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Phase transformation above T_m in $PbSc_{0.5}Ta_{0.5}O_3$ relaxor as seen via acoustic emission

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Chemically B-site disordered $PbSc_{1/2}Ta_{1/2}O_3$ relaxor crystals have been studied by means of dielectric and acoustic emission methods in the vicinity of $T_m \approx 280$ K. Along with the intrinsic cubic-to-rhombohedral phase transformation at $T_c = 261$ K, a phase transformation at $T_n = 293$ K is evidently detected by acoustic emission. Under an external dc electric field T_c gradually increases with increasing the field, whereas T_n exhibits nontrivial behavior, namely, initially decreases and then starts increasing, similarly to T_c. The characteristic temperature T_n is attributed to the occurrence of incommensurate modulated antiferroelectric regions, which have previously been suggested to coexist with both the cubic paraelectric and rhombohedral ferroelectric phases in the vicinity of T_m. The nontrivial behavior of T_n under an external dc electric field is also discussed.

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Relaxor ferroelectrics (FEs) of perovskite-type $Pb(B'_{1-x}B''_{x})O_3$ exhibit a diffusive, smeared, wide maximum at T_m in the temperature dependence of the dielectric permittivity (ε) shifting to high temperatures with increasing frequency.[1] Canonical relaxors possess no phase transformation at T_m, i.e., at low temperatures there is no long-range FE order detectible by diffraction analysis. Nowadays it is generally accepted that the strong dielectric relaxation of T_m is related to two crucial factors: (i) quenched random electric fields arising from the existing B-site chemical disorder and the resultant difference in ionic charges and radii between the different kinds of B-site cations, and (ii) fluctuating polar nanoregions dispersed within a cubic nonpolar paraelectric (PE) phase, appearing below the Burns temperature (T_d), which is considerably higher than T_m.[2] On cooling the polar nanoregions start to correlate and consequently, become larger and quasistatic at the so called T^* (Ref. 3) and freeze at T_f (in the case of canonical relaxors) or evolve into normal FE domains at the Curie temperature T_c, as both T_f and T_c are below but close to T_m. The sequence of characteristic temperatures $T_d \to T^* \to T_m \to T_f$ (or T_c) has been confirmed for a number of relaxor compounds by x-ray diffraction (XRD) (Refs. 4–6), vibrational spectroscopy[5–7] and acoustic emission (AE).[8,9]

A large number of B-site complex perovskite-type relaxors are characterized by local chemical 1:1 B-site order (CBO) along the cubic $\langle 100 \rangle$ crystallographic direction.[10] Compounds with the general formula $A(B'_{0.5}B''_{0.5})O_3$ may also exhibit long-range CBO and it has been shown that the degree of CBO influences the relaxor properties, supporting the idea that the existence of charge imbalance related with chemically B-site disordered regions is a key factor for the suppression of long-range FE order.[11] However, it has been recently shown that local elastic fields associated with isovalent A-site substitution as well as oxygen vacancies affect even more strongly the formation of FE state at low temperatures,[5,6,12] indicating that additional structural features may also be responsible for restraining the development of polar nanoregions into long-range ordered FE domains.

A typical relaxor compound of the type $A(B'_{0.5}B''_{0.5})O_3$ is $PbSc_{0.5}Ta_{0.5}O_3$ (PST) undergoes a spontaneous cubic-to-rhombohedral FE phase transformation just below $T_m \sim 280$ K. The phase transformation is weakly first order, as revealed by the volume discontinuity at T_c, but approaching tricritical behavior, considering the $T^{1/4}$ dependence of the rhombohedral unit cell angle below T_c.[13] The increase in the degree of long-range CBO sharpens the $\varepsilon(T)$ peak of PST and shifts T_c closer to T_m. The application of a dc external electric field (E) also shifts T_c to higher temperatures, without changing T_m.[14–16] The degree of CBO can be quantified using the Bragg reflection intensities as the ratio $S = \rho_{\text{experimental}} / \rho_{\text{theoretical}}$, $\rho = I(111)/I(200)$,[17] (Bragg peak indices given in $Fm\bar{3}m$, which is the symmetry of the perovskite-type structure if the B-site cations are ordered). Recently, using transmission electron microscopy (TEM), a phase in the vicinity of T_m was discovered for highly chemically B-site ordered ($S > 0.85$) single crystals of PST.[18,19] This phase was qualified as incommensurate modulated antiferroelectric (MAFE) and shown to coexist with both PE and FE phases. The temperature range of existence of the MAFE state is extended above and below T_m and is wider for crystals with a higher degree of CBO. However, the MAFE domains are continuous across the crystal and not confined inside the CBO domains, suggesting that MAFE regions may also be present in chemically B-site disordered relaxors. Indeed, Brillouin scattering shows a clearly pronounced inflection at 297 K for well-disordered PST ($S \approx 0.29$) with T_m of about 280 K,[20] which has been assigned to be some structural changes.

