Letter

Weak low-temperature polarity in a PbZrO₃ single crystal

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We report the existence of a low-temperature polar phase in PbZrO₃ below 270 K. The temperature dependence of resultant polarization was assigned from pyroelectric current changes measured after poling the single crystal or ceramic in a DC electric field. This was observed in single crystals and ceramics and may have a connection with the presence of polar (ferrielectric) antiphase boundaries inside the antiferroelectric phase. The transition point is demonstrated by changes in domain structure and anomalies in dielectric permittivity and losses in as-grown single crystals and ceramic samples.

I. INTRODUCTION

The discovery of lead zirconate in the 1950s became of considerable interest to scientists working on the fundamentals of antiferroelectricity and the theory of phase transitions. If not for that discovery, the perovskite $PbZr_xTi_{1-x}O_3$ (PZT) oxide ferroelectrics, with its enormous number and variety of piezoelectric applications, would not exist. More importantly, as the first antiferroelectric material ever discovered [1], it has become the archetype for antiferroelectricity and the basis for research on related functionalities such as energy storage or the negative electrocaloric effect [2,3]. On the other hand, the nature of antiferroelectricity in $PbZrO_3$ (PZ) and the complexity of its phase diagram continue to surprise. Despite being a 70-year-old material, in just the last decade discoveries have been made regarding its complex phase transition mechanism at T_C [4–6]; an unconventional paraelectric phase with polar regions and a triple point at which the cubic phase, modulated phase, and unmodulated phase coexist [7]; jerky domain wall propagation [8]; a flexoelectric effect [9]; giant negative electrocaloric effect [2,3,10]; a unit-cell-wise energy storage pathway and transient phase with cycloidal order of polarization [11]; and anomalously slow relaxation times for changes in the order parameter in response to an induced shear strain [12]. It was also reported that the thermal conductivity of antiferroelectric PZ can be bidirectionally switched upon the application of an electric field or thermal excitation [13].

In this context, perhaps the greatest unsolved question about PZ is the crystal symmetry of its ground state, particularly whether it is truly antipolar. As early as 1951, Roberts [14] reported that ceramic PZ is polar at room temperature based on observation of a piezoelectric effect of the order of 10^{-13} pm/C. That same year, in the paper where the antiferroelectric crystal structure of PZ was reported [15], Sawaguchi *et al.* stated that PZ could be ferroelectric if only Pb ions, independently from their in-pair antiparallel shifts in the orthorhombic *ab* plane, can make a small displacement along the *c* axis. Many structural and lattice dynamics experiments dealing with the symmetry of the PZ phase at room temperatures have established that this phase is both centrosymmetric and antiferroelectric. These examples illustrate that the antipolar vs polar question of PZ is as old as the material itself.

This paper presents experiments showing evidence of a low-temperature transition in ceramics and single crystals of PZ. The experimental evidence includes dielectric, pyroelectric, Raman scattering, and optical domain structures in PZ single crystals. So far such properties have not been studied from room to liquid nitrogen temperature; however, there is an article by Lawless [16] describing some glasslike properties of ceramic PZ below 40 K but not a phase transition.

II. EXPERIMENTAL METHODS

Investigations were made on two PZ single crystals denoted as A and B and one ceramic sample. The sizes of the single crystals A and B were $3.25 \times 3.375 \times 0.19$ mm (thickness) and $2.069 \times 1.797 \times 0.04$ mm (thickness), respectively, and the ceramic was $3.95 \times 4.125 \times 0.19$ mm (thickness). Details of the experimental techniques used are contained in the Supplemental Material [17].

