

Polarization Rotation via a Monoclinic Phase in the Piezoelectric 92% PbZn_{1/3}Nb_{2/3}O₃-8% PbTiO₃

B. Noheda,^{1,*} D. E. Cox,¹ G. Shirane,¹ S.-E. Park,^{2,†} L. E. Cross,² and Z. Zhong³

¹Physics Department, Brookhaven National Laboratory, Upton, New York 11973

²Materials Research Laboratory, Pennsylvania State University, University Park, Pennsylvania 16802

³National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973

(Received 18 September 2000)

The origin of ultrahigh piezoelectricity in the relaxor ferroelectric PbZn_{1/3}Nb_{2/3}O₃-PbTiO₃ was studied with an electric field applied along the [001] direction. The zero-field rhombohedral *R* phase starts to follow the direct polarization path to tetragonal symmetry via an intermediate monoclinic *M* phase, but then jumps irreversibly to an alternate path involving a different type of monoclinic distortion. Details of the structure and domain configuration of this novel phase are described. This result suggests that there is a nearby *R*-*M* phase boundary as found in the Pb(Ti, Zr)O₃ system.

DOI: 10.1103/PhysRevLett.86.3891

PACS numbers: 77.65.-j, 61.10.Nz, 77.84.Dy

Recently, two important advances have been made in searching for the origin of high piezo response in the perovskite oxides. One is a theoretical consideration [1–3] of the polarization rotation path under an electric field, emphasized by Fu and Cohen [1]. The second is the experimental discovery of a monoclinic phase in Pb(Ti, Zr)O₃ [4,5] close to a “morphotropic” phase boundary (MPB), a nearly vertical line between the rhombohedral and tetragonal phases. In this paper we demonstrate that these two seemingly disparate aspects are closely connected.

Solid solutions of Pb(Zn_{1/3}Nb_{2/3})O₃ containing a few percent of PbTiO₃ (PZN-*x*PT) are relaxor ferroelectrics with ultrahigh piezoelectric responses an order of magnitude larger than those of conventional piezoelectric ceramics [6–8]. They have a cubic perovskite-type structure at high temperatures, but undergo a diffuse ferroelectric phase transition at lower temperatures [6]. Materials in the ferroelectric region have structures with either rhombohedral or tetragonal symmetry, separated by a morphotropic phase boundary at *x* ≈ 10%, similar to that of the well-known piezoelectric system PbZr_{1-*x*}Ti_{*x*}O₃ (PZT) [9]. Extraordinarily high levels of electromechanical coupling and strain have been reported by Park and Shrout [8] in rhombohedral crystals that are poled along [001], despite the fact that the polar axis lies along [111] [7,10].

A typical strain-field loop for the rhombohedral composition 92%PbZn_{1/3}Nb_{2/3}O₃-8%PbTiO₃ (PZN-8%PT) (close to the MPB) with an electric field applied along [001] is plotted in Fig. 1 (top), after Durbin *et al.* [11]. For this poling configuration, the strain behaves linearly below a certain threshold field, which is smaller for compositions closer to the MPB [8,10]. This feature, together with the high strain levels obtained, makes these materials very promising for actuator applications. Above the threshold field, the strain shows a sharp jump, nonlinear behavior, and hysteresis. X-ray diffraction experiments performed on PZN-8%PT crystals under an applied electric field [11] have shown that the lattice parameter vs field loop exactly

reflects the strain behavior, confirming that the high macroscopic strain levels observed are due to the microscopic strain of the crystal lattice. The jump observed at the threshold field was attributed to a structural phase transition between the rhombohedral and the tetragonal phases. Very recently, it was also reported that the high-field tetragonal phase changes, after removal of the field, into a mixture of a dominant monoclinic phase with a remnant tetragonal phase [12].

