

Acoustic emission study of phase transitions and polar nanoregions in relaxor-based systems: Application to the $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ family of single crystals

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The restored strain energy in $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PZN) and 9% PbTiO_3 -doped PZN (PZN-9%PT) relaxor crystals has been studied by means of acoustic emission (AE). Two types of AE activity signals have been recorded: (i) related to temperature- or electric-field-induced macroscopic phase transitions and (ii) associated with formation/disappearance of intrinsic polar nanoregions. Monitoring of AE under varying [001] electric fields has allowed a unique *in situ* observation of a low-field (1 kV/cm) irreversible orthorhombic-to- M_C phase transition within the morphotropic phase boundary region of PZN-9%PT.

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Single crystals of relaxor-based solid solutions, such as $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - PbTiO_3 (PMN-PT) and $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - PbTiO_3 (PZN-PT), are known to exhibit exceptionally large electromechanical coupling and piezoelectric responses when poled along the pseudocubic [001] direction.¹⁻⁴ Substantial efforts aimed at the understanding of their remarkable properties have been made during the last five years. Theoretical and experimental works have shown that these unusual properties occur in the so-called morphotropic phase boundary (MPB) region, which is related to a low-symmetry monoclinic phase separating a rhombohedral PT-poor phase from a tetragonal PT-rich phase of PZN-PT. As a consequence, instead of being constrained to alignment along a symmetry axis, the polarization can easily rotate within a monoclinic plane under temperature variation, atomic substitution,⁵ electric field,⁶ or pressure stress.⁷ In fact, the pathway followed by the polarization appears to be much more complex in certain cases. For example, it has been demonstrated recently that the complex path in relaxor-based solid solutions can only occur if some inhomogeneous chemically ordered regions exist on the nanometer scale.⁸

Generally, it is not easy to deal with phase inhomogeneities as their observation depends on the length and time scale of the experimental probe. For relaxors, the broadening and the frequency dependence of the dielectric anomaly reflect the presence of polar nanoregions (PNRs) - the main feature in such systems - which appear hundreds of degrees above the temperature of maximum dielectric permittivity T_{max} . The first evidence of these inhomogeneities was provided by Burns and Dacol,⁹ who observed a deviation from the linear temperature dependence of the optical index of refraction below a certain temperature T_d during cooling of La-doped $\text{PbZr}_{(1-x)}\text{Ti}_x\text{O}_3$ (PLZT) samples. In pure PZN this temperature, referred to as Burns temperature, is close to 750 K whereas T_{max} is slightly above 400 K.¹⁰ Even though the PNRs strongly affect the relaxor properties, only weak phenomena reflecting their presence are detected: deviation from the Curie-Weiss law,¹¹ dynamic slowing down through the Vögel-Fulcher relationship,¹² change in the structural lattice constants or thermal expansion coefficient,^{13,14} appear-

ance of diffuse scattering,¹⁵ and anomalies in the specific heat.¹⁶

Concurrently, the acoustic emission (AE) method has been successfully used to investigate the macrodomain structure due to the first-order phase transitions in ordinary ferroelectrics of BaTiO_3 type.¹⁷ In particular, the formation of a domain twin structure due to relaxation of mechanical stresses has been evidenced through the appearance of AE signals at the Curie temperature (T_c). In general, AE is attributed to a sudden release of stored elastic energy, although the details of the mechanism are generally system specific. Spontaneous formation of microcracks, discontinuous motion of domain walls clamped by structural defects or instantaneous formation of a domain wall of finite size can be considered as possible origins of AE in ferroelectrics. The growing interest in this nondestructive technique lies in the fact that it is highly sensitive to relatively small structural changes. For example, it has been demonstrated that in the case of the ferroelectric-antiferroelectric phase transition in PbZrO_3 crystals an AE signal is recorded, whereas practically no thermal expansion change is detected.¹⁸ Recently, both AE and thermal expansion measurements have been simultaneously applied to studying the structural features of relaxor PMN crystals at high temperatures.¹⁹ It has been established that AE radiation accompanies the deviation of thermal expansion from linearity close to $T_d \approx 620$ K.

Recently, we have shown that AE signals can be related also to the electric-field-induced phase transitions in PMN.²⁰ In the present communication we report on the first detection of AE activity in PZN and PZN-PT crystals under varying temperature and applied electric field conditions. We show that the AE technique appears to be a powerful tool for detecting even minor stress changes within a material, including the new structural features related to the formation of PNRs and electric-field-induced phase transitions in PZN-PT single crystals of compositions close to the MPB.