Dielectric properties. Examples of the temperature dependence of the permittivity $\varepsilon\prime$ and dielectric losses $\varepsilon\prime\prime$ at a frequency of 10 kHz for a single crystal and ceramic with
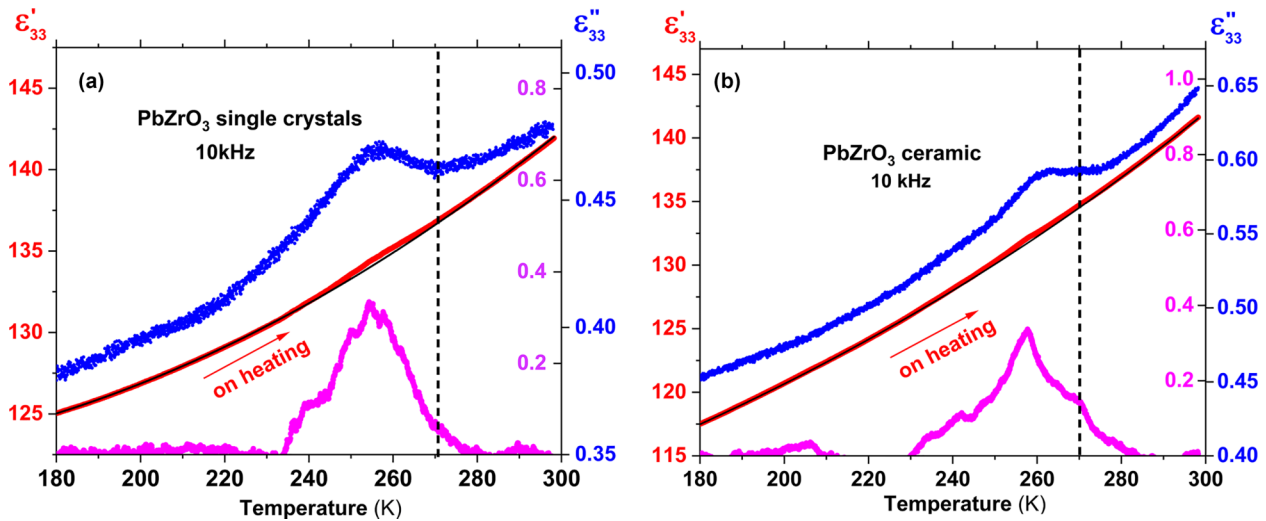
FIG. 1. (a) Low-temperature dependence of the real $\varepsilon\prime$ and imaginary $\varepsilon\prime\prime$ permittivity for a single crystal A in the [001] pseudocubic direction and (b) ceramic of $PbZrO_3$. The continuous black line is a fit to an exponential function to show that the difference between the experimental and exponential fit (pink curves) has an anomaly near 270 K, where the pyroelectric effect is observed (see Fig. 2).

silver electrodes are presented in Fig. 1. Between 230 and 280 K, the permittivity and the dielectric losses reveal a bump with a diffused maximum near 260 K. This maximum was observed for each frequency used and was not dependent on the frequency, as it is observed for relaxors. Although the dependence on heating and cooling was similar, the dielectric losses shifted about 20 K towards lower temperatures.

III. PYROELECTRIC PROPERTIES

Distinct changes of the pyroelectric current $I_p(T)$ reveal an inflection point in the $P(T)$ dependence (two I_p peaks), consistent with the existence of at least one transition, and possibly two from a polar to a nonpolar phase upon heating (Fig. 2). The polarization values for the single crystals and ceramics are different. This will be discussed further below. In Figs. 2(b) and 2(c), immediately after the transition point, small negative changes in polarization, characteristic of vanishing space charges, partly screening the polarization of the order of 0.1 and 0.25 nC/cm^2 were observed.

We also tried to observe the polarization-electric field hysteresis loop. For the PZ single crystal, for which the pyroelectric effect was observed, no such hysteresis was observed up to electric field of 150 kV/cm. Thus, the low-temperature polar phase, if it is switchable, has a coercive field bigger than the breakdown field of the sample. Double-hysteresis loops in bulk antiferroelectric PZ could only be measured near the transition to the paraelectric state at 508 K [2,18].

IV. OPTICAL PROPERTIES–DOMAIN POPULATIONS

During a structural transition a change in domain structure takes place. The Metripol setup allowed observation of the distribution of the optical indicatrix orientations in a multidomain PZ crystal. It can be recognized in Fig. 3 that complex indicatrix orientations in the as-grown PZ single crystal of thickness 25 µm undergo temperature changes. In the orthorhombic symmetry of the antiferroelectric phase,

the indicatrix may take the 0°, 45°, 90°, 135°, and 180° orientations to the [100] pseudocubic axis [19], and all of these orientations, but mostly at 0° and 180°, are present in Fig. 3(a). These other orientations may appear due to the observed transition to the predicted *Ima*2 orthorhombic phase [19]. Although this phase also has orthorhombic symmetry, like *Pbam*, and therefore should have the same optical indicatrix properties and no drastic optical change at transition, it does not exclude the appearance of additional orientations of domains (optical indicatrices) during the transition, probably because of stresses induced by domain walls or extended defects. That is why the birefringence experiments distinguished the two phases, below and above 270 K: the red-shadowed region in Figs. 3(a) and 3(b) indicate exemplary changes in the population of the indicatrix oriented at 135°. This diffuse behavior in the indicatrix orientations [green and brown lines in Fig. 3(c)] takes place in temperatures at which the changes of the dielectric and pyroelectric properties were observed (Figs. 1 and 2).

