

**Elastic softening and polarization memory in PZN-PT relaxor ferroelectrics**S. M. Farnsworth,<sup>1</sup> E. H. Kisi,<sup>1</sup> and M. A. Carpenter<sup>2</sup><sup>1</sup>*School of Engineering, University of Newcastle, Callaghan NSW 2308, Australia*<sup>2</sup>*Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, United Kingdom*

(Received 10 November 2011; published 30 November 2011)

Substantial elastic softening in the cubic phase of PZN-PT relaxor ferroelectric crystals is observed as a large hysteresis between the RUS frequencies from poled and depoled crystals. This is due to static switchable polar nanoregions (PNR) at  $T^*$ , well below the conventional Burns temperature but  $\sim 50$  K above the ferroelectric transition. Elastic softening due to polarization of the PNR shows polarization memory through two phase transitions and is greater than the softening associated with polarization of the ferroelectric phases. This emphasizes that PNR dominate the material properties at all temperatures below  $T^*$ .

DOI: [10.1103/PhysRevB.84.174124](https://doi.org/10.1103/PhysRevB.84.174124)

PACS number(s): 77.80.Jk, 77.80.B-, 77.84.Cg, 85.50.Gk

**I. INTRODUCTION**

Piezoelectric interconversion of electrical and mechanical energy is critical to a wide range of applications in control, energy production, and medical imaging.<sup>1</sup> Materials exhibiting the highest piezoelectric coefficients ( $\sim 2000$  pC/N) and strains ( $\leq 1.7\%$ ) occur in the system  $\text{Pb}(\text{Nb}_{2/3}\text{Zn}_{1/3})\text{O}_3\text{-PbTiO}_3$  (PZN-PT). Distinctive properties of technological interest are considered to arise from polarization rotation to low-symmetry phases<sup>2</sup> or elastic softening<sup>3</sup> (giant electrostriction) or to the structural and dynamic properties of polar nanoregions (PNR) in the relaxor state (electrooptic effect and large dielectric constant).<sup>4-6</sup> It might be expected that relaxor behavior in the stability field of the cubic ( $c$ ) paraelectric phase below the Burns temperature,  $T_B$ , would be replaced by long-range ferroelectric order at the ferroelectric transition temperature,  $T_F$ , to a tetragonal ( $t$ ) or rhombohedral ( $r$ ) structure. However, evidence from neutron and x-ray diffuse scattering shows that the PNR persist within the ferroelectric phases.<sup>7-12</sup> They have their own distinctive response to electric fields,<sup>7-12</sup> and PZN-8%PT crystals can retain a “memory” of an externally applied electric field even when heated into the macroscopically disordered cubic phase.<sup>8</sup> There has been evidence of a crossover from dynamic to long-lived (quasi-static) behavior of the PNR at a characteristic temperature,  $T^*$ , which is below  $T_B$  but above  $T_F$  and which is related to the frequency-dependent Vogel-Fulcher freezing interval from dielectric spectroscopy.<sup>13-17</sup> An acoustic emission peak at  $\sim 500$  K, also between  $T_B$  and  $T_F$ , is more typical of a *ferroelastic* phase transition.<sup>18,19</sup> The same combination of crossover dynamics relating to PNR and acoustic emission suggestive of a transformation microstructure in the classic relaxor  $\text{Pb}(\text{Mn}_{2/3}\text{Nb}_{1/3})\text{O}_3$  (PMN) has been interpreted as the condensation of PNR with permanent local distortions.<sup>20-22</sup>

We present resonant ultrasound spectroscopy (RUS) results showing extraordinary elastic softening in electrically poled PZN-PT crystals leading, through the electromechanical coupling, to the exaggerated piezoelectric properties. The softening is greatest in the relaxor state between  $T_F$  and  $T_B$  at  $T^* \approx T_F + 50$  K, strongly implicating PNR. Lastly, elastic hysteresis between poled and unpoled states in the interval 10 K to  $T^*$  is readily observable using RUS and correlates with the memory effect observed in diffuse neutron scattering.<sup>8</sup> The elastic memory effect survives the ferroelectric phase

transitions indicating robust static *mechanical* poling of PNR up to  $T^*$  although no electrical poling is sustained above  $T_F$ .

**II. EXPERIMENTAL METHODS**

RUS is a well established method for determining elastic and anelastic properties of samples up to a few cubic millimeters in size.<sup>5,23</sup> The frequency squared for each resonant mode,  $f^2$ , depends on elastic and piezoelectric (piezoelastic) moduli in the sample. The width of resonance peaks at half height,  $\Delta f$ , depends on anelastic relaxations and is often sensitive to transformation-related microstructure. Resonance modes of a multidomain crystal are determined by both the intrinsic single-crystal moduli and the ensemble of domains and domain walls. Differences between RUS spectra from poled and unpoled crystals therefore provide direct evidence of the effect of poling on microstructure.