{001}-cut single crystal plates ($3 \times 3 \times 0.3$ mm³) of both pure PZN and PZN-9%PT were studied using a dedicated acoustic emission technique described in detail in Ref. 21. Each sample was coupled with silver epoxy to the polished

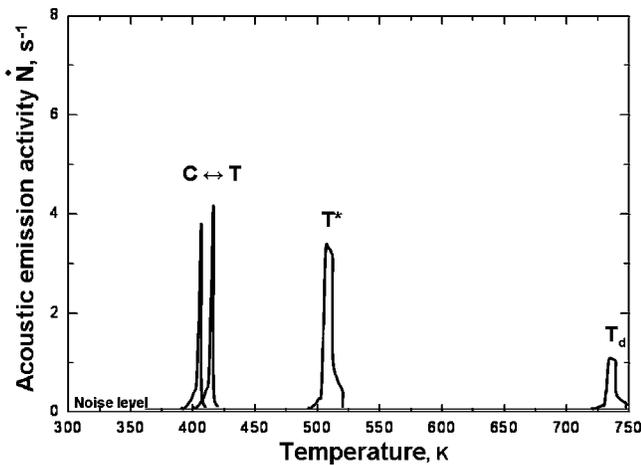


FIG. 1. AE activity as a function of temperature during thermal cycling of a PZN crystal; arrows indicate the heating and cooling directions.

side of an acoustic silica waveguide. A PZT-19 piezoelectric sensor was attached to the rear end of the waveguide. The sensor was electrically coupled to a 500 kHz band-pass pre-amplifier with a reduced noise level of $\leq 1 \mu\text{V}$. A Cu-K thermocouple junction was glued to the waveguide near the sample. The sample with the adjacent part of the waveguide was mounted in a resistance element furnace for AE activity (\dot{N}, s^{-1}) measurements from room temperature up to 750 K at an average heating/cooling rate of 1 K s^{-1} . In the case of the PZN-9%PT sample, room temperature AE measurements were carried out also under bias; dc electric field of up to 18 kV/cm was applied at a rate of about 10 V min^{-1} through two silver epoxy contacts pasted on opposite sides of the crystal, while the sample was submerged in an oil bath.

Figure 1 shows the AE activity variation as a function of temperature for pure PZN in the heating and cooling regimes. A sharp AE signal with a thermal hysteresis of about 10 K occurs around $T_c \approx 413 \text{ K}$. This signal corresponds to the structural phase transition from the cubic (high-temperature) to rhombohedral symmetry, as originally described by Kuwata *et al.*,²² and it shows the I -order character related to this transition. The more striking and peculiar features are the two higher temperature AE signals detected in the cubic phase at $T \approx 505$ and 730 K . These unusual anomalies are quite different from the AE activity corresponding to the phase transition; they are broader (at least three times) and do not show any thermal hysteresis. The highest-temperature peak (730 K) corresponds to the Burns temperature T_d associated with formation of locally polarized nanoregions, or PNRs, in relaxors.¹⁰ The PNRs begin to appear at $T_d \gg T_c$, namely, well within the paraelectric phase, due to compositional inhomogeneities in the disordered crystal and disappear as a result of local ferroelectric phase transitions followed by atomic displacements and associated release of stored strain energy.²³ This result is also in agreement with our recent data on PMN.¹⁹ The 505 K peak, which we denote as T^* , exhibits the same AE features as the T_d peak, e.g., in terms of the peak width, and we presume that it is also related to the PNRs and especially to the initiation of increase

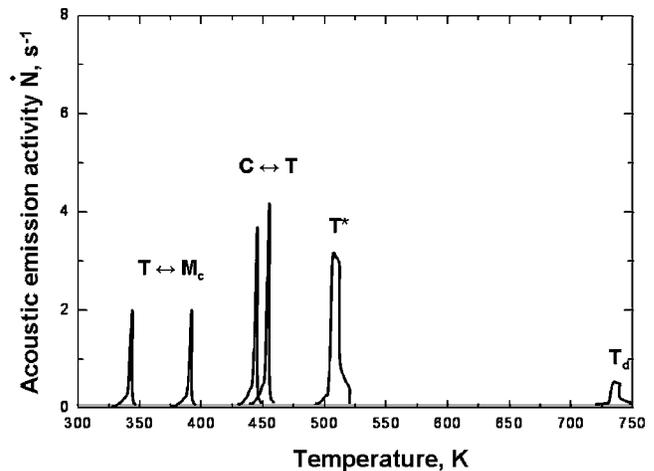


FIG. 2. AE activity as a function of temperature during thermal cycling of a PZN-9%PT crystal; arrows indicate the heating and cooling directions.