V. RAMAN SCATTERING

Raman scattering is an extremely sensitive method for monitoring changes in lattice vibration frequencies at a transition. The measurements were performed for a PZ single crystal with the light spot focused on a single domain. Some Raman lines disappear at various temperatures, with most of the changes [notably in the Zr-O stretching modes and the lowest-frequency Pb−(ZrO_3) lattice mode] taking place in the temperature range in which the dielectric and pyroelectric anomalies were detected. We did not record any high-frequency Raman lines from OH bond vibrations in all the measured spectra (this excludes the presence of water turning into ice around the critical temperatures).

Low-temperature Raman and IR scattering experiments were reported in the article [5]. This article presents the temperature dependence of squared frequencies of the detected modes at low temperatures. Although the number of
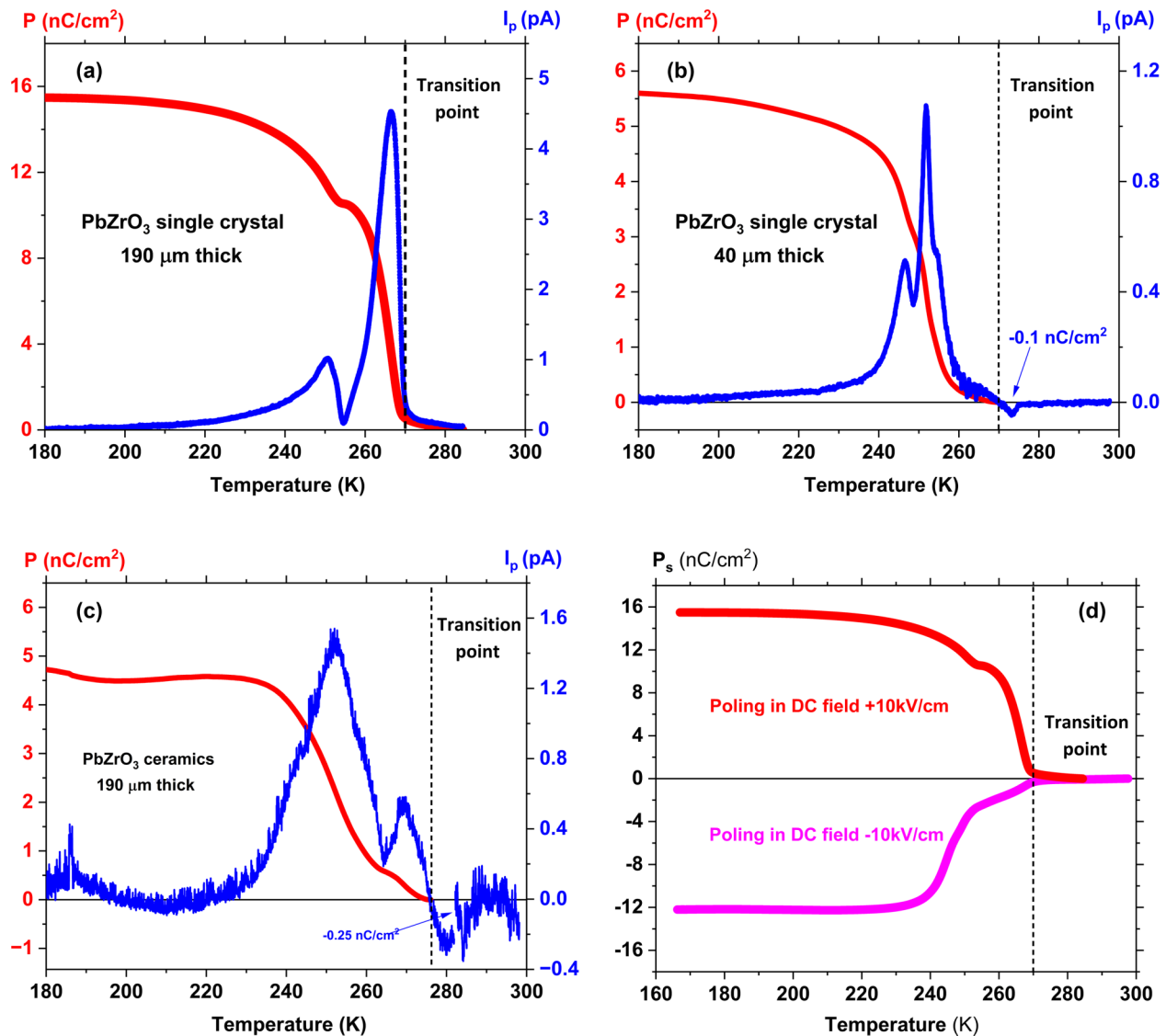
FIG. 2. Polarization P calculated from temperature changes of the total pyroelectric current I_p, on heating, for the PZ single crystals (a) A, (b) B, and (c) ceramic. The I_p originates from the primary and secondary pyroelectric effects. (d) Reversibility of the pyroelectric signal for crystal A poled in a DC field of intensity +10 and -10 kV/cm. The inequality in polarization may be due to the inability of the polarization to be completely reversible owing, e.g., to its partial pinning on structural defects.

