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Evidence of local anisotropic strains in relaxor ferroelectrics below intermediate temperature T^* detected by acoustic emission

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Abstract
Oriented {100}-, {110}-, and {111}-cuts of $Pb_{0.78}Ba_{0.22}Sc_{0.5}Ta_{0.5}O_3$ single crystals have been studied by means of the acoustic emission (AE) method during their thermal cycling in the temperature range of 300–600 K. For all crystal orientations pronounced AE signals have been detected near 490 K, which corresponds to the intermediate temperature T^*. However, the highest AE count rate has been detected from {110}-oriented cuts, revealing strong anisotropic coupling between the existing polar species that at T^* merge into larger regions of polarization (PNRs). The temperature's hysteresis is revealed to be 15 K, indicating that the transformation processes at T^* can be considered as local Martensitic-like ferroelectric transitions inside PNRs. The interplay between PNRs and ultrahigh local strains of perovskite-type relaxor ferroelectrics is discussed.

Relaxors and relaxor-based ferroelectrics exhibit fascinating dielectric, electromechanical and optoelectrical properties, due to the presence of nanometre-scale regions of polarization, also called polar nanoregions (PNRs), embedded within a non-polar cubic matrix. PNRs nucleate at the Burns temperature T_d, which is usually above 600 K [1]. Below T_d and above a maximum of the dielectric permittivity maximum the PNRs flip between possible orientation states, resulting in mobile dipole moments. On cooling, the dynamics of PNRs slows down and freezes at T_f, which is usually below 200 K, leading to a nonergodic state [1]. Neutron scattering experiments on $PbZn_{1/3}Nb_{2/3}O_3 - xPbTiO_3$ (PZN–xPT) crystals suggested that between T_d and T_f there exits another characteristic temperature T^* associated with structural transformations of PNRs [2]. Further x-ray diffraction (XRD), infrared spectroscopic, Raman spectroscopic and acoustic emission (AE) studies on other compounds revealed that the intermediate temperature T^* is a general feature of all perovskite-type relaxor and relaxor-related ferroelectrics [3–7]. The local structural transformations that occur at T^* reflect the temperature evolution of phonon peaks associated with the existing polar species, while the response of the average structure leads to a kink in the temperature dependence of the pseudocubic unit-cell volume and a strong AE signal. In contrast to T_d, T^* turns out to be steady enough, lying in a relatively narrow range near 500 K for a large number of compounds, whereas T_d is found to vary between ∼620 and ∼740 K [7].

The exact structural features of PNRs are still not clarified. Recent molecular dynamic simulations based on a simple consideration of individual B-site cation pairs indicate that at T_d the ferroelectrically active B-site cations within a few unit cells group to form clusters of slowly responding dipole moments [8]. According to this theoretical study, B-site

chemical inhomogeneity on the long-range scale, as well as correlation between PNRs, is not necessary to give rise to the relaxor behaviour. On the other hand, temperature dependent phonon inelastic and diffraction analyses indicate that below T^* PNRs strongly correlate and are of rhombohedral type [9–11], i.e. PNRs undergo a rhombohedral-like structural transformation and become monopolarized as well. The rhombohedral distortions give rise to a steep increase in the elastic diffuse neutron scattering at T^*. Neutron diffuse scattering results indicate that PNRs in pure PZN have an ellipsoidal form extended along the cubic $\langle 111 \rangle$ direction, which is consistent with their rhombohedral polarization [2] and is in agreement with the conclusions drawn on the basis of Brillouin spectroscopy [9]. In contrast, in mixed PZN–xPT ($x = 0.45$ and 0.9) PNRs are extended within the cubic {001}–{110} planes, whereas the polarization persists along the cubic $\langle 111 \rangle$ direction [2]. The latter conclusion was however refuted by high-energy x-ray diffuse scattering experiments on PZN–xPT ($x = 0.45$ and 0.8) crystals, which clearly showed that PNRs persist with a $\langle 111 \rangle$-oriented polarization independently of the content x [12].

