

Thermal expansion of phase transformations in $(1-x)\text{Pb}(\text{Mg}_{1/3}, \text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$: Evidence for preferred domain alignment in one of the $\langle 001 \rangle$ directions for melt-grown crystals

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Thermal expansion measurements on *unpoled*, multidomain, single crystals of PMN-PT in the MPB region reveal that one of the $\langle 001 \rangle$ directions is different than the other two, contrary to the crystallographic equivalency that is expected for threefold rotations about $\langle 111 \rangle$ derived from the prototypic-cubic phase. This unexpected behavior may be related to the method of seeded crystal growth. On heating into the tetragonal phase, the unique axis persists, consistent with the preferential alignment of c -axis domains. Poling along the unique direction further enhances the anisotropy in thermal expansion coefficients, leading to an increase in the magnitude of the strain induced on heating through the subsequent rhombohedral-to-tetragonal and tetragonal-to-cubic phase transformations. Room-temperature poling in the rhombohedral phase in a direction normal to the unique direction reorients the preferred domain alignment in the higher temperature tetragonal phase. This realignment disappears upon further heating into the high-temperature cubic phase, i.e., thermal depoling reestablishes the original unique direction. When the room-temperature poled crystals are heated under open-circuit conditions, the temperature at which the tetragonal-to-cubic phase transformation is completed is shifted to higher temperatures relative to unpoled crystals, indicating an increase in the temperature range of stability for the tetragonal phase as a result of incomplete randomization of domain orientations at the rhombohedral-to-tetragonal phase transformation. Under short-circuit conditions, the tetragonal-to-cubic phase transformation temperature is not shifted, indicating a complete randomization of polarization directions on heating above the rhombohedral-to-tetragonal phase transformation temperature. The thermal expansion characteristics for the phase transformation behavior are related to poling conditions and dielectric properties.

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I. INTRODUCTION

Remarkable properties have been reported in recent years for an emerging class of piezoelectric crystals based on lead magnesium niobate (PMN), or lead zinc niobate (PZN), substituted with lead titanate (PT).¹ These new material systems [e.g., $(1-x)\text{Pb}(\text{Mg}_{1/3}, \text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN-PT)] can have exceptionally large piezoelectric coefficients (e.g., $d_{33} = 3000$ pC/N, $d_{31} = -1800$ pC/N, $d_{15} = 5000$ pC/N) and electromechanical coupling factors (e.g., $k_{33} = 0.94$).² The latter implies over 90 % electro-mechanical energy conversion (k^2), and the former are approximately an order-of-magnitude greater than commercially available piezoelectrics based on polycrystalline lead zirconate titanate (PZT).³ Little is known about the basic properties of these piezoelectric crystals, or the mechanisms by which large electromechanical responses can be obtained, i.e., field-induced displacement of strain or stress-induced displacement of bound charge. These effects are enhanced by a softening of the lattice and are known to maximize in the vicinity of phase transformations. We report here thermal expansion measurements on bulk PMN-PT crystals, and give data for thermal-induced strains at phase transformations. The information should be useful for an understanding of the basic properties of PMN-PT crystals. Un-expectedly, we discover a preferred alignment of domains along one of the $\langle 001 \rangle$ directions and

document the effect on thermal expansion characteristics and high dielectric constant values ($K \approx 10^4 - 10^5$), especially in the vicinity of phase transformations.

Crystalline solutions in the PMN-PT system have a perovskite structure where the symmetry changes from rhombohedral⁴ (and/or monoclinic^{5,6}) to tetragonal at a morphotropic phase boundary (MPB), near $x = 35$ % at room temperature. The MPB is nearly composition independent at lower temperatures, but tends toward the PMN-rich side of the diagram with increasing temperature, intersecting the rhombohedral-to-cubic phase transformation line at approximately $x = 28$ %.⁴ Thus the composition range from $x = 28 - 35$ % is referred to as the morphotropic phase boundary region. It is the MPB region that is investigated in this paper.

