

Ferroelectric precursor behavior of highly cation-ordered $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ detected by acoustic emission: tweed and polar nanoregions

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Highly cation-ordered, ferroelectric $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (PST) crystals have been studied by acoustic emission over a wide temperature range. The high degree of order leads to a non-dispersive dielectric anomaly at $T_{\text{trans}} = 300$ K of a weakly first order phase transition. Acoustic emission (AE) was found at three characteristic temperatures, 330 K, 409 K and ~ 600 K, but none between these temperatures. These temperatures are close to those known from cation-disordered relaxor PST, containing polar nano regions (PNRs). The microstructure in our ferroelectric PST contains structural tweed rather than PNRs. The coincidence of the AE temperatures points towards a close structural relationship between PNRs and tweed. Furthermore, when electric fields are applied, we observe shifts of these temperatures which are similar to ‘critical end point’ behavior. The similarity of AE signals in relaxors and tweed ferroelectrics proves that AE detects signals in a wider parameter space than previously expected.

Random fields and local phase transitions are commonly evoked when symmetry changes in heterogeneous systems. While some models predict a well-defined transition behavior, such as the spherical random-bond-random-field (SRBRF),^{1,2} where the system transforms at a well-defined temperature from a paraelectric phase to a spherical glass phase without long range order. Other approaches predict smeared cross-overs such as Vugmeister and Rabitz,³ and the traditional composition fluctuations model,⁴ and the super-paraelectric model by Cross.⁵ In none of these cases would a classic criticality analysis in terms of Wilson exponents of single thermodynamic order parameters be applicable. Experimentally, smeared crossovers are indeed seen in relaxor ferroelectrics (RFEs). These are materials with wide frequency dispersions of the dielectric response in the transition region. In addition, the transition between a paraelectric and a ferroelectric phase is not only smeared but also split into a number of other singularities which are commonly ascribed to the existence and temperature evolution of polar nanosized regions (PNRs),^{6,7} The structural properties of PNRs are still not fully understood with few studies focused on atomic-level correlation effects between PNRs.⁸

Smooth crossover near the Burns temperature T_d at high temperature range is seen in RFEs by the temperature evolution of the refractive index,^{9–11} dielectrics and Brillouin light scattering,^{12–19} polarized Raman spectra,^{20,21} thermal expansion,^{22–24} and acoustic emission (AE).^{25–29} Similar behavior is found near the intermediate temperature T^* .^{12–21,30–35} On further cooling, a smeared frequency dependent temperature maximum of the dielectric response occurs near T_m and, slightly below T_m the freezing occurs at the freezing temperature T_f , similar to polar-glass phases.^{36–39}

In contrast to these observations, one finds that AE studies^{12–19,22,23,25–30} show extremely sharp singularities at T_d and T^* , which is sometimes related to changes of the thermal expansion.⁴⁰ While this behavior is unlikely when the anomaly is close to the Widom line and far away from the transition point,⁴¹ we will also show in this paper that AE persists even without any changes in thermal expansion. Another common property of AE spectroscopy is that the AE signals are usually related to avalanche ‘crackling’ noise,^{42,43} but AE signals in ordered PST seem not to follow the predicted statistical power law distribution. Computer simulation of AE, on the other hand, has shown that even smooth processes can lead to discontinuous (jerky) AE signals when, e.g., a cluster of nano-domains collapses at conditions far from equilibrium,⁴⁴ while repeating the AE experiments should lead to a broad probability distribution. Such features have not been reported for RFEs.

We will show in this paper that an even more surprising feature occurs when a relaxor PST sample is annealed so that a classic ferroelectric phase transition replaces the relaxor transition. The transition is now sharp with no frequency dispersion of the dielectric response,⁴⁵ Previous studies using transmission electron microscopy have shown that structural modulations and complex strain pattern exist in all PST samples examined, independent of their degree of order.^{46–49} These structural modulations are related to the relaxor behavior in disordered PST as PNRs. Structural modulations in ferroelectric PST also break the cubic symmetry at $T > T_{\text{trans}}$ so that polar behavior is observed in the nominally cubic phase. No relaxor behavior is now observed so that we call these structural modulations ‘tweed’^{50–54} to distinguish them from the relaxor related PNRs. Such ‘tweed’ precursor structures are already known for paraelectric

BaTiO₃ where local symmetry breaking equally leads to the appearance of polarity and elastic softening.⁵⁵ In analogy with BaTiO₃ we might have expected AE signals in ferroelectric PST only to indicate the phase transition at T_{trans} and the onset of the precursor tweed formation,^{50,53} at higher temperatures. This is not the case, however, and we still observe AE signals in ferroelectric PST near the corresponding temperatures of relaxor PST. This result shows that AE is not restricted to relaxor materials (and is hence not a fingerprint for polar nano-regions) but has wider applicability and lower specificity with respect to tweed structures.

