the search for lead-free alternatives for the ubiquitous $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT), the solid solution $(1-x)(0.94\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3-0.06\text{BaTiO}_3)-x\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (BNT-6BT-xKNN) has been demonstrated to exhibit a range of peculiar features that render this material interesting for both science and application with its exceptionally large actuating performance.[1][2] It was shown that the physical mechanism for this high strain took place with a reversible field-induced phase transition between a 'pseudocubic' and an obvious non-cubic phase.[3][4] Later, it was suggested that this 'pseudocubic' phase is an ergodic relaxor that can convert into a ferroelectric phase on the application of electric field. [5] Here we present a comprehensive study by means of piezoresponse force microscopy on a bulk lead-free compositional series BNT-6BT-xKNN with $0\% \leq x \leq 18\%$ to have better insight into the proposed mechanism at nanoscales, relevant to probing relaxor to ferroelectric transitions. It is demonstrated that BNT-6BT ($x=0\%$) is a nonergodic relaxor where domains and ferroelectric switching can be induced for sufficiently high fields. The addition of KNN gradually increases ergodicity and consequently the critical field that is required for the transition into the long-range-ordered state increases notably. When the KNN content is increased to $x=3\%$, the field induced domains become unstable and are prone to a time-dependent relaxation, i.e. the amplitude of the piezoresponse diminishes to virtually zero. For even higher KNN contents, no long range order can be imaged, but on the nanoscale polarization loops are obtained for very high fields. These results offer a new perspective on lead-free relaxor ferroelectrics and they allow for a discussion on the interrelation between macroscopic and nanoscopic material properties.

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Influence of bipolar electric cycling on the macroscopic and structural properties of BNT-based lead-free piezoceramics

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Bismuth-sodium-titanate- barium-titanate (BNT-xBT) compositions close to the morphotropic phase boundary exhibit a transition from a pseudo-cubic structure in the unpoled state to a ferroelectric phase upon application of an electric field. Depending on composition and dopants this ferroelectric phase sustains or vanishes after the electric field is removed. This transition and the general characteristics of these materials can be described as relaxor-like.

In our study we investigated the influence of bipolar electric cycling on the properties of BNT-6(BZ_(1-x)T_x) ceramics (Z is Zr) in order to understand the processes leading to electric fatigue and their relation to the relaxor-like behaviour. In-situ neutron diffraction studies on BNT-6BT showed the expected peak splitting during the first bipolar cycle, related to the transition to the ferroelectric state. The peak splitting becomes stronger during the next few cycles then vanishes again at higher cycle numbers, so that the pattern resembles a cubic structure. The evolution of the macroscopic properties polarization, strain and permittivity with cycle number reflects the transition to the ferroelectric state as well. However, in the cycling region where the peak splitting has already vanished, hysteretic polarization and strain loops are still observed.

The addition of Zr leads to local lattice distortions and presumably to stronger relaxor-like behaviour. With increasing Zr content the samples become more sensitive to electric cycling, passing through the above mentioned regions at lower cycle numbers already.

These results indicate that the relaxor-like characteristics determine the change in properties due to bipolar electric cycling and therefore have to be taken into account when discussing fatigue degradation.

Lead-free composite relaxor ferroelectrics for high strain actuator applications

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Over the last two decades there has been an enormous amount of work focused on the development of lead-free piezoceramics, since environmental and health concerns, underpinned by EU legislation, restrict the use of market-dominating lead-containing piezoceramics. Promising lead-free alternatives for actuator applications are Bi-based piezoceramics with high achievable strains due to a reversible electric-field-induced phase transformation from ergodic relaxor to ferroelectric phase. In these materials relatively high fields of 6 kV/mm have been required to induce this phase transformation and therefore to obtain the desirable property.