As stated, the remarkable electromechanical properties of PMN-PT crystals in the MPB region make them of interest for new piezoelectric applications.^{7,8} Crystals with compositions in the MPB region go through two phase transformations as temperature is increased. The lower temperature transformation is between rhombohedral and tetragonal ($R \rightarrow T$) phases, and the higher temperature transformation is between tetragonal and cubic ($T \rightarrow C$) phases. The rhombohedral ($3m$) and tetragonal ($4mm$) phases are ferroelectric, with domain structures of spontaneous polarization (P_S). In addition to the temperature- and composition-driven phase

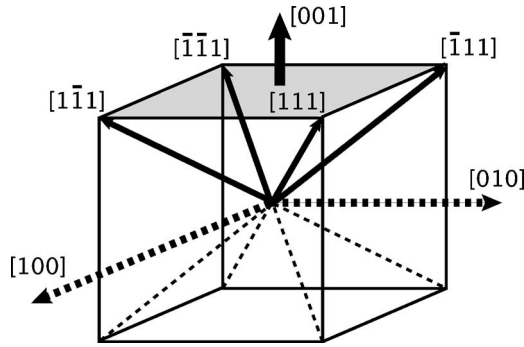


FIG. 1. Field-induced domain alignment for a crystal with rhombohedral symmetry for an electric field applied along $\langle 001 \rangle$.

transformations, application of an electric field can also induce transformations in MPB crystals.^{1,9} For materials that are in the MPB region, application of an electric field at room temperature along a $\langle 001 \rangle$ direction may lead to the poling of a domain (average)¹⁰ engineered¹ state, consistent with macroscopic $4mm$ (tetragonal) symmetry (Fig. 1).

Crystals in the MPB region are rhombohedral at room temperature, thus their polar axis is along $\langle 111 \rangle$, but the properties are maximized by poling along $\langle 001 \rangle$. The high performance realized for this orientation is believed to be due to induced macroscopic symmetries.¹ No distinction has been made between the $\langle 001 \rangle$ directions in previous reports because they are *indistinguishable* by x-ray diffraction (XRD), as is the case in this study, but the thermal expansion measurements reported here reveal that there is a unique direction along which domains preferentially align, indicating that the $\langle 001 \rangle$ directions are not energetically equivalent for the melt-grown crystals. This result is unexpected from consideration of domain states that transform from a high temperature, nonpolar, cubic ($m3m$) prototypic state, to a low-temperature, polar, rhombohedral ($3m$), ferroelectric state.¹⁰ We now report experimental results for anomalous thermal expansion behavior for both unpoled and poled crystals and give dielectric data. The anisotropy in thermal expansion along $\langle 001 \rangle$ is observed to increase with increasing PT content for compositions in the MPB region that exhibit the sequence of phase transformations $R(3m) \rightarrow T(4mm) \rightarrow C(m3m)$ on heating, with increasing stability for the intermediary tetragonal phase, even for rhombohedral crystals at room temperature.

II. EXPERIMENTAL PROCEDURE

The crystals used in this work (H.C. Materials Corp., Urbana, IL) were grown from the melt by a modified Bridgman method using a zone-refining approach for improved quality control. Mixed-oxide powders of the stoichiometric formulation ($x=0.31$) were loaded over a $\langle 211 \rangle$ seed crystal placed at the bottom of a sealed platinum crucible, and the melt zone was gradually moved upward, creating a temperature profile that promoted dissolution and crystal growth. Zone refining minimized compositional variations along the length of the crystal that are known to become titanium rich. The crystals were ~ 10 cm in length by 5 cm in diameter, and weighed

over 1.5 kg. Crystal specimens were cut from the center of the boule, and the orientations were such that the major faces were $\{001\}$. Since the three directions— $[100]$, $[010]$, and $[001]$ —are *indistinguishable* by XRD due to the presence of a threefold axis of rotation along $\langle 111 \rangle$ (Fig. 1), the faces are referred to hereafter as A , B , and C .

Thermal expansion measurements were made on bulk specimens ($5 \times 5 \times 1.5$ mm) on a Netzsch STA 409 horizontal dilatometer with a claimed resolution of 1 nm. A fused silica push rod and sample holder were used to minimize any contribution from the equipment to the overall thermal expansion for the PMN-PT crystals during controlled heating at $2^\circ\text{C}/\text{min}$ in static air. Usually, the measurements were made in open-circuit conditions unless stated otherwise. To obtain short-circuit boundary conditions, the two electroded surfaces of the poled crystal were connected by aluminum foil.

Weak-field capacitance measurements were made on the same specimens using an HP4284A Precision LCR Meter at 1 V/mm ac when heated in air at $2^\circ\text{C}/\text{min}$. Measurements were made at various frequencies between 100 and 10 kHz, and the dielectric constant K values were calculated. Piezoelectric measurements were made on a modified Berlincourt d_{33} meter and ferroelectric measurements on a RT-66A test system (Radiant Technologies).