RUS spectra were collected from three 2-mm<sup>3</sup> cube-shaped PZN-PT single crystals using equipment described elsewhere.<sup>24,25</sup> Crystals 1 and 3 were PZN-4.5%PT and PZN-8%PT respectively, both poled along  $[001]_c$ ; crystal 2 was PZN-4.5%PT poled along  $[111]_c$ . Spectra were collected in the frequency range 0.05–1.8 MHz during heating and cooling sequences between 10 and 550 K, with equilibration for 10–15 minutes before data collection at each temperature. The frequency and half-width of significant resonance modes as a function of temperature were determined by fitting an asymmetric Lorentzian function. Error estimates for the frequencies based upon the fitting statistics are generally  $< 1\%$ . A partial fit of elastic moduli to resonance frequencies of crystal 1 measured at 500 K (i.e., in the cubic phase) allowed a calibration of  $1/2(C_{11}-C_{12})$  in terms of  $f^2$  for the lowest frequency mode. This is consistent with room-temperature data from the literature for PZN-4.5%PT and PZN-8%PT poled along  $[001]$  that show that deviations from cubic symmetry for the elastic moduli are small and, in terms of average cubic parameters,  $1/2(C_{11}-C_{12})$  is substantially smaller than  $C_{44}$ .<sup>26</sup> Peak widths were used to follow the temperature dependence of acoustic dissipation through the inverse mechanical quality factor  $Q^{-1}$  ( $=\Delta f/f$ ).

**III. RESULTS**

Figure 1 shows spectra collected during heating of crystal 1 above room temperature illustrating mode softening at the

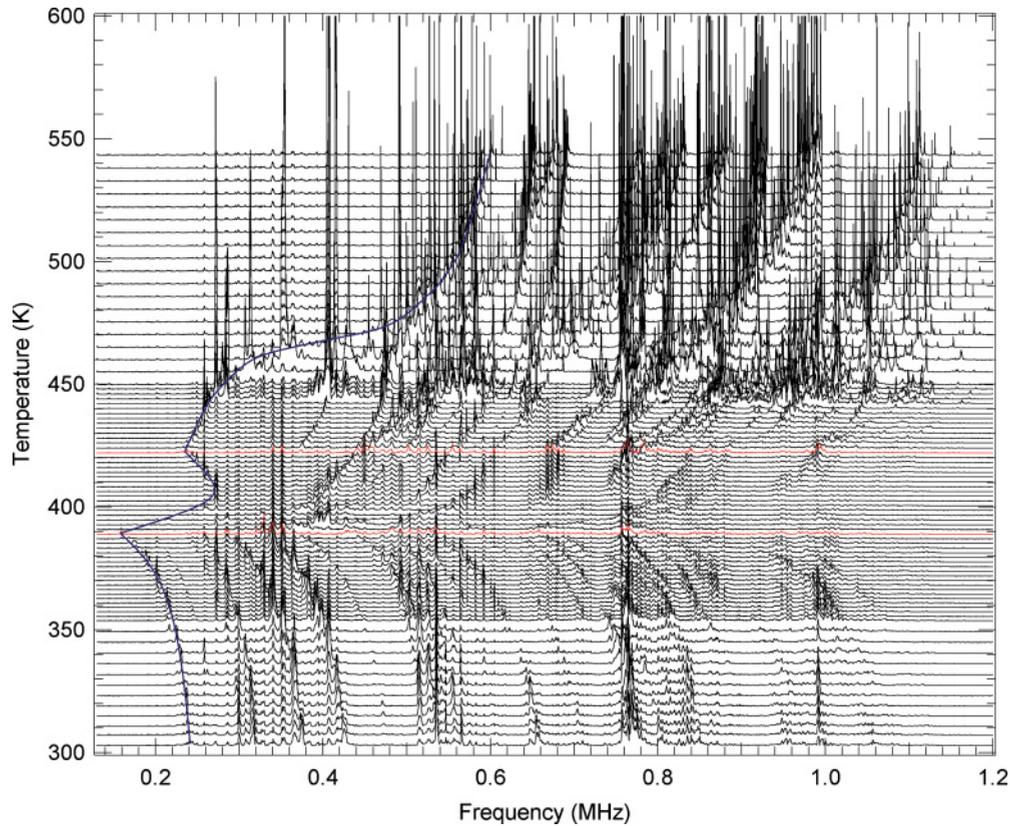


FIG. 1. (Color online) Lower frequency portion of RUS spectra during heating of the [001]c poled PZN-4.5%PT crystal offset in the y axis (amplitude) proportional to temperature. The blue line follows the lowest frequency mode and red spectra mark long-range ferroelectric transitions.