We use highly ordered PbSc_{0.5}Ta_{0.5}O₃ (PST) for our experiment and contrast these results with those of disordered material with the same chemical composition. PST with $s = 65\%$ (PST-65 for short) cation order has been studied using dielectric, x-ray and resonant piezoelectric spectroscopy (RPS).⁴⁵ The dielectric constant ϵ exhibits a sharp, frequency independent maximum at the phase transition point at $T_{\text{trans}} = 300$ K. Thermal expansion of the lattice constant a , derived from x-ray diffraction, is constant between 700 K and 425 K in contrast with disordered PST.²³ Below 425 K the thermal expansion increases when tweed precursor ordering of the ferroelectric transition commences.⁴⁵ In the precursor regime the sample is locally polar similar to other ferroelectric materials like BaTiO₃,⁵⁵ as well as alloys and ferroelastics.^{51,52}

Disordered PST is a RFE undergoing a spontaneous cubic-to-rhombohedral ($Pm\bar{3}m$ to $R\bar{3}$) phase transition at Curie temperature T_c just below T_m .⁵⁶ T_m shifts to higher temperatures as the dielectric frequencies increase.^{36,57} When the ordering of Sc/Ta cations increases, in addition to the enlargement of the unit cell from $Pm\bar{3}m$ to $Fm\bar{3}m$, the peak shape near T_m becomes sharper and frequency independent,³⁶ and the relaxor to ferroelectric crossover occurs with $T_m \approx T_c$.⁵⁸ In addition, an incommensurate phase near T_m was claimed for highly B-site ordered ($s > 85\%$) single crystals of PST by transmission electron microscopy. This phase coincides within the paraelectric and ferroelectric phases and demonstrates the non-equilibrium nature of disordered PST. The field dependence of $T_c = 261$ K, the incommensurate transition temperature $T_n = 293$ K,⁵⁷ and $T^* = 450$ K,³³ were previously measured by AE for disordered PST-8. T_c increases monotonically in agreement with small-angle light scattering data.⁵⁹ T^* increases linearly, but the T_n changes non-linearly.⁵⁷ Similar to T_m in RFEs,^{27,28,60-62} in disordered PST T_n initially decreases and then reaches a minimum at $E_{\text{th}} = 0.125$ kV/cm, and then increases.⁵⁷

Details of the AE technique employed in this study were described before.²⁶ The PST samples⁴⁵ with the sizes of $4 \times 5 \times 1$ mm³ were coated with fired silver contacts and pasted with a silver epoxy onto the polished side of a fused silica acoustic rod waveguide. A PZT-19 disk piezoelectric sensor was attached to the rear end of the waveguide. 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 Cr-Al thermocouple junction was glued to the waveguide near the crystal. The acoustic waveguide with the sample pasted was vertically mounted from below into the tube resistance furnace. Both the thermocouple and detector-amplifier outputs were interfaced with a PC for readout. The silver contacts of the crystal were connected to a high voltage power supply. Temperature dependences of the AE count rate \dot{N} (dN/dT , s⁻¹) were measured at several fixed values of bias voltage upon heating from 300 to 700 K with rate of about 1 K/min.

Fig. 1 shows the temperature evolution of the AE count rate of PST-65, combined with the lattice parameter a , previously obtained for the same crystal.⁴⁵ AE exhibits three peaks: at 330 K, at 409 K and around 592-602 K. The peak at 330 K with $\dot{N} = 4.9$ s⁻¹ appears 30 K above $T_{\text{trans}} = 300$ K.⁴⁵ In disordered PST-8 T_n was observed 32 K above the equivalent T_c ,⁶³ so that these two features can be correlated. A second peak at 409 K with $\dot{N} = 7.0$ s⁻¹ is 16 K below the onset temperature of tweed structure at 425 K.⁴⁵ A similar peak exists in more disordered PST (with unspecified degree of order) at $T^* = 500$ K together with a break in thermal expansion.²³ This temperature is called T_{tw}^* . A third peak near 600 K with $\dot{N} = 1.8$ s⁻¹ is equivalent to T_d where polar nanostructures first appear. In disordered PST a break of the thermal expansion occurs near this temperature but not in ordered PST. Nevertheless the AE signals are seen, the temperature is then called T_d^{pn} to emphasize the correspondence with the relaxor temperature T_d . The AE of T_d is slightly smeared over a finite range of T in contrast with the sharp peak at T^* , and also provides a smaller \dot{N} compared with the \dot{N} of T^* .²⁹ We have not endeavored to explore the history dependence of the AE signals.