Local structural transformations inside PNRs and/or reorientation of PNRs should induce large mechanical stresses on the boundaries between the rhombohedral PNRs and the surrounding paraelectric cubic crystal matrix. These stresses are released in the form of an acoustic emission (AE), usually accompanying structural ferroelectric phase transitions [13]. This explains the fact that AE has repeatedly been detected in the range of $T^* \sim 500$ K for a great diversity of relaxor single crystals and ceramics, e.g., $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and PZN [7]; PZN–xPT, $x = 0.45, 0.6, 0.7, 0.9$ and 0.12, [4, 14]; and $PbFe_{2/3}W_{1/3}O_3$–xPbTiO$_3$ (PFW-xPT), $x = 0, 0.25$ and 0.37 [15]. In addition, AE is known to be controlled by processes of reorientation and reshaping of domains and is therefore highly susceptible to the crystallographic orientation of the material [16]. For example, in the case of formation of rhombohedral PNRs elongated or flattened along the cubic body diagonal directions, one would expect the accompanying AE to have the highest count rate along the cubic $\langle 111 \rangle$ direction.

The objective of the current letter is to study the AE response near T^* along different crystallographic directions. We have chosen $Pb_{0.78}Ba_{0.22}Sc_{0.5}Ta_{0.5}O_3$ (PBST) as a model compound because it remains cubic, according to XRD, down to 10 K, i.e. it is a canonical relaxor. Hence, the AE signals are expected to be entirely related to the polar nanoregions and not masked by the possible coexistence of long-range ordered ferroelectric domains of various symmetry, as is the case for mixed relaxor–normal ferroelectric crystals. PBST has not been studied by AE so far, but, according to a combined Raman scattering and x-ray diffraction analysis, exhibit $T^* \sim$ 490 K [5]. The performed anisotropic AE measurements reported here clearly demonstrate that the coupling between initially nucleated small polar clusters is strongly anisotropic.

Cubic-shaped single crystals of PBST were synthesized by the high-temperature solution growth method [17]. For AE experiments plate-like oriented specimens parallel to the cubic crystallographic {100}, {110}, and {111} planes were cut
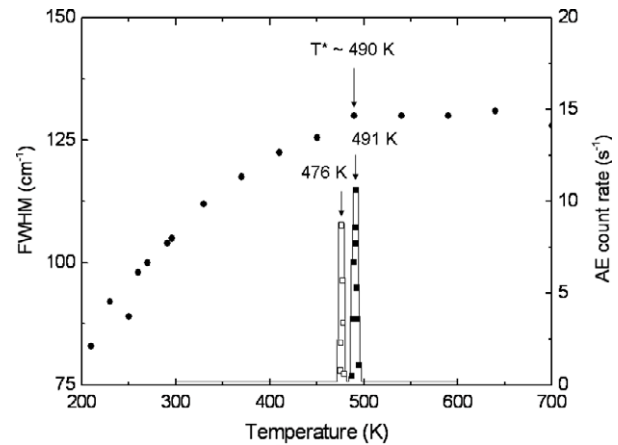

Figure 1. Temperature dependence of the full-width at half-maximum (FWHM) of the Raman peak near 245 cm^{-1} (filled circles), which arises from B-cation localized phonon modes in polar clusters [13], and the acoustic emission from {110}-oriented cuts measured on cooling (open squares) and on heating (filled squares).

from a single boule by a diamond wire saw. To eliminate any possible artificial influence of factors such as differences in the size and mass of the samples on the AE count rate, special care was taken to prepare cuts free of cracks and of approximately the same size, 2.0 mm × 2.0 mm × 0.8 mm, as the variation in the thickness from a sample to sample was of order of 10 μm. The AE technique is described in great detail elsewhere [14]. Each specimen was pasted with a heat conducting silicon fluid to the polished side of a fused silica acoustic rod waveguide. A PZT-19 disc piezoelectric sensor favourable for receiving longitudinal acoustic waves was attached to the rear end of the waveguide. The use of such a sensor helps to avoid the contribution of scattered AE waves and assures that only AE signals perpendicular to the surface of the sample are detected. The sensor was electrically coupled to a 500 kHz band-pass low noise variable (up to 40 db) preamplifier connected to a detector-amplifier (40 db). A CH–AL thermocouple junction was glued to the waveguide near the sample. The higher part of the acoustic waveguide with the pasted sample was mounted in a resistance element tube furnace. Both thermocouple and amplifier outputs were interfaced with a PC for a coupled readout. AE count rate $\dot{N}$ (dN/dt, s^{-1}) measurements were performed from 300 up to 600 K during the thermal cycling with an average heating/cooling rate of about 1–3 K min^{-1}. The AE count rate gives excellent information on moving objects such as the PNRs' (domain) walls. The repeatability of the results was verified on several cuts, and the magnitude of the heating/cooling rate was found to have a negligible effects on the results.