Thus, the objective of our study was to apply AE, a method quite sensitive to nanoscale structural transformations in FEs, in order to check the existence of MAFE regions in PST with poor CBO. In the present Rapid Communication we report the occurrence of both FE $\to$ PE and MAFE $\to$ PE transformation processes in well B-site disordered PST crystals as well as the dependences of the critical temperatures on an external dc E.

Optically homogeneous cubic-shaped single crystals of

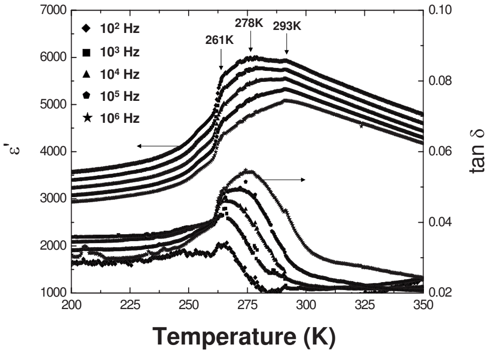

FIG. 1. Dielectric permittivity $\varepsilon(T)$ and dielectric losses tan $\delta(T)$ for PST single crystals measured at several frequencies in the absence of an external electric field.

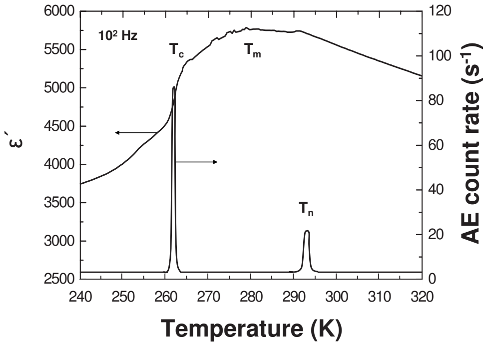

FIG. 2. Dielectric permittivity $\varepsilon(T)$ at 100 Hz and AE count rate (T) for PST single crystals in the absence of an external electric field.

PST were synthesized by the high-temperature solution growth method.[21] The chemical composition and homogeneity were verified by microprobe analysis (Camebax microbeam SX100 scanning electron microscopy system). The degree of CBO $S \approx 0.13$ was determined by powder XRD (Philips X'Pert diffractometer), following the commonly accepted routine[17] applicable for ceramics as well as for single crystals. The degree of CBO can be defined also via the site occupation factors (SOFs) of the (4*a*) or (4*b*) Wyckoff position in $Fm\bar{3}m$, as equal to $\eta = |\mathrm{SOF(Ta)} - \mathrm{SOF(Sc)}| / |\mathrm{SOF(Ta)} + \mathrm{SOF(Sc)}|$. The degree of CBO calculated from SOFs obtained from structure refinements to synchrotron single-crystal XRD data is 0.08,[22] which confirms the low degree of CBO in the single-crystal sample studied. The mean size of CBO domains was determined to be ~6.4 nm, using the Scherrer equation applied to the 111 Bragg reflection. Samples from the same synthesis batch were subjected to dielectric and AE experiments. Platelike {100}-oriented specimens sized of about $3 \times 2 \times 1\ \mathrm{mm}^3$ were cut with a diamond wire saw. Dielectric measurements were conducted on heating inside a cryostat at a rate of $5\ \mathrm{K\ min}^{-1}$ using an *LCR*-meter HP4284A with a tickle voltage of 100 mV ac.