Our current study with high-energy x rays of 67 keV gives a very different picture. We show that the rhombohedral phase in the unpoled sample transforms into a purely monoclinic phase by the application of an electric field along the [001] direction which, surprisingly, remains monoclinic after the field is removed. This monoclinic phase, in which *b_m* is directed along the pseudocubic [010] axis, is not the same as that observed in PZT, in which *b_m* lies along pseudocubic [110] [4]. The monoclinic phase in PZT represents the *a-g-f-e* path (see Fig. 1, bottom) proposed by Fu and Cohen [1] for the polarization to rotate between the rhombohedral and the tetragonal phases, while the monoclinic PZN-8%PT phase represents the rotation path along *a-c-d-e*.

Four crystals with composition PZN-8%PT, grown by the high temperature flux technique [8,13], were kindly provided by the authors of Refs. [11,12]. The crystals were oriented using a Laue backreflection camera as described previously [8], and cut into 2 × 2 × 2 mm³ cubes with their faces perpendicular to the ⟨100⟩ directions.

Synchrotron x-ray diffraction measurements were initially performed at beamline X7A, at the National Synchrotron Light Source (NSLS), with x rays of about 18 keV from a Si(111) double-crystal monochromator. Because of the high lead content, the samples are quite opaque at these energies, with a penetration depth of only about 1 μm, at the typical scattering angles used, and the measurements are therefore sensitive to inhomogeneous piezoelectric strains close to the surface (skin effect). In order to avoid this

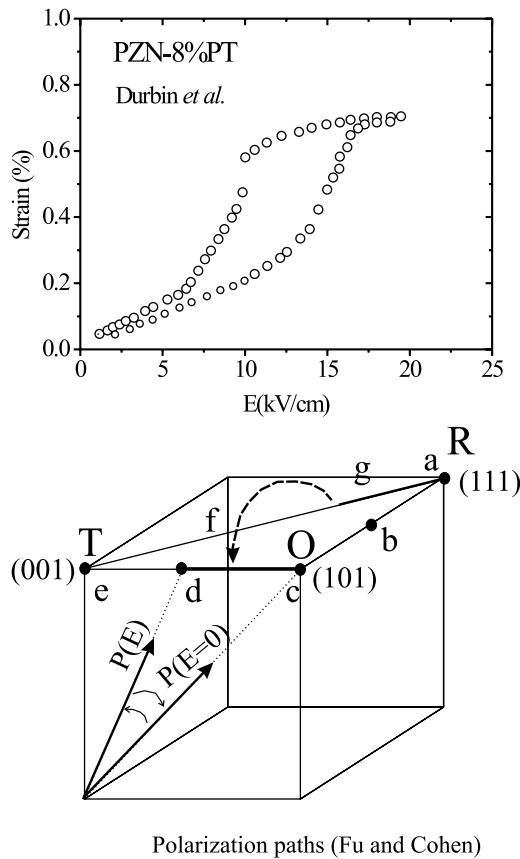


FIG. 1. Top: strain-field loop for PZN-8%PT (after Durbin *et al.* [11]). Bottom: scheme of the two possible paths (R - T and R - O - T) for the polarization direction to change from $[111]$ in the rhombohedral (R) phase to $[001]$ in the tetragonal (T) phase, as proposed by Fu and Cohen [1]. The thickest lines represent the path followed by the polarization in PZN-8%PT under the application of the electric field, as demonstrated by this work. The solid arrows illustrate the orientation of the polarization in a particular domain with and without an electric field.

effect, high-energy x-ray experiments were performed at 67 keV at the superconducting-Wiggler beamline X17B at the NSLS.

The 67-keV x rays were obtained with a Si(220) Laue-Bragg monochromator, and the measurements were made on a four-circle Huber diffractometer equipped with a Si(220) analyzer, with an electric field applied to the crystal *in situ*. For this purpose thin wires were attached to the sample electrodes using a small drop of conducting epoxy, and a silicon grease with a high dielectrical breakdown was used to prevent arcing.

As-grown crystals of the composition under study are rhombohedral [6,8] (see Table I). However, when an electric field above a certain value is applied, the crystal symmetry changes and the rhombohedral phase can only be recovered either by annealing above the Curie temperature or by crushing the crystal. The initial rhombohedral state and the phase transition(s) undergone during the first field cycle are currently under investigation by Ohwada [14].