of their correlation length, or of size of the polar nanoregions. The intensity of the AE activity at T^* is three times stronger than that at T_d reflecting, therefore, larger elastic strains stored. Apparently, enhanced growth of the PNRs occurs around this temperature, and the interaction between larger PNRs of different polarizations generates intense transient elastic waves during the reorientational motion of polar nanoregions. This assumption is supported by an earlier analysis of the diffuse neutron-scattering data.²³ Indeed, the correlation length extracted according to the Ornstein-Zernike model increases roughly below 500 K in PZN and PZN-4.5%PT. This observation can also be related to the observations (based on inelastic neutron scattering analysis) at 500 K of both an anomalous ridge of inelastic scattering at roughly $q=0.2 \text{ \AA}^{-1}$ from the zone center, resembling a “waterfall effect,” and a significant change in the elastic cross section near this specific wave number.²⁴ It is important to emphasize hereby that such T^* -type temperature is also evidenced in another prototypical relaxor PMN at about 350 K by means of x-ray diffraction,²⁵ Raman spectroscopy,²⁶ and dielectric measurements.¹¹ We also note that at temperatures below T_d it has been demonstrated that the transverse acoustic phonon branch shows a broader linewidth in PMN.²⁷ The cumulative experimental results obtained with both PZN and PMN point to the fact that T^* is a peculiar and specific temperature in relaxor systems, which is directly related to the presence of PNRs. The explicit intense AE activity peak at around $T^*=505 \text{ K}$ indicates the thermal range of enhanced growth and stronger interaction between the polar nanoregions in PZN.

It is interesting to compare the AE response of the pure PZN single crystal with a solid solution crystal, especially with the PZN-9%PT composition corresponding to the MPB. The AE activity for such compound is shown in Fig. 2. PZN-9%PT undergoes two macroscopic phase transitions evidenced by sharp AE signals. The peak close to 450 K (with about a 10 K thermal hysteresis, similarly to the 413 K peak in PZN) is I order and corresponds to an abrupt cubic-to-tetragonal (C - T) phase transition. An additional transition is

characterized by a 380 K peak on heating and a 340 K peak on cooling exhibiting a very large thermal hysteresis of about 40 K. Similar features have been observed in the course of low-angle light scattering studies of PZN-9%PT (Ref. 28) and Brillouin backscattering spectroscopy of PZN-8.5%PT.²⁹ The PZN-9%PT composition belongs to the MPB, and there is a competition between the structures of different symmetries with free energies very close to each others, which hampers the straightforward assignment of the transition involved. It has been shown that the room temperature phase of PZN-9%PT can be either monoclinic³⁰ (M_C in Vanderbilt and Cohen notation³¹) or orthorhombic³² or a mix of both phases.³³ For the sake of clarity we assume in the following that the room temperature phase is orthorhombic being the limiting case of the monoclinic M_C -type phase.³⁵ The strength of the AE response for such tetragonal-to-monoclinic (T - M_C) phase transition is two times weaker than that corresponding to the C - T transition (at ~ 450 K). The large thermal hysteresis of 40 K shows that the restored elastic strain energy is small and may be indicative of a rather gradual growth of the tetragonal into the monoclinic (M_C) phase. We thus assume that there is a continuous change of the polarization from the [001] tetragonal to, ultimately, the [011] orthorhombic direction in the monoclinic (010) plane, which is consistent with the diffuse first-order transition model.³²

A surprising result of the AE measurements during thermal cycling is the persistence of the two high-temperature responses, namely, the T^* and T_d peaks, in the cubic paraelectric phase of the PZN-9%PT crystal at temperatures very close to those of pure PZN. Only a weak increase of T_d is observed for PZN-9%PT ($T_d \approx 736$ K). The T^* value remains practically constant, although it is expected to increase through the $T^* = T_c + \delta T$ relationship, with δT increasing at higher PT concentrations.²³ This discrepancy may be sample dependent, but also other PZN- x PT compositions must be studied before the dynamics of polar region reorientation is understood in more depth.

More insight into the MPB composition and phase transitions can be gained from studying the AE activity under an external dc electric field. The AE measurements at room temperature on the PZN-9%PT crystal sample under a dc electric field applied along the [001] direction is shown on Fig. 3. When the field value increases, two sharp AE activity peaks are detected around 1 and 17 kV/cm. We focus initially on the 1 kV/cm peak. X-ray studies of PZN-9%PT demonstrate that the room temperature structure of this material within the MPB is orthorhombic³⁴ in the absence of an electric field. Single crystals of PZN-9%PT poled along the [001] direction become monoclinic, and complex monoclinic domain states are obtained with the polar axis making an angle of about 45° relatively to the poling direction.³⁵ Due to the low static elastic energy of these domain states in PZN-9%PT,³⁶ a 3D network of small size (< 100 nm) monoclinic phase domains with a large interfacial is formed in the orthorhombic matrix. The emergence, expansion and disappearance of such interphase domain boundaries are accompanied by an acoustic emission activity peaking at 1 kV/cm under the [001] electric field. The relatively low field required reflects the very low energy barrier existing in PZN- x PT between the O