The AE technique is described in great detail elsewhere.[8] Silver contacts were prepared on both sides of the platelike specimen. The sample was pasted with a silver epoxy to the polished side of a fused silica acoustic rod waveguide. A $\mathrm{Pb(ZrTi)O_3}$-19 disk piezoelectric sensor was attached to the rear end of the waveguide. The sensor was electrically coupled to a 500 kHz bandpass 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 sample pasted was mounted in a resistance element tube furnace. Both the thermocouple and amplifier outputs were interfaced with a PC for a coupled readout. The silver contacts of the sample were connected to a high voltage power supply. Temperature dependences of the AE count rate $\dot{N}(dN/dT, \mathrm{s}^{-1})$ were measured at several fixed values of bias voltage upon heating from 200 to 400 K with rate of about 1–3 K/min.

The temperature dependence of the dielectric permittivity $\varepsilon(T)$ of the studied PST sample is shown in Fig. 1. As can be seen, both the real part of the dielectric permittivity $\varepsilon'(T)$ and the dielectric losses tan $\delta(T)$ exhibit a broad, frequency-dispersed peak, typical of chemically *B*-site disordered compounds. For low frequencies the maximum of $\varepsilon'(T)$ as well as that of tan $\delta(T)$ is near $T_m \approx 280$ K. The clearly visible frequency-independent step of $\varepsilon'(T)$ and tan $\delta(T)$ at 261 K indicates the phase transformation to a normal FE state. This temperature corresponds well to T_c determined by XRD from the rhombohedral distortion of the unit cell[5] as well as by Raman scattering from the depolarization of the spectra due to the development of normal FE domains.[23] A similar trend of $\varepsilon'(T)$ revealing T_c near 260 K has been observed for other PST compounds with a low degree of CBO.[24]

The combined plot of $\varepsilon'(T)$ measured at 100 Hz and the AE count rate $\dot{N}(T)$ is shown in Fig. 2. As can be seen, the steep slope in the $\varepsilon'(T)$ curve at $T_c = 261$ K is accompanied by a strong AE signal with $\dot{N} = 84\ \mathrm{s}^{-1}$ related to the FE → PE phase transformation. However, above T_m another well-pronounced AE signal with $\dot{N} = 22\ \mathrm{s}^{-1}$ is observed at 293 K. This temperature value coincides with the temperature at which one can see a slight maximum of $\varepsilon'(T)$ as well as a slight visible notch of tan $\delta(T)$ at higher frequencies, and in a certain extent marks the higher-temperature border of the low-frequency $\varepsilon'(T)$ peak (Fig. 1). Note that for PST the intermediate characteristic temperature T^* is near 450 K (Ref. 5) and therefore, the AE and dielectric features detected at 293 K cannot be attributed to the structural changes occurring at T^*. The temperature value of 293 K is closed to the temperature range where a MAFE → PE phase transformation would be expected (298 K) (Ref. 18) and where a sharp damping of the longitudinal acoustic phonons assigned to a phase transformation has been detected (297 K) (Ref. 20) in chemically *B*-site disordered crystals. Thus, one can conclude that a phase transformation does take place at $T_n = 293$ K, just above T_m, and most probably, it is due to the formation of MAFE regions. The difference in the $\dot{N}$ values, corresponding to the FE → PE and MAFE → PE phase transformations, is proportional to the difference in the phase volumes embedded.