We now report the field dependence of all characteristic

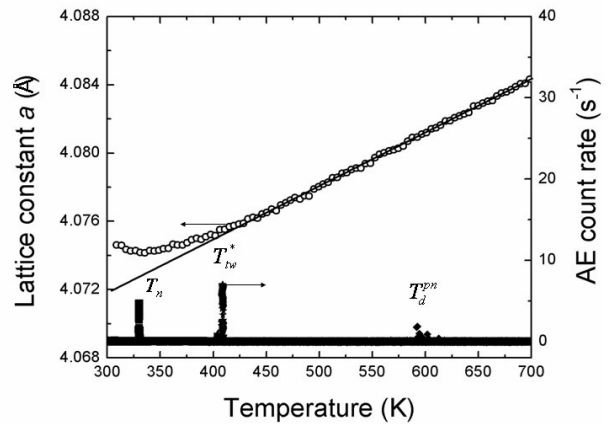


FIG. 1. Plot of of the temperature evolution of the pseudocubic lattice parameter a (Ref. 45) and AE count rate \dot{N} (right axis) when dc electric field $E = 0$.

temperatures, T_n , T_{tw}^* , and T_d^{pn} , detected by AE. Fig. 2 shows AE count rates data as functions of T and E . All the temperatures are influenced by E . T_n and T_{tw}^* exhibit the characteristic minimum at $E_{th} = 0.3$ kV/cm similar to those previously observed in other RFEs.^{27,28,60–62} T_d^{pn} exhibits the non-linear behavior with an anomaly near the same electric field, $E_{th} = 0.3$ kV/cm, but without any minimum: it monotonically increases and saturates for $E > E_{th}$.

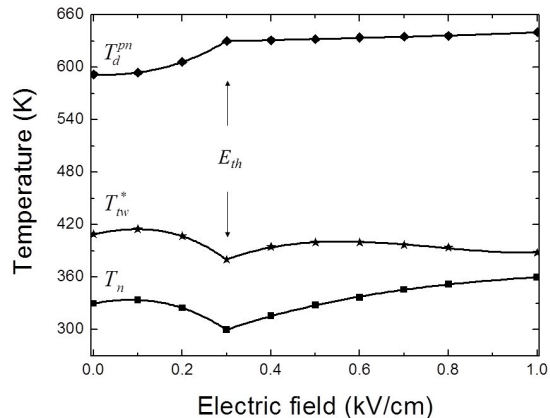


FIG. 2. Plots of the MAFE-PE phase transition temperature T_n , intermediate temperature T_{tw}^* , and Burns temperature T_d^{pn} , detected by AE, in dependence on dc electric field E .

The count rate \dot{N} at T_n depends strongly on the applied field E (Fig. 3). \dot{N} exhibits a pronounced maximum at 0.4 kV/cm, slightly above E_{th} in reasonable agreement with previous observations.^{27,28,61,62} At this point a ‘giant’ piezoelectric response has been postulated,^{41,64,65} and thus this maximum may relate to a critical end point (CEP) in the $E - T$ phase diagrams of RFEs.^{41,64}

In this scenario the $T_n(E)$ curve consists of two segments where fields $E < 0.3$ kV/cm are insufficient to break the internal random polarity of the tweed structures, while fields $E > 0.3$ kV/cm generate fully polarized tweed. These two phases have different transition temperatures $T_n(E)$ and hence generate a phase diagram with a singularity where the two phase transition temperatures coincide. We denote this point by T_n^{\max} and note that, based on our available experimental data, it remains impossible to distinguish between the various models for the origin of this singularity. Nevertheless, the close similarity of T_n^{\max} in highly ordered PST-65 and the same effect near morphotropic boundaries make us speculate that the ‘critical end point’ structure plays a similar role as the interplay of orthorhombic and monoclinic phases near the morphotropic phase boundary,^{53,54,66,67} and hence increases the AE signature.