ferroelectric phase transitions. Figure 2 shows the temperature dependence of  $1/2(C_{11}-C_{12})$  during heating of the initially poled crystal and subsequent cooling of the depoled crystal. Note that the small discontinuities in frequency data at 295 K are an artifact arising from the switch between high- and low-temperature instruments. On heating, a minimum at  $\sim 385$  K indicates the  $r \leftrightarrow t$  transition and at  $419 \pm 1$  K a

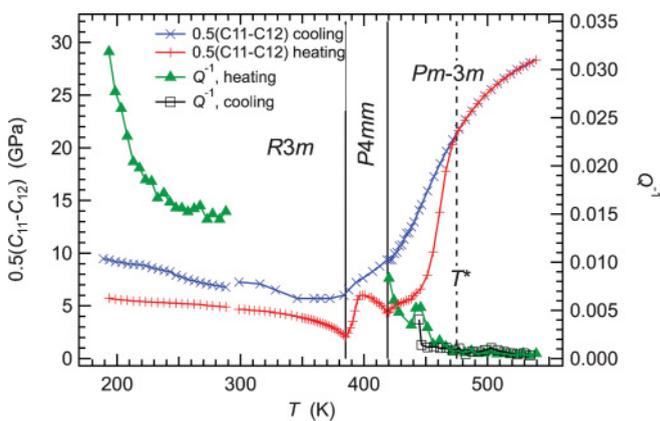


FIG. 2. (Color online) Data for  $1/2(C_{11}-C_{12})$  from the lowest frequency resonance mode in Fig. 1 of the poled crystal during heating (+,  $\blacktriangle$ ) and the depoled crystal after heating to  $\sim 550$  K ( $\times$ ,  $\square$ ).  $T^*$  ( $\sim 475$  K) marks the onset of hysteresis in elastic properties. Precision is generally  $\pm$  a few percent for the elastic constants though data on cooling  $450 \rightarrow 300$  K are less precise.

further minimum shows the  $t \leftrightarrow c$  transition ( $T_F$ ) previously observed at  $421 \pm 2$  K using neutron diffraction<sup>27</sup>. The stiffness  $1/2(C_{11}-C_{12})$  then rises steeply above 419 K, until at 550 K it is a factor of  $\sim 6$  greater than at room temperature. During cooling of the now depoled crystal,  $1/2(C_{11}-C_{12})$  reveals a large hysteresis starting  $\sim 50$  K above  $T_F$  at 475 K, which we term  $T^*$ . At all temperatures below this, the poled crystal is elastically softer than its depoled equivalent. This means that, on heating, the crystal is not *mechanically* depoled until  $T^*$  despite having passed through two phase transitions known from neutron diffraction to depole the ferroelectric domains formerly present in the  $r$  phase.<sup>12,27</sup> Therefore below  $T^*$ , there is a static elastic *polarization memory* built into the structure/microstructure that does not lead to remanent electric polarization at  $T_F < T < T^*$ . A separate resonance peak from crystal 1, determined primarily by  $C_{44}$ , shows a similar though smaller hysteresis at about the same temperature. Changes in the resonance frequencies in spectra from crystals 2 and 3 also occurred at the temperatures expected for the known phase transitions. The onset of hysteresis was also  $\sim 50$  K above  $T_F$  at  $\sim 470$  K for crystal 2 and at  $\sim 505$  K for crystal 3.

Typical  $Q^{-1}$  data are illustrated in Fig. 2 for the lowest frequency resonance of crystal 1. Above  $\sim 460$  K, low values ( $\sim 0.001$ ) signify very low attenuation, which was larger below  $\sim 455$  K on heating and below 445 K during cooling. Below these temperatures, all peaks were even broader but interference from alumina rod resonances meant accurate

$Q^{-1}$  values could not be obtained. Better resolution from the low-temperature instrument allowed  $Q^{-1}$  to be determined for the heating sequence at  $>200$  K. These show high attenuation, diminishing with increasing temperature. Resonances from depoled crystals were notably broader than those of poled crystals at all temperatures below  $\sim T_F + 20$  K (440 K in crystal 1).