Further, we have examined the behavior of both the characteristic temperature T_n and the critical temperature T_c under a dc E. The $T_c(E)$ dependence is shown in Fig. 3. As can be expected, the FE → PE phase transition temperature T_c gradually increases with increasing E, approaching a satura-

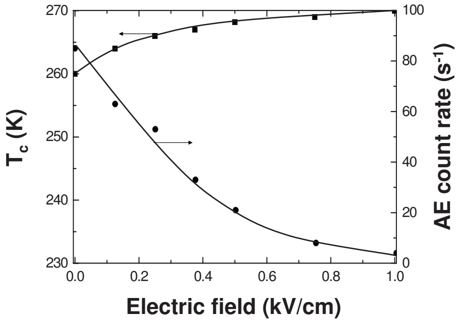

FIG. 3. FE→PE phase transformation temperature T_c and the corresponding AE count rate $\dot{N}$ for PST single crystals as a function of a dc external electric field.

tion value at high E. Similar behavior of $T_c(E)$ was observed for PST with a high degree of CBO, $S \approx 0.9$ (Ref. 16) and $S \approx 0.65$.[25] The corresponding $\dot{N}(E)$ weakens approximately exponentially at lower E values and approaches saturation at higher E. This is a reasonable behavior because the application of E moves the phase transition to the tricritical point lying at the end of the first-order phase transition line,[26] where no embryos of the another phase arise. Hence, the corresponding volume jump of the crystal vanishes and no discontinuity in any thermodynamic variables (including the strain, which is the AE source) is expected. A similar $\dot{N}(E)$ dependence of T_c was recently observed in $BaTiO_3$ crystals.[27]

The observed characteristic temperature T_n exhibits nontrivial behavior upon a small E (see Fig. 4). Initially, T_n decreases with increasing E, and then increases, while the corresponding AE count rate $\dot{N}$ first increases and then decreases with increasing E, as the maximum of $\dot{N}(E)$ coincides with the minimum of $T_n(E)$. This nontrivial $T_n(E)$ dependence strongly supports the suggestion that T_n is related to the occurrence of AFE regions, because it is well known that in crystals with AFE long-range order the AFE-PE phase-transition temperature initially decreases with the increase in E and then starts increasing,[28] similarly to the data presented in Fig. 4. On the other hand, a similar V-type shape has been observed at small E for the $T_m(E)$ dependence of $(1-x)PbMg_{1/3}Nb_{2/3}O_3$-$xPbTiO_3$ (PMN-xPT) relaxors, which are known to possess no AFE phase at all, using dielectric (x=0.06, 0.1, 0.13, 0.25, 0.35, and 0.4) (Ref. 29) and AE (x=0.33) methods.[30] Therefore, the nontrivial $T_n(E)$ dependence cannot be explained only within the framework of classical AFE-PE transitions and other mechanism should be considered. Such a mechanism is suggested to result from the presence of random electric fields due to chemical B-site disorder in relaxors. The random electric fields have a reorientational component adjustable by E. In particular, the emergence of the macroscopic polarization in a sample is accompanied by alignment of the reorientational component along the E. The longitudinal random electric fields component giving a contribution to the dielectric susceptibility could be described as[31]

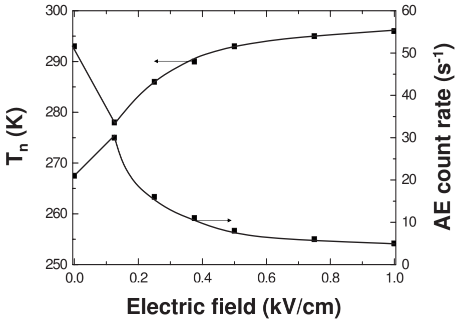

FIG. 4. The characteristic temperature T_n and the corresponding AE count rate $\dot{N}$ for PST single crystals as a function of a dc external electric field.

$$\langle \chi_{\mathrm{II}} \rangle \approx \{ |E+e|^{7/2} - |E-e|^{7/2} + \cdots \}, \tag{1}$$

where e is the random electric fields value. The experimental data obtained for the $T_m(E)$ dependence in PMN-xPT were satisfactorily model by using Eq. (1).[29,30] According to this model, T_m has a minimum when E reaches the threshold value equaled to the random electric field, $E_{\mathrm{th}}=e$, and, then, T_m increases as happens in normal FEs with a second-order phase transition. The above distribution of the random electric fields longitudinal component could also explain the $\dot{N}$ behavior. Indeed, as E enhances the random electric fields longitudinal component increases quadratically as const $+AE^2$ in weak fields, passes through a sharp maximum, and then decreases as $E^{-1/2}$ (Fig. 2 in Ref. 30). We assume that similar processes occur in PST near T_n. The reorienting random electric fields electric dipoles contributing to the longitudinal susceptibility induce the strains within the lattice and, consequently, radiate AE. Hence, the $\dot{N}$ maximum coincides with the T_n minimum, thus reflecting the strong interaction between the external E and the internal random electric fields leading to a nontrivial behavior of T_n in PST crystal as well.