Once the rhombohedral phase is irreversibly transformed into the monoclinic one, the monoclinic lattice

TABLE I. Lattice parameters, unit cell volume, and symmetry of PZN-8%PT as-grown, under a high field of 20 kV/cm, and after the field is removed. S denotes the crystal symmetry.

	a (Å)	b (Å)	c (Å)	α/β (°)	V (Å ³)	S
As-grown, $E = 0^a$	4.053	4.053	4.053	89.90	66.58	R
$E = 20$ kV/cm ^b	4.047	4.029	4.086	90.16	66.62	M
After field, $E = 0^{a,b}$	4.061	4.030	4.061	90.15	66.46	M

^aFrom powder diffraction.

^bFrom single crystal diffraction.

shows reversible changes as a function of the electric field, as shown in Fig. 2 (see also Table I). The monoclinic angle, $\beta = 90.15^\circ$, and the monoclinic axis, b_m , are field independent in the studied range between 0 and 20 kV/cm. c_m increases with the electric field and shows a jump at about 15 kV/cm and hysteresis, in agreement with Durbin *et al.* [11], while a_m decreases as the field is increased and approaches the c_m value in the $E = 0$ limit [15].

The domain configuration observed in this experiment is illustrated in the representations of the reciprocal space shown in Fig. 3 [16]. Usually monoclinic symmetry leads to a very complicated domain configuration. However, once the field is applied, a much simpler situation prevails. The c axis is now fixed along the field direction. As shown in the representation of the HK0 plane in Fig. 3a, there are only two b domains related by a 90° rotation about the c axis. Each of these b domains contains two a domains in which a_m forms angles of either β or $180^\circ - \beta$, respectively, with c_m (see Fig. 3b). The polarization vectors in each of the four domains, which rotate under the electric field within the ac plane, form identical angles with the $[001]$ direction. It is evident from Fig. 3a that the domain twinning confers upon the lattice a pseudotetragonal symmetry, which might account for the previous assignment of tetragonal symmetry to this phase based on optical measurements [13].

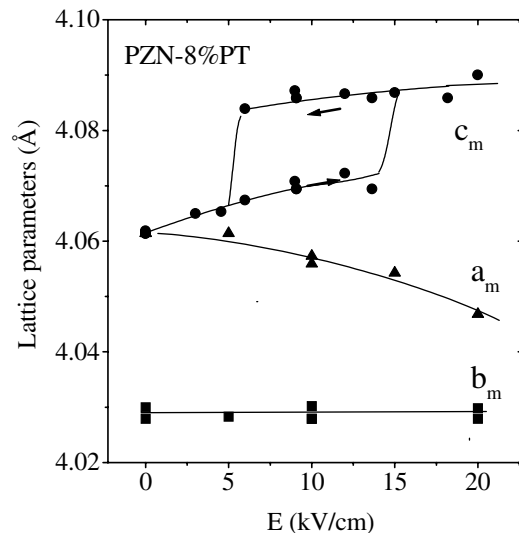


FIG. 2. Evolution of the lattice parameters, a_m , b_m , and c_m , of PZN-8%PT with electric field. No change in the monoclinic angle, β , is observed in this range of fields.

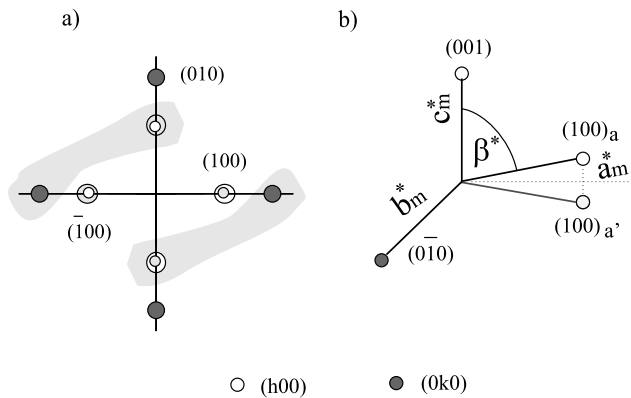


FIG. 3. (a) HK0 plane in reciprocal space for monoclinic PZN-8%PT showing the two b domains at 90° , shaded and unshaded, in which H and K are interchanged with respect to each other. The double circles represent the two a domains, illustrated in b. (b) Scheme of the reciprocal unit cell of one of the b domains showing the two a domains, a and a' , respectively.