All crystal samples radiate sharp AE bursts at 491 K on heating and 476 K on cooling, which corresponds very well to the T^*-value determined by polarized Raman spectroscopy [5] (see figure 1). It should be underlined that AE experiments allow for a much better precision in the determination of the actual magnitude of T^*, while Raman spectroscopy can reveal the atomistic origin of T^*. A thorough analysis of the Raman spectra of several model relaxor compounds

revealed that the Raman peak near 245 cm^{-1} is related to the cubic triple degenerate infrared active mode F$_{1u}$ involving B-cation motion [5]. Hence, the paraelectric matrix does not contribute to the Raman scattering near 245 cm^{-1} and this Raman signal is strictly associated with off-centre displacements of B-cations in polar nanoregions. Thus, the structural heterogeneity (coexistence of cubic and rhombohedral symmetry) has no significance on the width of the Raman peak near 245 cm^{-1}, the temperature evolution of which is predominantly determined by the structural transformation of polar nanoregions comprising B-cation off-centre displacements. The excellent agreement between T^*, as determined from AE and from the temperature dependence of the full-width at half-maximum (FWHM) of the Raman peak arising from off-centre octahedral cation shifts, confirms that T^* is related to coupling of off-centred cation-oxygen octahedra between adjacent small polar sub-clusters (embryos that occur at T_d), which merge to form larger nanoregions possessing polarization PNRs [5, 18]. The temperature hysteresis determined from AE experiments on PBST is 15 K, which is typical of a Martensite-like ferroelectric phase transition in normal ferroelectrics [13]. The similarity between Martensite phase transitions in metals and phase transitions in ferroelectrics, as well as the mechanism of formation of a Martensite-like domain structure in ferroelectrics, were previously discussed in [19]. The phase transition-related stresses relax by breaking up the ferroelectric embryos into head-to-tail arranged 90°-domain-twins. Such a Martensite-like domain structure was observed in BaTiO$_3$ crystals from a phase transition accompanied by AE [20]. Ferroelectric twin domains were also observed in PbTiO$_3$ crystals, and the first order phase transition was accompanied by an AE hysteresis resembling that of a Martensite transition [13]. Similar hysteresis dependencies of AE were observed in PbZrO$_3$ and PbHfO$_3$ crystals through their first order Martensite-like phase transitions [13]. Therefore, our results on PBST once again confirm the previously proposed model that the structural transformations occurring at T^* can be considered as local Martensite-like ferroic phase transitions inside PNRs, which in turn are embedded in a non-ferroic matrix [14].

The $\dot{N}$ values were found to be essentially different depending on the sample orientation (see table 1). Our findings clearly show that the AE rate accompanying T^* indeed depends on the crystallographic orientation. Surprisingly, the highest $\dot{N}$ values have been detected from ⟨110⟩-oriented single-crystal cuts instead from ⟨111⟩-oriented ones, as one would expect for rhombohedral-like PNRs elongated or flattened along the cubic body diagonal. This fact can be explained by assuming that the predominant orientation of the PNRs coincides with the orientation of the studied single-crystal specimen. Consequently, one can conclude that below T^* the PNRs are mainly shaped in such a way that the orientation of the interface between the PNRs and the surrounding cubic matrix is predominantly parallel to the cubic {110} crystallographic planes. Due to the specific shape of the polar species that couple at T^*, the motion and merging of the interface boundaries is along the cubic ⟨110⟩ directions and, hence, the strongest release of elastic energy is also along

Table 1. Acoustic emission count rate measured on cooling and heating from differently oriented single-crystal specimens.