#### IV. DISCUSSION

Small elastic hysteresis between cooling and heating of unpoled PZN-4.5%PT through the  $t \leftrightarrow c$  transition has been observed previously<sup>28</sup> and is typical of first-order transitions. Some elastic hysteresis between poled and unpoled crystals was also expected since the bulk piezoelectric properties of a preferential alignment of  $t$  or  $r$  domains will differ from those of a crystal with randomly oriented domains. A small hysteresis ( $\sim 2$  standard deviations) in the NMR relaxation time  $T_2$  and a small surface strain difference due to poling in PMN crystals have been reported.<sup>29,30</sup> More obviously connected to this work is the memory effect in diffuse neutron scattering from PZN-8%PT. In that work, field cooling from above  $T_F$  (their  $T_C$ ) enhanced one side of the diffuse scattering at 300 K whilst the other side remained unchanged. Heating to 500 K ( $>T_F$  but  $<T^*$ ) removed the effect, i.e., it is clearly associated with the *ferroelectric* phase below  $T_F$  via domain walls or wall-PNR interactions. Remarkably though, the effect was remembered upon returning the same crystal to 300 K in zero field. The effect survived many cycles of heating to 500 K but was lost when the crystal was heated to 525 K (above our  $T^*$ ). The cause could not be pinpointed as the diffuse scattering is insensitive to differences between poled and unpoled crystals above  $T_F$ .

In contrast, the piezoelectric polarization memory observed here persists well beyond the  $t \rightarrow c$  transition, to  $T^* \approx 470$ –475 K in the 4.5%PT crystals and to  $T^* \approx 505$  K in the 8% PT crystal. The source of the diffuse scattering memory effect is revealed as poling induced elastic softening. Some structural feature of PZN-PT crystals remains statically mechanically polarized up to  $\sim 50$  K above  $T_F$ , and it seems inescapable that this is the PNR. In other words, our  $T^*$  ( $\approx T_F + 50$  K) represents a temperature below which the PNR form a stable, static microstructure that is dynamically polarizable by an electric field, is retained within the matrix of rhombohedral and tetragonal phases, and is not disrupted by  $r \rightarrow t$  or  $t \rightarrow c$  transitions. Recalling that there is no static electric polarization above  $T_F$ ,<sup>31</sup> theories of the relaxor state in these materials must now explain structures at  $T < T^*$  that are *mechanically* polarized (i.e., show elastic softening in RUS due to poling) and yet retain no net *electric* polarization in zero field.

An equally striking result is that a large proportion of the elastic softening on poling can be directly attributed to the PNR. This is emphasized by the difference  $\Delta 1/2(C_{11}-C_{12})$ , shown in Fig. 3. With falling temperature below  $T_B$  ( $\sim 750$  K in PZN<sup>31</sup>) softening of elastic constants in cubic PMN and PZN-PT has been reported<sup>17,32</sup> and is visible for PZN-4.5PT in Fig. 2. However, in the cubic phase above  $T_F$ , there should not be differences between poled and unpoled crystals so long as the average PNR lifetime is short. Instead, the figure demonstrates that the hysteresis below  $T^*$  for PZN-4.5%PT reaches a maximum value at  $\sim 450$  K, well within the cubic phase. In other words, the influence on the elastic properties of

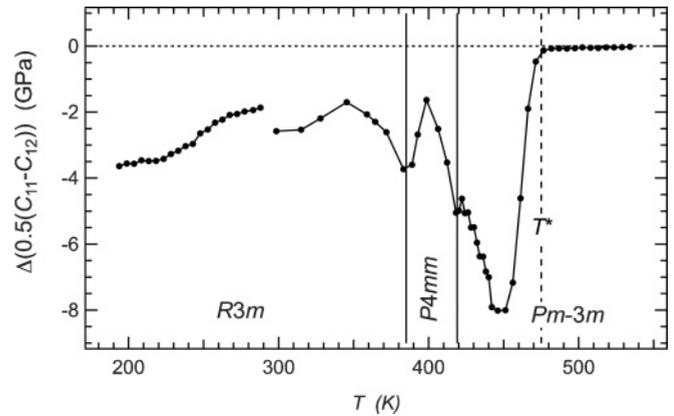


FIG. 3. Piezoelectric softening due to poling shown as the difference  $\Delta 1/2(C_{11}-C_{12})$  between poled and depoled states in Fig. 2. Stability ranges for the  $r$ ,  $t$ , and  $c$  phases are shown.

polarized PNR alone is far greater than the effect of polarizing conventional  $r$  or  $t$  ferroelectric domains.