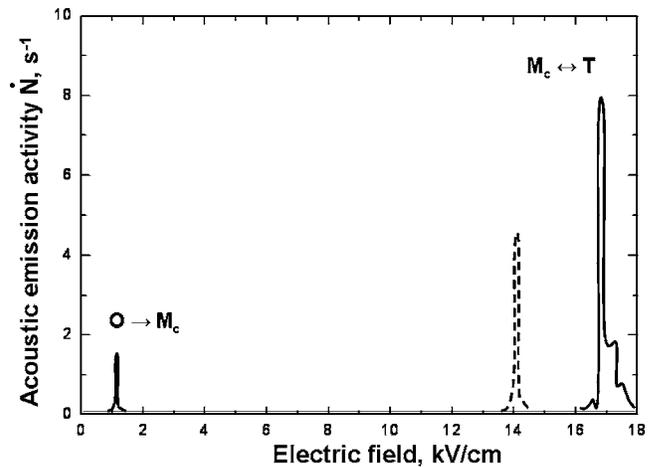


FIG. 3. AE activity as a function of electric field applied in the [001] direction at room temperature.

and M_C states, which also allows the O polar axis [101] to rotate easily in the monoclinic (010) plane.³² Although large macroscopic strains and electric polarization have been observed in PZN- x PT crystals of compositions close to the MPB, they change linearly in the low-field region, and no anomalies characteristic of the orthorhombic- or rhombohedral-to- M_C phase transition are revealed in their electric field responses.

The strong second peak of AE activity, at 17 kV/cm, emerging upon further increase of the externally applied [001] field clearly corresponds to the M_C - T phase transition. This transition is very energetic and corresponds to high strain restitution at this field value, as it is common for highly piezoelectric materials. Two weaker sub-peaks detected on the right side of the 17 kV peak may be related to surface effects or responses from other parts of the sample due to the sample inhomogeneity. Fields of similar magnitude have been determined for the same structural transition in PZN-8%PT single crystals from unipolar measurements of electric-field dependences of the polarization and strain responses.^{6,37} The latter show a hysteresis loop, namely, a reverse T - M_C phase transition at fields a few kV/cm lower upon decrease of the applied field. A corresponding hysteresis peak at 14 kV/cm appears on the AE activity curve, in the decreasing field regime, as shown in Fig. 3. It is noteworthy that no other peak appears upon the field decrease down to 0 kV/cm, which implies that the M_C phase remains stable under zero field at room temperature, without an immediate reverse M_C - O transition. However, repeated measurements of field-induced AE with a time gap of 24 hours reveal the 1 kV/cm again, showing that the M_C phase relaxes into the more stable orthorhombic phase in terms of hours rather than weeks as reported for the M_A - X room temperature transition in PZN-8%PT.⁶

In summary, we have shown that the AE method is a powerful tool for studying the relaxor-based systems. It allows one to detect the structural changes accompanied by strain relief due to all macroscopic phase transitions (thermally activated or induced by application of an electric field) and especially due to the formation and interaction of PNRs that are responsible for the exceptional piezoelectric and

electrostrictive properties of relaxor ferroelectrics. The peculiar AE signature related to the PNRs has allowed us to accurately determine the temperatures of their nucleation and enhanced growth of their correlation length. A surprising result of the related measurements is that these temperatures do not seem to depend on the PT content in PZN-*x*PT, although only two compositions (pure PZN and PZN-9%PT) have been employed. This issue has not been studied systematically yet, and will be one of the subjects of our future AE investigations using samples of different compositions. Electric-field-induced phase transitions in the PZN-9%PT crystal, corresponding to the MPB composition, have been

studied at room temperature. On the field increase, the transition sequence follows the $O-M_C-T$ path, but only the reversible $T-M_C$ transition is observed in the AE measurement on field decrease. The elusive irreversible $O-M_C$ transition at the low field of 1 kV/cm can be revealed explicitly, virtually *in situ*, only by the AE method giving the most illuminating example of its advantages in studying the PZN-based and other relaxor materials. We believe that the present results will stimulate further research of phase transitions as well as nucleation, growth and interaction of PNRs in various relaxor and similar systems (with embedded nano/microregions in the parent matrix) using the AE technique.

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