A new approach to overcome this drawback is to build up composites, composed of such a large strain ergodic relaxor and small amounts of nonergodic relaxor or ferroelectric material to reduce the field level required to trigger relaxor-to-ferroelectric transition. In this work a series of composites with various ratios of nonergodic BNT-7BT (93 Bi_{0.5}Na_{0.5}TiO₃ - 7 BaTiO₃) and ergodic BNT-6BT-2KNN (92 Bi_{0.5}Na_{0.5}TiO₃ - 6 BaTiO₃ - 2 K_{0.5}Na_{0.5}NbO₃) is presented. The evolution of properties as a function of compositions is studied by electromechanical techniques, such as bipolar and unipolar strain and polarization loops at different fields and temperatures. The depolarization temperature T_d of the composites is determined by measuring thermally stimulated depolarization currents (TSDC). The results reveal that the composite approach provides another degree of freedom in finding a suitable lead-free piezoceramic for actuator applications. The optimum composite for applications at 4 kV/mm consists of 10 % nonergodic and 90 % ergodic relaxor phase, where a normalized strain ($d_{33}^* = S_{\max}/E_{\max}$) of 680 pm/V could be achieved.

We present a phenomenological model using an equivalent circuit model, where we introduced our assumption that the nucleation of ferroelectric domains into the ergodic relaxor phase is aided by interfacial charges from the electrically-induced ferroelectric phase out of nonergodic relaxor phase.

Different Doping Concepts for Nb in BNT and Their Influence on Electric Properties

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Bismuth-alkaline titanates (for example BNT $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ or BKT $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$) are promising candidates to replace lead-zirconate-titanates in certain applications. This compositional system offers good piezoelectric properties and is highly modifiable through doping with alkaline earth and rare earth metals.

In literature, different attempts of doping with iso- and aliovalent metal ions are described. This work focuses on B-site doping of BNT with Niobium. Since Niobium has a higher valence state than Titanium and acts as a donor, two possibilities of compensation may occur. Niobium can replace Titanium stoichiometrically which leads to vacancies on A-sites (either V_A'''' or V_A' depending whether Bi^{3+} or Na^+ leaves the perovskite structure). The second possibility is to replace Titanium preserving charge neutrality by substituting Titanium with only 4/5 Niobium, which favours B-site vacancies in the system.

This work shows the influences of the different doping concepts for Nb in BNT, using common analysis techniques. The microstructure was investigated using SEM, coupled with EDX for elemental analysis. Lattice parameters were analyzed with XRD. Small signal piezoelectric parameters were measured by impedance analysis and a Berlincourt piezometer. Large signal data of polarization and strain were obtained with the aixACCT Piezoelectric Evaluation System.

Waterfall effect in relaxor ferroelectrics

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Waterfall effect [1] is an apparent vertical dispersion that has been observed in low frequency transverse phonon branches in many perovskite materials: from monodomain ferroelectric BaTiO₃ [2] to relaxor ferroelectrics like PMN [3]. One possible scenario how to interpret this effect is a coupling model between transverse acoustic (TA) and soft transverse optic (TO) branches [4].

From inelastic neutron scattering data on monodomain tetragonal BaTiO₃ single crystal [2], it is obvious that the waterfall effect arises from an interaction between the low-frequency E_1 component of the split F_{1u} (TO1) polar mode (of cubic phase) and the TA acoustic mode. One can expect that the waterfall effect can occur in other perovskite materials if they have a low frequency E_1 component of the TO mode.

In relaxors with macroscopically cubic perovskite structure in general, the F_{1u} (TO₁) polar mode splits also because of the low-symmetry local structure. For example in PMN, the F_{1u} mode splits into A_1 and E_1 components below Burns temperature (T_d) as shown recently from Hyper-Raman scattering experiment [5]. In this contribution, we would like to show that knowledge of A_1 and E_1 mode parameters allowed us to use the coupling model for the waterfall effect in PMN relaxor [6]. Then, we will discuss the waterfall effect in the morphotropic NBBT single crystal (see Fig.1) [7] and strong inhomogeneities of both A_1 and E_1 components in NBBT that have been studied by streamline Raman spectroscopy [8].