There are, however, some indications that the phenomena taking place near T_m are influenced by additional force fields, existing along with the random *electric* fields induced by chemical B-site disorder: (i) the maximum drop in T_n for PST is ~15 K, i.e., much stronger than the corresponding change in T_m (~5 K) for PMN-0.33PT (Ref. 30); (ii) as discussed above, T_n is most probably related to the occurrence of MAFE regions, which near T_m coexist with polar nanoregions and therefore, the structural species typical of MAFE and polar nanoregions compete to each other thus enhancing local *elastic* fields. Therefore, inhomogeneous local strains arising from the simultaneous presence of polar and antiferrodistortive atomic arrangements may considerably contribute to the V-type shape of the $T_n(E)$ dependence for PST. Note that this assumption does not contradict to the general idea of the random field model, if inhomogeneous local strains and corresponding elastoelectric coupling are considered.

Finally, we present a complete E-T phase diagram for PST based on our AE data (Fig. 5). There are two transformation processes taking place in the considered temperature range. The first one is the well-known spontaneous transformation from the long-range R to C phase. Its T_c rate is approximately 6 K cm/kV in the linear part of the curve,

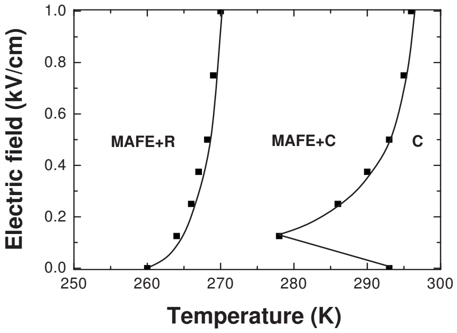

FIG. 5. *E*-*T* diagram for PST single crystals with low degree of chemical *B*-site order ($S \approx 0.13$).

which is of the same order of magnitude ~ 1 K cm/kV as compared to PST with a high degree of CBO, $S \approx 0.9$ ($T_c \approx 270$ K) (Ref. 16) and $S \approx 0.65$ ($T_c \approx 260$ K) (Ref. 25) measured using the dielectric and small-angle light scattering methods, respectively. The second phase transformation occurs within the C phase and may be attributed to the MAFE regions→*c* phase, previously detected near 297 K by TEM.[20] The *E* dependence of T_n corresponding to this phase transformation exhibits a nontrivial minimum, similarly to the $T_m(E)$ behavior that has been previously observed for PMN-*x*PT relaxors at small *E*.[29,30] It is obvious that such a behavior is an intrinsic feature of the relaxors materials caused by existence of the internal random electric fields.

In summary, we have evidenced a phase transformation, namely, a formation of MAFE regions inside the PE matrix at T_n (just above T_m) in chemically *B*-site disordered relaxor FE PST. The $T_n(E)$ dependence exhibits a nontrivial minimum at small $E = 0.125$ kV/cm. Our results indicate that within a certain temperature range between T_c and T_n, the structure of PST comprises both polar nanoregions and antiferrodistortive regions. Based on x-ray diffuse scattering analysis,[32,33] a local antiferrodistortive order and coexistence of FE and AFE regions has also been proposed for chemically *B*-site ordered $PbSc_{0.5}Nb_{0.5}O_3$. The dependence of T_m on electric field for PMN-PT indicates that such a structural state might be universal for all perovskite-type relaxor and relaxor-based ferroelectrics, but for compounds with stoichiometry differing from $PbB'_{0.5}B''_{0.5}O_3$, the temperature of formation of local antiferrodistortive order is too close to T_m to be distinguished.

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