FIG. 3. Temperature dependence of the domain populations δ_d on (a) heating and (b) cooling, calculated for the yellow highlighted rectangle shown on an exemplary orientational map in 230 K in (c). The a, b, and c axis in (c) mark the pseudocubic axes. To observe continuous changes in the domain populations, presented only for certain temperature points in (a) and (b), see the Supplemental Material [17].

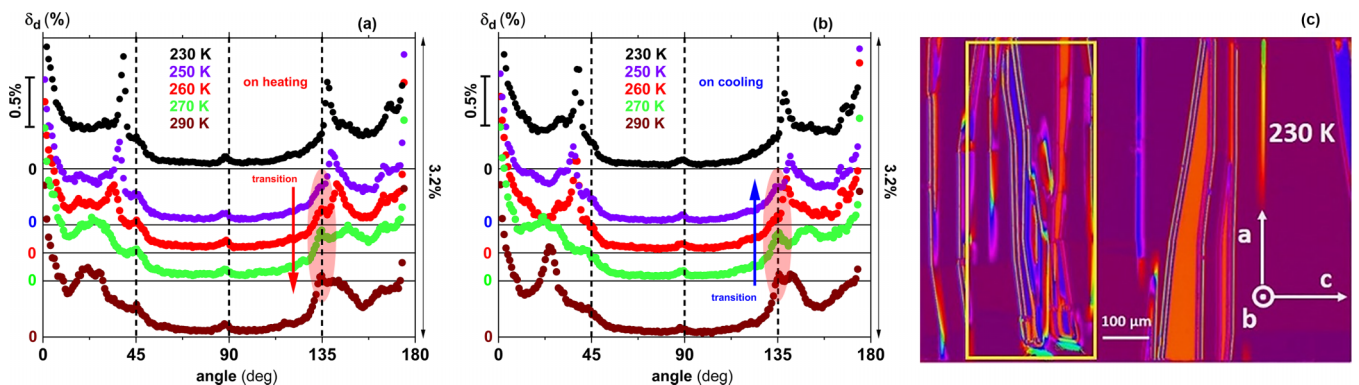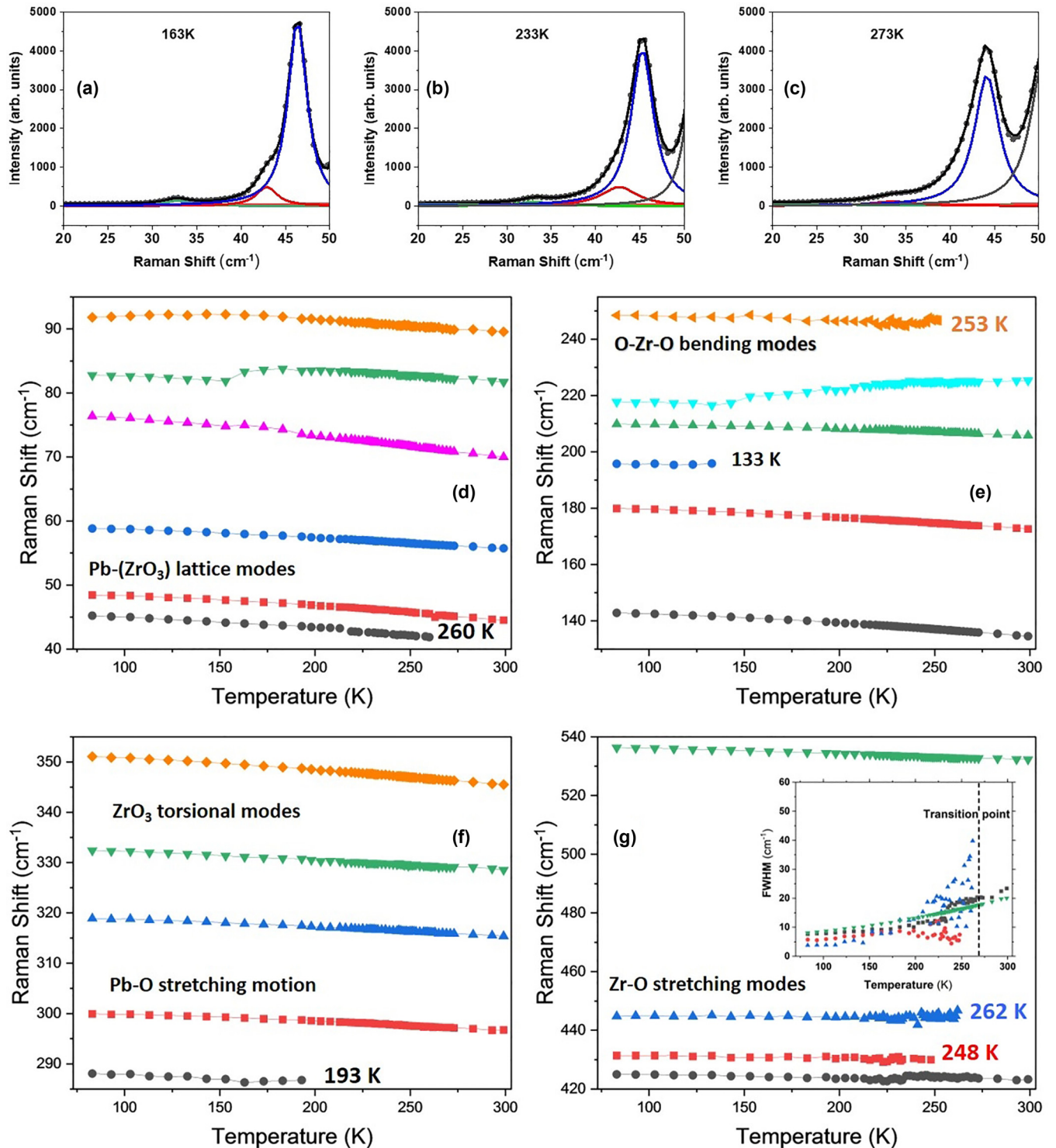FIG. 4. (a–c) An example of the disappearance of the low-frequency Raman line (red line) near the observed transition. (e–g) Temperature dependencies of all Raman modes in the PZ single domain detected in the [001] pseudocubic direction on heating. Note the temperatures at which some Raman lines disappear. Two lines in (g) (red and blue) disappear at the temperature corresponding to the transition in Figs. 1–3. The assignment of frequencies to lattice modes has been made based on data in Refs. [5,21–23]. The inset in (g) shows the temperature dependence of the FWHM for Zr-O stretching modes.

experimental points is much smaller than in our Fig. 4, it might be recognized that some modes (Fig. 4(g) in Ref. [5]) disappear at the temperature point where the phase transition, discussed in this paper, occurs.

Discussion. This paper presents experiments showing evidence of a low-temperature transition in ceramics and single crystals of PZ. The onset of a pyroelectric current suggests a polar low-T phase, but the polarization found is orders of

magnitude lower than the recent predicted (ferrielectric) polarization [20]. Therefore this transition likely has an alternate origin, as discussed in this Letter.

The subtle and weak magnitude of the polarization raises questions. The first is whether this is a bulk transition between two intrinsically stable states or a locally confined one associated with defects like skin layers, dislocations, or vacancies. The small value of the polarization might reflect no SHG signal observations for powder and single crystals down to 90 K (Fig. 2). One possibility is that the transition is confined within a surface skin layer [24,25]. If so, one would expect the polarization for poled ceramics (consisting of small grains and thus with a larger surface-to-volume ratio) to be greater than for the single crystal. Yet the data in Fig. 2 contradict this: the largest polarization was measured in the thickest single crystal. Suppose defects like dislocations or vacancies are the origin. In that case the problem is the reverse: how come the magnitude of the polarization is so similar across the samples despite their very different morphologies?