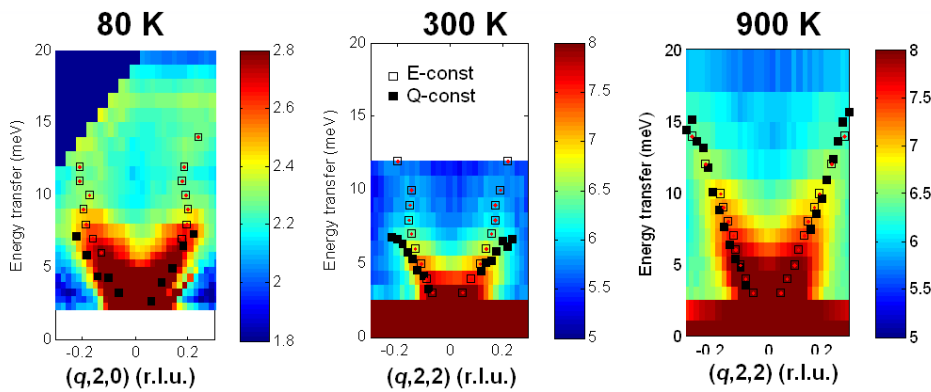


Fig. 1: Phonon dispersions of NBT-4%BT in the (220) and (020) Brillouin zones along the transverse direction at several temperatures. The collected data were independently analyzed as constant-energy scan sets (open squares: positions of Lorentzian bands) and constant-Q scan sets (full squares: frequencies of damped)

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Lone-pair effect in Bismuth Sodium Titanate based ceramics investigated by temperature dependent Raman spectrometry

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The isoelectronic structure of Pb²⁺ and Bi³⁺ encouraged researchers to look at Bismuth based ferroelectrics in order to replace Lead zirconate titanate, because the coupling of the stereochemically active electron pair of Pb²⁺ towards the oxygen ions is considered responsible for the enhanced polarization in this compound. An outbreak of research activities was triggered by revealing an extended strain phenomenon under high electric field that provides sufficient strain for actuator applications. The investigation of structure-property relationships is hampered by a complex succession of phase transitions that are visible in the dielectric response but difficult to connect to structural features by powder diffraction methods due to a more or less pseudo-cubic system with minimal distortions to rhombohedral or tetragonal symmetries.

Using a high resolution Raman spectrometer with a temperature stage and an improved cut-off filter that enabled the measurement of spectra down to a wavenumber of 50 cm⁻¹ we could monitor the Ti-oxygen, the TiO₆-octahedra and the A-site (Bi/K/Na)-oxygen vibrational modes of the lattice as a function of temperature. Using this symmetry and chemically sensitive technique we were able to show that the transition points observed in the temperature dependence of the permittivity are correlated to a change in wavenumber at the A-O modes denoting a weakening of interatomic spring constants. This was accompanied by a symmetry change in the whole unit cell affecting the other modes of the system, too. We explain these phenomena by a weakening of the sp hybridization between Bi³⁺ and oxygen (“lone pair effect”) affecting the dsp-hybridisation between oxygen and Ti⁴⁺. Since these changes occur abruptly we regard this as breaking of a bond leading to a phase transition first from a ferroelectric to an antiferroelectric state with an electrostrictive behavior, which is to a great extent responsible for the extended strains observed.

Ferroelectric and Relaxor aging in acceptor doped (1-x)BNT-xBT

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Aging in acceptor-doped conventional ferroelectrics such as barium titanate or lead zirconate titanate is a well described phenomenon. In literature, it is mainly ascribed to the clamping of domain walls and a resulting suppression of their movement by oriented defect dipoles or space charge regions. A second type of aging occurs in relaxor ferroelectrics. It is related to the rearrangement of polar nanoregions within the energy landscape. Relaxor aging mainly affects the permittivity at the aging temperature which decreases with aging time. This leads to “holes” in the temperature dependent permittivity, which occur at the aging temperature, but does not necessarily effect domain wall motion and hysteretic properties.

Like undoped (1-x)(Bi_{1/2}Na_{1/2})NaTiO₃-xBaTiO₃ (BNT-xBT), acceptor-doped (BNT-xBT) exhibits relaxor properties in the virgin state, but ferroelectric behavior can be induced by poling. Therefore, acceptor-doped BNT-xBT should be susceptible to both aging mechanisms described above, depending on the poling state. To examine the aging of permittivity and large signal polarization, the time dependent behavior of both poled and unpoled BNT-xBT:Fe was studied. In the unpoled material, hole-aging occurs at the aging temperature where the degree of decrease in permittivity depends on aging time. Like in other relaxor materials, only the permittivity in the vicinity of the aging temperature is reduced, while the $\epsilon(T)$ curve at temperatures far away from the aging temperature remains unaffected. In poled material, the polarization hysteresis shifts along the field-axis like in conventional ferroelectrics, but the effect is smaller than that observed for lead zirconate titanate. The results will be discussed with respect to the symmetry of the crystallographic unit cells.