Fig. 4 shows the behavior of characteristic temperatures of PST samples with very different degrees of cation order. These temperatures typically fall into four groups

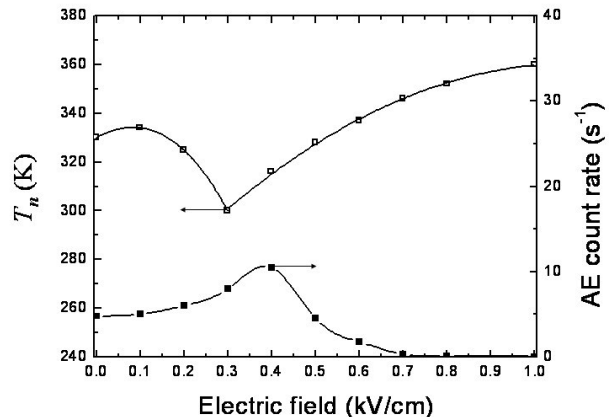


FIG. 3. Plot of the MAFE-PE phase transition temperature T_n detected by AE (left axis) and AE count rate \dot{N} in dependence on dc electric field E .

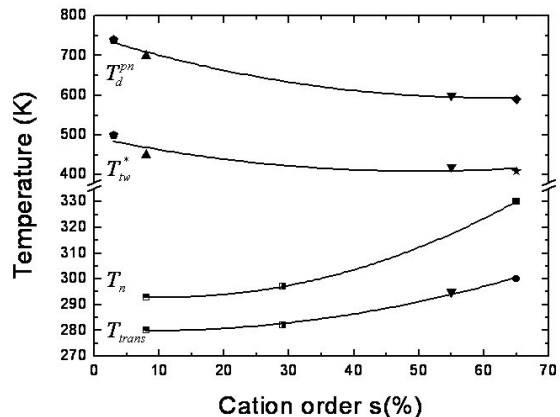


FIG. 4. Variation of characteristic temperatures T_m , T_n , T_{tw}^* , and T_d^{pn} with B-site Sc/Ta cation order, as detected by AE. For $s = 65\%$, temperatures T_n , T_{tw}^* , and T_d^{pn} are obtained from the data presented in Fig. 1. Other data are from Refs. 20, 23, 33, 45, 68, and 69. Continuous lines are guide to the eye.

which show smooth dependences on the degree of order. These groups are T_d^{pn} , T_{tw}^* , T_n , and T_m (which corresponds to T_{trans}). Acoustic emission was observed in sample $s = 65\%$ for the upper three temperatures while T_{trans} is the transition temperature of the sample⁴⁵ where no measurable AE was found. The observation that the characteristic temperatures seem to follow the same trend in samples with very different microstructures, such as PNRs and tweed, shows a much closer relationship between them than previously anticipated. The nucleation temperature of tweed is then correlated with the Burns temperature of PNRs, the coherency temperature is related to T^* while T_n seems to relate to the point of a

local maximum of the sample density (minimum of the lattice parameters in Fig. 1) where the linear elasticity is no longer appropriate to describe the structural modulations. The fact that the s -dependence is rather small also rules out the the cation disorder is the direct origin for the relaxor behavior in PST: samples with small disorder ($s < 10\%$) show similar characteristic temperatures as samples with $s = 65\%$ cation disorder.

We conclude that AE operates over a wider parameter space than has been anticipated: it is irrelevant whether microstructural changes of PNRs (nucleation, coherency, static deformation, freezing) or tweed are investigated. In both cases we find very similar signals so that one may be tempted to argue that the detailed microstructure of PNRs is not dissimilar to tweed. This would mean that we see PNRs as a dense array of polar clusters with little or no paraelectric matrix in between. If the borders between the individual PNRs are sufficiently continuous (no hard domain walls) there is indeed very little difference between dense PNR patterns and tweed structures. Conversely, one can describe the PNRs scenario as a squared-up tweed structure similar to the behavior of incommensurate phases.⁷⁰ This interpretation depends on the insensitivity of AE on detailed structural changes. The AE signal indicates that something happens but not what and hardly how much. We are still far from a comprehensive structural model for relaxors and tweed, which would allow us to quantitatively comprehend the occurrence of AE signals. Furthermore, it is unclear why AE signals are much more constrained in temperature than the extend of the fluctuation intervals, which are determined by other techniques, and why AE statistics does not follow the statistical fingerprint for avalanche dynamics. Further work is therefore highly desirable.

I. ACKNOWLEDGMENTS

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