Some examples of the x-ray peak profiles are shown in Fig. 4. The longitudinal scans over the (002) reflection at 0 kV/cm and at 20 kV/cm shown in the upper left of the figure illustrate the drastic change of the c axis with the electric field ($L = 2$ corresponds to the $c_m = a_m$ value at $E = 0$). The very narrow mosaic at high fields is apparent in the upper right of the figure, which shows a transverse scan (L scan) over the (020) Bragg peak at $E = 20$ kV/cm ($K = 2$ corresponds to the $c_m = a_m$ value at $E = 0$ so $K = 2.015$ means $b_m/a_m = 2/2.015$). The lower part of the figure is a contour map of the HOL zone around (200) after removal of the field, which shows the b domain containing the two a domains illustrated in Fig. 3a and 3b. The symmetric splitting along the transverse direction (L scan), corresponds to the twin angle between the a domains, so the L coordinate of 0.005 corresponds to a monoclinic angle $\beta = 90.16^\circ$ that is found to be independent of the electric field. Although the (020) peak is very narrow, a small shoulder can be observed at positive L values (also present at 20 kV/cm, in the upper-right plot), which probably results from the crystal mosaic.

The low-energy experiments at 18 keV essentially reproduce the results obtained by Durbin *et al.* [11,12]. The c_m lattice parameter along the field direction [001] exhibits the same strongly nonlinear field dependence illustrated in Fig. 2. Measurements made with the scattering vector perpendicular to the field direction after the field was removed show the same characteristic diffraction features as recently reported [12], namely, a very broad peak on the low-angle side and a very sharp peak on the high-angle side, corresponding to $H = 2.000$ and $K = 2.015$, respectively. The broad peak changes with field while the sharp peak is field independent, in agreement with our high-energy x-ray results described above. The markedly different widths of these two peaks led Durbin *et al.* to postulate the coexistence of two phases (monoclinic and tetragonal) at $E = 0$ kV/cm, with very different domain sizes. However, since the broadening of the (h00) peaks was not ob-

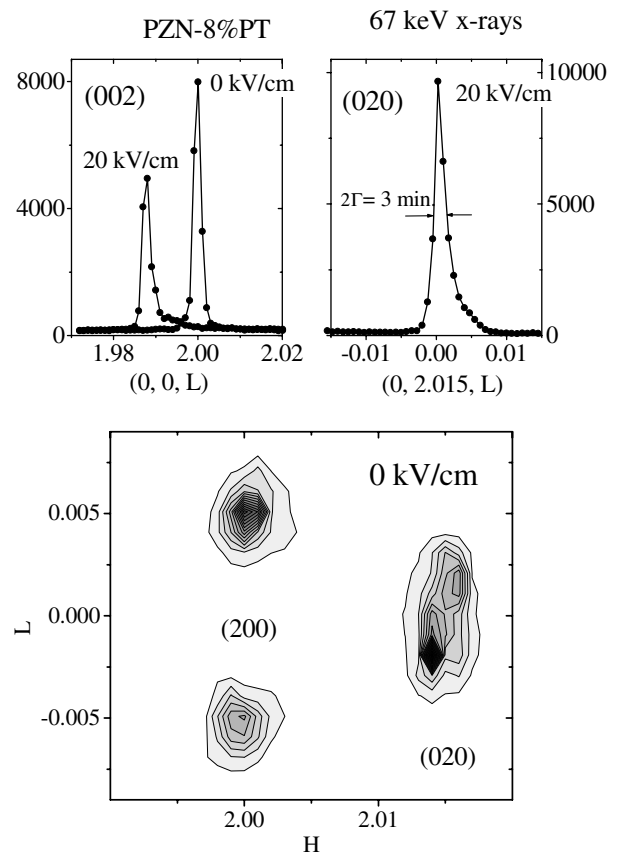


FIG. 4. Radial (L) scans over the (002) reflection at 20 kV/cm and at 0 kV/cm, after the field is removed (top left). The transverse (L) scan around (0, 2.015, 0) at 20 kV/cm is shown (top right). Bottom: an HOL mesh scan around the (200) Bragg reflection after the removal of the electric field. $H = K = L = 2.0$ have been defined to correspond to the a_m value at $E = 0$ kV/cm.

served with high-energy x rays, it can be attributed to a “skin” effect.