Single crystal relaxor $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3-x\text{BaTiO}_3$: Direction dependence of electrical properties

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Research in lead-free piezoceramics is focused on solid solutions with end members belonging to the perovskite family with different crystal systems in the hope of finding a morphotropic phase boundary (MPB) with properties favorable to applications. This is despite the fact that the physical reasons for the good piezoelectric properties at the MPB are poorly understood in both classical ferroelectrics and relaxors; in fact, it is even not certain if the concept of an MPB can be extended to non-lead-containing systems. For PMN-PT at least, there is some agreement in that the enhancement of the piezoelectric properties at the MPB is connected to the possibility of polarization rotation in rhombohedral systems from the (111)-direction into the (100)-direction. It is unclear whether this approach can be extended to lead-free systems like $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3-x\text{BaTiO}_3$ (BNT-BT), as no equivalent research has been done so far. The picture is further complicated by the relaxor nature of BNT-BT, which allows the existence of nanosized polar clusters of different symmetries in addition to ferroelectric domains with long-range order.

In this work, we determine the electrical properties of BNT-BT single crystals on both the rhombohedral and the tetragonal side of the MPB in different directions with respect to the crystallographic axes. Cuts in both (111) and (100) directions are examined for both symmetries to check whether a rotation of the polarization vector from one symmetry into the other is possible under external electric fields. The crystal structure and quality is checked by XRD. The phase transition behavior is determined in temperature-dependent measurements of the permittivity in the frequency range from 100 Hz to 10 MHz. As polarization rotation will cause drastic changes in domain wall densities depending on the orientation of the crystal axes with respect to the external field, we examine the hysteretic behavior of polarization P , strain S , dielectric coefficient and piezoelectric coefficient d . Finally, the depolarization behavior of differently poled samples is investigated by thermally stimulated discharge current (TSDC) to obtain evidence of a two-step depolarization process that can go along with polarization rotation. The results of the measurements on the single crystals are compared with that obtained from polycrystalline ceramics to further assess crystal quality, estimate the potential benefit of single crystals in applications over polycrystals, and to reveal possible differences in the relaxor behavior.

Electric field and mechanical stress induced strains, domain switching, and phase transformations in $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-(x)\text{BaTiO}_3$

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Piezoelectric materials are used in many applications due to their ability to strain when an electric field is applied to them, and generate charge displacement when mechanically stressed. Because piezoelectrics are used in both these capacities, it is important to study their response to both electric fields and mechanical stresses. The lead-free piezoelectric material system $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-(x)\text{BaTiO}_3$ (NBT-xBT) is currently being heavily researched as a replacement for Pb-containing commercial piezoelectrics. NBT-xBT exhibits a morphotropic phase boundary (MPB) near 6-7% BT with superior mechanical properties, and this work examines the response to electric fields and mechanical stresses of bulk polycrystalline samples with selected compositions spanning the MPB [1].

In situ neutron diffraction experiments were conducted separately with applied mechanical stresses and electric fields at the instruments VULCAN at the Spallation Neutron Source at Oak Ridge National Laboratory in Oak Ridge, Tennessee and WOMBAT at the Australian Nuclear Science and Technology Organisation in Lucas Heights, Australia, respectively. Lattice strains and domain switching were quantified by fitting selected Bragg reflections with Gaussian profiles. Highlighted results from the mechanical loading experiment include determination of the elastic stiffness anisotropy for each composition, which supports the existence of a monoclinic phase at low BT content [2], a rhombohedral phase at the MPB, and a tetragonal phase at high BT content. From the electrical loading experiment, we determined the extent to which MPB compositions develop mixed rhombohedral and tetragonal phases from a pseudo-cubic phase during static and cyclic electric field loading.