Variations in  $Q^{-1}$  highlight strain-related dynamic effects associated with the PNR. The steep increase in  $Q^{-1}$  below  $\sim 445$ –460 K in PZN-4.5%PT is typical of a phase transition giving a *ferroelastic* microstructure, except that it occurs above  $T_F$ . This is consistent with acoustic dissipation, evidence that at  $\sim 500$  K a microstructure depending on strain relaxations appears within the macroscopically cubic phase of PZN-PT.<sup>18,19</sup> Both this and the polarization memory effect are consistent with the development of local order coupled to static strain fields but not correlated over sufficient distance to break the macroscopic symmetry.

A higher density of conventional (improper ferroelastic) twin walls in the depoled crystals is expected to contribute additional anelastic losses at  $T < T_F$ , and the markedly weaker/broader resonance peaks observed during cooling confirm this. The depoled crystals became almost superattenuating as observed for  $\text{LaAlO}_3$ .<sup>33</sup> An additional change in acoustic dissipation below  $\sim 200$  K, well within the rhombohedral stability field, is not understood but perhaps relates to freezing of twin wall and/or PNR interface motion. Freezing of macroscopic domain wall motion in PZN-PT crystals (without an external electric field) has previously been reported near 243 K.<sup>34</sup>

Evidence for a stable, static PNR microstructure at  $T < T^*$  in PZN-4.5%PT must be reconciled with evidence for dynamical effects in the same temperature range. The effective correlation length of local ordering increases with falling temperature but the increase appears to be steepest between 500 and 450 K, where it goes from  $\sim 20$  to  $\sim 50$  Å.<sup>14</sup> Brillouin scattering central peak line widths indicate a concomitant slowing of relaxational modes.<sup>16,17</sup> The central peak is characteristic of relaxor ferroelectrics and is clearly related to the atomic displacements within PNR. In PZN-PT, it persists down to at least room temperature, showing that relaxation processes do not fully freeze out at  $T^*$  or at  $T_F$ .<sup>17</sup> Neutron diffuse scattering has provided ample evidence for the geometry of atomic displacements but the recent addition of spin-echo measurements has shown that the *static* component changes from  $\sim 35\%$  at 550 K to  $\sim 56\%$  at 400 K,  $\sim 74\%$  at 300 K, and  $90\%$  at 200 K.<sup>12</sup> Similarly, high-temperature dielectric

spectroscopy shows frequency independence of the real part of the complex permittivity and then frequency-dependent maxima in the temperature range  $\sim 420\text{--}450$  K at  $0.5\text{--}500$  kHz.<sup>35</sup> This frequency dependence is well understood as a slowing down of flipping motions of the locally polarized regions. The issue then comes down to the length scale and timescale over which the correlated changes in polarization occur. The macroscopic perspective provided by the polarization memory observed here is consistent with an emerging consensus for both PZN-PT and PMN that  $T_B$  determined from electro-optic and related techniques<sup>31</sup> marks the appearance of purely dynamic PNR, but  $T^*$  marks a structural transition that produces statically polarizable nanodomains.<sup>13–17,20–22,36,37</sup> The dynamics above  $\sim T^*$  are of the entire ensemble of PNR, while the dynamics below  $\sim T^*$  are effectively of the allowed polarizations ( $\pm 180^\circ$ ) within mechanically (elastically) static PNR. It has been argued from high energy-resolution neutron scattering experiments on PMN that this lower characteristic temperature  $T^*$  better fits Burns and Dacol's definition<sup>31</sup> and is therefore the true Burns temperature  $T_B$ .<sup>38</sup> This depends on interpretation of the original definition<sup>31</sup> that does not explicitly

state whether the local polarizations are static or dynamic. Although PNR in poled crystals below  $T^*$  are static in terms of their elastic and related properties, it must be recalled that they display no electric polarization. They therefore have distinct preferred orientations within the crystals (are mechanically poled) but must experience random  $180^\circ$  flipping of the electric polarization in zero field over a wide temperature range. Given that the exact nature of the PNR is yet to be understood, we feel the current definitions  $T_B$  and  $T^*$  are sufficient for the present.

We close by reemphasising that in PZN-PT the influence of poling the PNR on the piezoelectric properties [e.g.,  $1/2(C_{11}-C_{12})$ ] is much greater than the influence of poling the ferroelectric domains and may be the most important contributing factor to the remarkable macroscopic properties of relaxor ferroelectrics.

This work was supported by ARC grants DP0666166 and LE0453426, AINSE, and AMRFP. RUS facilities at Cambridge were established through grant NE/B505738/1 from the NERC. Our thanks to Chris Howard for many helpful discussions.

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