Powder diffraction data collected from a sample prepared by crushing a small crystal piece after the application and removal of an electric field have confirmed that the monoclinic indexing of our single-crystal experiments is correct. Lattice parameters $a_m = c_m = 4.061$ Å, $b_m = 4.030$ Å, and $\beta = 90.15^\circ$ were extracted, in complete agreement with the single-crystal data. In this case, however, the monoclinic phase was found to coexist with a rhombohedral phase with $a_r = 4.054$ Å and $\alpha = 89.9^\circ$ (see Table I).

Comparison of our experimental results with the theoretical model of Fu and Cohen [1] brings out several interesting features. These authors calculated the free energies along the polarization rotation paths between the rhombohedral R and tetragonal T points for BaTiO₃ (see Fig. 1), and concluded that the R - T path (a - g - f - e) is the most energetically favorable one. PZN-8%PT starts out at the R point in Fig. 1, since the as-grown crystal is rhombohedral, but then changes irreversibly to the O - T path (c - d - e), with monoclinic symmetry. As mentioned above, this process of change between the rhombohedral and the monoclinic

phases (dashed arrow in Fig. 1) is being studied elsewhere in detail [14]. When the field is decreased, the crystal remains on the O - T path. During this process a_m and c_m gradually approach each other until they eventually reach the same value at $E = 0$ kV/cm [15]. When the field is increased, a_m approaches b_m (see Fig. 2), while following the O - T path, approaching the T point in Fig. 1. The polarization of each domain rotates within the (010) plane, and the polarization direction gets closer to the tetragonal polar axis, [001], as the field is increased, as shown by the solid arrows in Fig. 1. However, the T point is not yet reached at the maximum electric fields ($E = 20$ kV/cm) used in this study. Work is being carried out on other compositions, such as PZN-4.5%PT and PZN-9%PT, to determine the compositional range in which this behavior is observed. The major remaining questions are why and how the sudden change at 15 kV/cm is reflected only in c_m . The jump observed in c_m is very sensitive to the mechanical stress and can be completely eliminated if the sample is slightly stressed [17]. Work is in progress to address this point.

The electric field experiments reported by Guo *et al.* [5] on rhombohedral PZT showed that, by poling at high temperatures, a monoclinic phase is also induced by the electric field and retained after the field is removed. This monoclinic cell is such that b_m lies along pseudocubic [110] [4], indicating that the polarization moves along the R - T (e - g - f - e) path when the field is applied. On the other hand, unpoled PZT has a monoclinic phase region from $x = 0.46$ to $x = 0.52$ at 20 K [18]. The existence of an irreversible rhombohedral-to-monoclinic phase transition induced by the application of an electric field in PZN-8%PT suggests that, as in the PZT case [5], a rhombohedral-to-monoclinic phase boundary exists close to $x = 8\%$ in the unpoled PZN-xPT phase diagram. This would clarify some of the apparent puzzles reported, such as the optical observation of symmetry lowering in PZN-9%PT [19,20]. If the monoclinic phase is found to exist in unpoled PZN-9%PT, then the phase diagram of PZN-PT becomes almost identical to that of PZT. Our current results suggest that the near degeneracy between the two monoclinic paths (R - T and R - O - T) might be responsible for the larger piezoelectric response in PZN-xPT, compared with that of PZT, in which only rotation is allowed. We expect that first-principles calculations may well clarify some of these important questions.

After submission of this Letter, the very relevant work by Vanderbilt and Cohen [21] came to our attention. By means of an eighth-order expansion of the Devonshire theory, these authors were able to predict three different monoclinic phases. Two of these, M_A and M_C , correspond, respectively, to that previously observed in PZT and the one in PZN-8%PT described above.