Pb$_{0.78}$Ba$_{0.22}$Sc$_{0.5}$Ta$_{0.5}$O$_3$ Direction	AE count rate (s^{-1})	
	Cooling	Heating
[100]	2.4	5.2
[110]	13.7	15.6
[111]	5.3	8.1

this direction. Such a scenario is in good agreement with the observed x-ray diffuse scattering streaks along the ⟨110⟩* reciprocal space direction for PBST [5]. Diffuse scattering streaks are typical of a large number of Pb-based relaxors, and two theoretical models have been developed to explain these streaks [21, 22]. Both models clearly indicate that the diffuse scattering is due to the existence of PNRs and, in particular, due to off-centred cation displacements that correlate within the {110} planes of the real space, without clearly specifying the energetically favourable direction of the cation displacements themselves. Paściak *et al* proposed that PNRs are isotropic and three-dimensional but with domain walls parallel to the cubic {110} planes [21], whereas Welberry and Goossens argued that PNRs are anisotropic and relatively thin, with their boundaries parallel to {110} planes [22]. Despite the shape of the PNRs, both theoretical models reveal that the predominant orientation of the interface between the PNRs and the surrounding non-polar matrix is parallel to the {110} planes, which strongly supports the suggestion that the transformation processes at T^* involve the motion of polar–cubic interface boundaries, similar to the domain wall motion in normal ferroelectrics. The structure of PNRs below T^* most probably resembles that of the low-temperature phase of relaxors which develop ferroelectric long-range order, i.e., it is rhombohedral-like. However, above T^* there might be a variety of sub-PNRs, comprising cation off-centre displacements along ⟨100⟩, ⟨110⟩, or ⟨111⟩, i.e., tetragonal-, orthorhombic-, or rhombohedral-like polar species. Their reorientation and alignment to form rhombohedral-like PNRs with permanently ⟨110⟩-oriented boundaries induce ultrahigh local strains in the overall structure. Therefore, the interface between polar and non-polar spatial regions contains the highest dislocation density, which is known to be the main source of AE [23], and hence the specific shaping of PNRs is responsible for the highest $\dot{N}$ count rate along the pseudocubic ⟨110⟩ direction at T^*.

Recently, using neutron inelastic scattering, a strong coupling between the PNRs and TA phonons polarized along ⟨110⟩ directions was discovered in PZN–0.45PT crystals at 200 K. Since PNRs can scatter only phonons having a parallel polarization, it was concluded that the lattice of the bulk remains virtually cubic, having only a slight rhombohedral distortion, but the material appears 'softer' along the ⟨110⟩ directions owing to the effects of the PNRs [24]. The theoretical treatments devoted to dipolar/strain fluctuations in perovskite relaxors [25] have unambiguously demonstrated that instability of TA mode with nanometre-scale modulation ($q \sim 0.1$ Å^{-1}) takes place prior the instability of the uniform optical mode, producing a static heterogeneous structure

concerning polarization as well as shear strain. For pure PMN the most probable direction of modulation was determined to be $\langle 110 \rangle$. This suggests that the intrinsic origin of the heterogeneity in relaxors is the distribution of $\langle 110 \rangle$-shaped PNRs.

In summary, it has been established that AE accompanying the intermediate temperature T^* of $Pb_{0.78}Ba_{0.22}Sc_{0.5}Ta_{0.5}O_3$ single crystals exhibits the highest count rate from {110}-oriented samples. The strong anisotropy of the AE rate indicates anisotropic coupling between the incipient ferroic species that occur at the Burns temperature and further merge in larger nanoregions of polarization at T^*. The reorientation and self-alignment of the initial polar sub-clusters to form large PNRs is realized via motion of the interface boundaries along the $\langle 110 \rangle$ directions, resulting in ultrahigh local strains. In solid solutions of relaxors and normal ferroelectrics such as PZN–PT and PMT-PT these intrinsic ultrahigh local stains are additionally enhanced by the higher chemical disorder on the B-site, causing a giant piezoelectric response.

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