We examine the bulk phase transition scenario as follows. The temperature dependence of the Raman lines is consistent with the existence of such a low-temperature transition near 270 K. The gradual disappearance at 193, 248, 253, and 260 K, and especially at 262 K prescribed to a Zr-O stretching mode (Σ_3 mode), occurs in a temperature zone where the pyroelectric current starts increasing and then disappears. Also, the local peak in the $I_p(T)$ plots before the transition point may testify to the gradual disappearance of vibrational modes. It is worth emphasizing that the Raman scattering experiments were done on a PZ single domain single crystal not subjected to external factors other than temperature. In addition, as mentioned earlier, there is a clear change in the domain populations approaching the transition point, as shown in Fig. 3 and the Supplemental Material [17]. It has to be added that the transition was robust and repeatable, i.e., it was observed on several heating and cooling cycles. Hence, we can conclude that between 250 and 270 K, a homogeneous phase transition occurs to a weakly polar low-temperature phase.

Most structural refinements have not dealt with the possibility of a structural transition at low temperatures, although some of us suggested, based on low-temperature x-ray diffraction and neutron diffraction, the possibility of an order–disorder transition involving the oxygens below room temperature [26]. In addition, we detected a definite, although small, approximately 0.008(4) Å, departure of the Zr atom from the $z = 0.25$, 0.75 planes, not previously visible in the earlier room-temperature structure determinations [26]. Thus the observed transition might be associated with a change in oxygen order. A piece of evidence for a low-temperature polar phase comes from high-field experiments by Fesenko *et al.* [27], who observed triple-hysteresis loops below 200 K.

An article by Aramberri *et al.* [20] raised the possible polarity of a PZ low-temperature phase. Using first-principles DFT simulations, the ferrielectric phase *Ima*2 becomes more stable than the *Pbam* (and the related *Pnam* proposed in [28]) at 0 K. Under the harmonic approximation, the PZ may not be

antiferroelectric even at ambient conditions. The *Ima*2 symmetry is orthorhombic like the *Pbam* antiferroelectric phase, which might explain no distinct changes in the morphology of the ferroelastic domains (Fig. 3) nor differences between high-*T* and low-*T* x-ray spectra. Also, the observed transition is close to 255 K, suggested in [20] as the lowest limit of the ferrielectric phase. However, the polarization predicted in that paper was $11 \, \mu C/cm^2$, which is about 1000 times bigger than our pyroelectric measurements. One possible explanation for the discrepancy might be that the poling fields are insufficient to saturate the polarization, although the application of DC poling fields greater than 10 kV/cm did not increase the polarization value in our field-cooling experiments. It is also worth stressing that both orthorhombic symmetries *Ima*2 and *Pbam* are not in a group-subgroup relation, and thus a transition between both phases would necessarily be discontinuous (possibly diffusive) and not mean field. Although we have experimental evidence about a phase transition in PZ in low *T*, we cannot attribute it to a homogeneously distributed phase, particularly the *Ima*2 phase.

Note, though, that the *Ima*2 symmetry has been identified in PZ within the polar translational boundaries (TBs) at room temperature [29]. It has to be mentioned that polar translation boundaries have already been reported theoretically [30] and experimentally [31,32]. Cooling the samples under a DC field might lead to the poling of these TBs in the DC field direction and/or their growth. This would also account for the small value of polarization observed in the pyroelectric experiments since the polarization is calculated for the area of the electrodes, not for the area occupied by TBs. The observed transition might thus be connected with, e.g., temperature changes in the magnitude of the polarity of the translational boundaries, clearly revealed when the DC electric field is applied.

We can thus conclude that we have identified an additional low-temperature transition in PZ, possibly due to an inhomogeneous phase associated with translational boundaries, and we have verified that the bulk crystal and ceramics are indeed weakly polar at low temperatures. This is opposite to the current understanding of the PZ, and thus we expect our discovery to stimulate further research into this difficult material.

APPENDIX

In the paper by Fujishita *et al.* [33], there are reported small unit cell changes at temperature, below which we have observed weak polarity of lead zirconate single crystal and ceramics.

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