We thank M. Durbin, Y. Fujii, P. Gehring, R. Guo, J. Hastings, K. Hirota, K. Ohwada, D. Vanderbilt, and

T. Vogt for helpful discussions. Financial support by the U.S. DOE under Contract No. DE-AC02-98CH10886, by ONR Grant No. N00014-98-1-0527, and project MURI (N00014-96-1-1173) is also acknowledged.

*Corresponding author.

Electronic address: noheda@bnl.gov

On leave from Universidad Autonoma de Madrid.

†Present address: Fraunhofer Technology Center, Hialeah, Florida 33010.

- [1] H. Fu and R. E. Cohen, *Nature (London)* **403**, 281 (2000).
- [2] A. Garcia and D. Vanderbilt, *Appl. Phys. Lett.* **72**, 2981 (1998).
- [3] L. Bellaiche, A. Garcia, and D. Vanderbilt, *Phys. Rev. Lett.* **84**, 5427 (2000).
- [4] B. Noheda, J. A. Gonzalo, L. E. Cross, R. Guo, S-E. Park, D. E. Cox, and G. Shirane, *Phys. Rev. B* **61**, 8687 (2000).
- [5] R. Guo, L. E. Cross, S-E. Park, B. Noheda, D. E. Cox, and G. Shirane, *Phys. Rev. Lett.* **84**, 5423 (2000).
- [6] J. Kuwata, K. Uchino, and S. Nomura, *Ferroelectrics* **37**, 579 (1981).
- [7] J. Kuwata, K. Uchino, and S. Nomura, *Jpn. J. Appl. Phys.* **21**, 1298 (1982).
- [8] S-E. Park and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).
- [9] B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics* (Academic Press, London, 1971).
- [10] S-F. Liu, S-E. Park, T. R. Shrout, and L. E. Cross, *J. Appl. Phys.* **85**, 2810 (1999).
- [11] M. K. Durbin, E. W. Jacobs, J. C. Hicks, and S-E. Park, *Appl. Phys. Lett.* **74**, 2848 (1999).
- [12] M. K. Durbin, J. C. Hicks, S-E. Park, and T. R. Shrout, *J. Appl. Phys.* **87**, 8159 (2000).
- [13] D-S. Paik, S-E. Park, S. Wada, S-F. Liu, and T. R. Shrout, *J. Appl. Phys.* **85**, 1080 (1999).
- [14] K. Ohwada (private communication).
- [15] In the limit at which $a_m = c_m$ and $\beta > 90^\circ$, the crystal symmetry becomes orthorhombic, corresponding to the O point in Fig. 1 (bottom). This orthorhombic cell is doubled in volume with respect to the monoclinic cell, with lattice parameters $a_0 = 2a_m \sin(\beta/2) = 5.751$ Å, $b_0 = b_m = 4.030$ Å, and $c_0 = 2a_m \cos(\beta/2) = 5.736$ Å. The space group is probably $Bmm2$, by analogy to the orthorhombic phase of BaTiO₃.
- [16] The real and the reciprocal lattice parameters are related by $a_m^* = 2\pi/(a_m \sin\beta)$, $b_m^* = 2\pi/b_m$, $c_m^* = 2\pi/(c_m \sin\beta)$, and $\beta^* = 180^\circ - \beta$.
- [17] D. Viehland, *J. Appl. Phys.* **88**, 4794 (2000).
- [18] B. Noheda, D. E. Cox, G. Shirane, R. Guo, B. Jones, and L. E. Cross, *Phys. Rev. B* **63**, 014103 (2001).
- [19] Y. Uesu, Y. Yamada, K. Fujishiro, H. Tazawa, S. Enokido, J.-M. Kiat, and B. Dkhil, *Ferroelectrics* **217**, 319 (1998).
- [20] K. Fujishiro, R. Vlokh, Y. Uesu, Y. Yamada, J.-M. Kiat, B. Dkhil, and Y. Yamashita, *Jpn. J. Appl. Phys.* **37**, 5246 (1998).
- [21] D. Vanderbilt and M. H. Cohen, *Phys. Rev. B* **63**, 094108 (2001).