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Relaxor Behavior and Phase Transitions in Bi(Zn_{1/2}Ti_{1/2})O₃ Solid Solutions

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While Bi(Zn_{1/2}Ti_{1/2})O₃ (BZT) is not stable under normal atmospheres and pressures, recent work has shown that BZT can form solid solutions with a large number of stable perovskites such as PbTiO₃ [1], BaTiO₃ [2-3], NaNbO₃ [4], and (Bi_{1/2}Na_{1/2})TiO₃ [5-6]. The addition of Bi(Zn_{1/2}Ti_{1/2})O₃ has a profound impact on the dielectric properties and symmetry of the perovskite structure. A number of different systems have been explored including BZT-BaTiO₃, BZT-NaNbO₃, and BZT-(Bi,K,Na)TiO₃. Typically these systems exhibit limited solubility with pseudo-cubic symmetry at BZT concentrations greater than 10 mol% as well as a diffuse phase transition in the vicinity of room temperature.

For example, in the Bi(Zn_{1/2}Ti_{1/2})O₃-BaTiO₃ system the Curie temperature decreased with a small addition of BZT along with a shift from a first-order phase transition to a diffuse phase transition. Above approximately 9 mol% BZT the dielectric maximum remained constant at approximately 10-30°C. This was also apparent in the polarization data, where compositions with less than 5 mol% of BZT exhibited loops characteristic of ferroelectric behavior gradually transitioned into narrow loops with minimal saturation at relatively high fields. Structural data on these compositions show a smooth transition between tetragonal symmetry to cubic symmetry over this same range in composition. The relaxor characteristics seen in this solid solution and many similar compounds are likely due to the chemical disorder introduced through the addition of Bi³⁺ onto the A-sublattice and Zn²⁺ onto the B-sublattice of the perovskite structure.

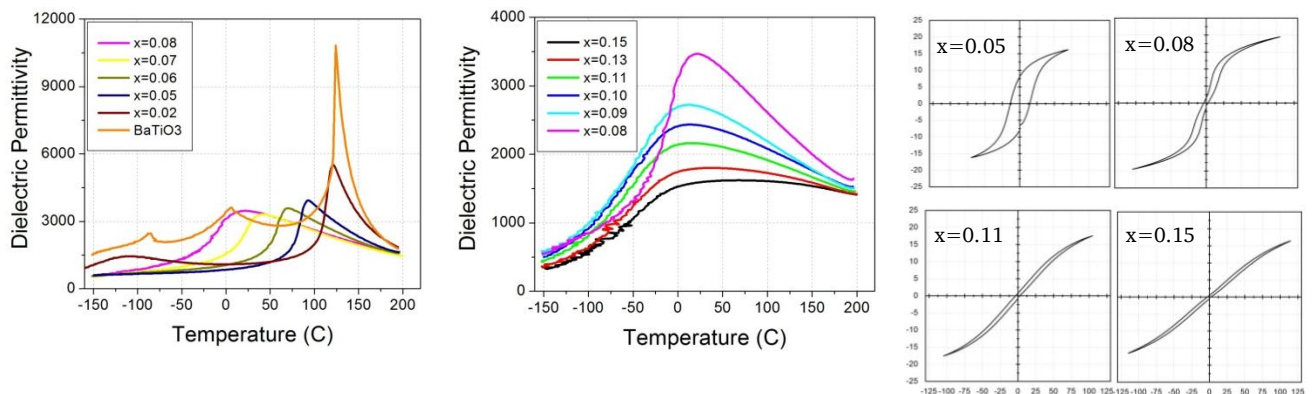


Fig. 1. Dielectric spectra and polarization hysteresis data for $x\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-(1-x)\text{BaTiO}_3$

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Low temperature processing and high performing of $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$ and $0.57\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{--}0.43\text{PbTiO}_3$ relaxor-ferroelectric ceramics

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The relaxor-ferroelectric ceramics, such as $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{--PbTiO}_3$ (PSN–PT), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PMN–PT) or $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PZN–PT) with a composition near to the morphotropic phase boundary (MPB), exhibit a high dielectric constant and excellent piezoelectric properties, and are suitable for applications in actuators, sensors and capacitive devices. The PMN–PT and PZN–PT ceramics possess relatively low Curie temperature T_c (around 170 °C for PMN–PT and 180 °C for PZN–PT at MPB), which may greatly limit their usefulness in many fields, where a broad operating-temperature range is required. However, the PSN–PT material with a composition near to the MPB, i.e., 0.57PSN–0.43PT, possess around 100 °C higher T_c and is therefore an attractive choice for applications at higher temperatures. On the other hand, the $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PSN) is also interesting composition. PSN is a relaxor, which spontaneously transform into the ferroelectric phase as reported in [1].

Stoichiometric PSN and 0.57PSN–0.43PT ceramics were prepared from a mechanochemically activated powder. The ceramics was sintered at 1000 °C, which is 200–400 °C lower than the previously reported data for the sintering temperature of PSN and PSN–PT ceramics. By sintering of ceramics at 1000 °C we were able to obtain PSN and PSN–PT ceramics with 97 % of theoretical density.

The dielectric, ferroelectric and piezoelectric properties of PSN and 0.57PSN–0.43PT ceramics were studied. The properties of 0.57PSN–0.43PT ceramics are comparable or even higher than properties of doped 0.57PSN–0.43PT ceramics, while in the literature it was proposed that the doping of PSN–PT ceramics with niobium enhances the electrical properties. The dielectric permittivity of 0.57PSN–0.43PT at kHz is 2200. The remnant polarization P_r , piezoelectric coefficient d_{33} and coupling coefficients k_p and k_t of ceramics prepared from mechanochemically activated powder are 43 C/cm², 570 pC/N, 0.71 and 0.56, respectively [2].

The dielectric permittivity of PSN ceramics at 1 kHz is 1200. The high temperature phase transition occurs at 102 °C. The PSN material at room temperature shows ferroelectric behaviour, it shows the hysteresis loop with remnant polarization P_r of 30 C/cm². Further, the piezoelectric properties of PSN ceramics were studied for the first time. The direct and inverse piezoelectric responses of the PSN ceramics were measured and the poling conditions of PSN ceramics were studied. The piezoelectric coefficient d_{33} of PSN ceramics poled by electric field of 4 kV/mm at 75 °C for 5 min and field-cooled to 25 °C and measured by piezometer is 80 pC/N. Also the coupling coefficients k_p and k_t of ceramics were determined, being 0.15 and 0.32, respectively.

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Lead-free relaxor ferroelectric $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$: On the stability and ferroic properties of chemically ordered nanoregions

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$\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ (NBT) is a model relaxor ferroelectric with a complex perovskite structure having two different cations on the A-site. Similarly to $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) or $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PSN), both relaxor ingredients are present, i.e. off-centering (Bi^{3+} for NBT and Pb^{2+} for PMN or PSN) and random cation distribution on the mixed cationic site. In addition, like in PMN- or PSN-based solid solutions, NBT-based materials show extraordinarily high strains and are thus promising environmentally friendly alternatives to the lead-containing standard piezoelectric materials.

In addition to the relaxor behavior NBT displays a complex temperature phase sequence. Despite intensive research effort, there are still open questions concerning the existence of chemical order, intermediate phases, lower-symmetry phases, etc. [1] The chemical order is of great interest as it might strongly affect the polar displacements and thus the local symmetry and it is believed to be the origin of the so-called polar nanoregions (PNRs) i.e. the key component of relaxor behavior.

In order to get more insights into these complex structural features, we used Density Functional Theory calculations to investigate the tendency for chemical ordering and its consequences on the local structure. Moreover, we studied phase stabilities depending on hydrostatic pressure and how polar and rotational modes as well as chemically induced displacive modes evolve under compressive and tensile conditions.

Our results support the existence of local chemical order and are in good agreement with an earlier experimental report showing {001}-like diffuse scattering [2]. We show that both local and average structures in NBT arise from a delicate balance between octahedral tilting, ferroelectric distortions and chemically induced ionic displacements depending on the local A-site configuration. Surprisingly, at zero pressure we find a mixed-phase state to be most stable, which consists of a chemically disordered matrix with an $R3c$ -like average structure and {001}-chemically ordered nanoregions possessing a $Pbnm$ -like average structure, which in fact are polar with considerable spontaneous polarizations comparable to that found for the $R3c$ -like structures.

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