III. RESULTS AND DISCUSSION

A. Unpoled crystal

The directional thermal strains, $\Delta l/l_0$ (along each of the $\langle 001 \rangle$ directions, A , B , or C) for an *unpoled* crystal are given in Fig. 2(a) as a function of temperature, together with the derivative thermal expansion coefficients $(\Delta l/l_0)/\Delta T$ in Fig. 2(b). The anisotropy in thermal expansion is indicated. The rhombohedral phase exhibited similar behavior along two of the measurement directions (in this case A and B), expanding initially by approximately +4 ppm/K, but contracted by approximately -10 ppm/K in the third direction (C). At the $R \rightarrow T$ transformation the crystal expanded along this unique direction (C) while contracting along the other two directions (A and B). Anisotropy in dielectric constant K was also detected for the unpoled rhombohedral phase at room temperature, where the K for the unique direction was approximately 4–5% greater than for the other two orthogonal directions.

The domain configuration should be random in an *unpoled* crystal, and therefore, properties are expected to be similar in each of the three $\langle 001 \rangle$ directions. In a random multidomain state, there is a one-third possibility of having c -oriented tetragonal domains in each of the $\langle 001 \rangle$ directions. For the PMN-PT crystals, $c^T > c^C = a^C > a^T$,¹¹ where C and T superscripts correspond to the cubic and tetragonal phases, and c and a to the lattice parameters. If one of the $\langle 001 \rangle$ directions has a greater amount of c -oriented domains than the other two, a contraction along that direction should be observed as the tetragonal phase approaches the $T \rightarrow C$ phase transformation ($c^T > a^C$). Correspondingly, an expansion should be observed in the orthogonal directions ($a^T < a^C$). The thermal strain measurements revealed uniaxial behavior.

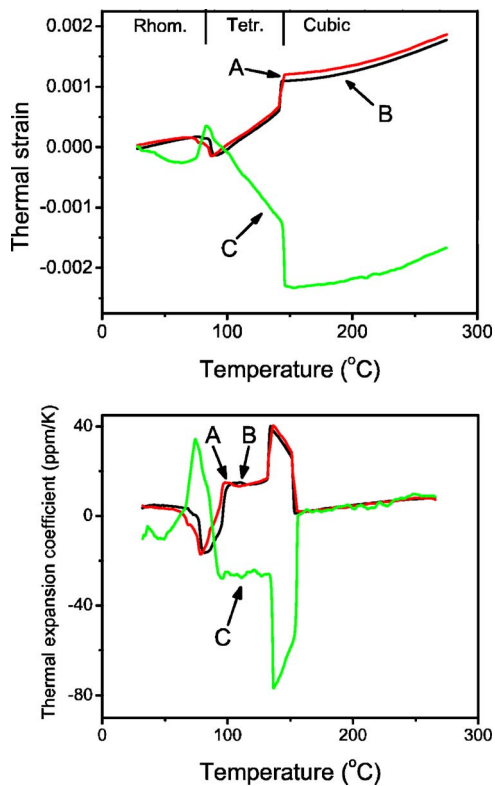


FIG. 2. (Color online) (a) Thermal strain for each $\langle 001 \rangle$ direction (labeled A, B, and C since they are indistinguishable by XRD) for an unpoled crystal, and (b) corresponding thermal expansion coefficients for each $\langle 001 \rangle$ direction for an unpoled crystal.

Once in the tetragonal phase, the crystal contracted in the unique direction (C) with increasing temperature and expanded in the other two directions, A and B [Figs. 2(a) and 2(b)]. This behavior mimicked that of a single-domain tetragonal crystal, but was determined for an *unpoled* multidomain crystal. The measurements revealed that a larger amount of tetragonal domains were somehow spontaneously aligned with their *c*-direction parallel to the unique direction than for the other two orthogonal directions. The thermal expansion coefficients for the crystal in the tetragonal phase were approximately -25 ppm/K for the unique direction, and $+14$ ppm/K for the other two directions. From Figs. 2(a) and 2(b), it can be seen that the tetragonal phase transformed sharply into the cubic phase at 156°C , as the crystal contracted in the unique direction and expanded in the other two orthogonal directions, discontinuously. All three $\langle 001 \rangle$ directions in the cubic phase have the same thermal expansion coefficient (as to be expected), approximately linear $+17$ ppm/K by 266°C . What was unexpected was the anomalous anisotropy below 156°C , in the multidomain states. Apparently, there was a *preferred* domain orientation along one of the $\langle 001 \rangle$ directions. The angle between the $\langle 211 \rangle$ seed direction and two of the $\langle 001 \rangle$ cut directions is 65.90° , whereas it is 35.26° for the other $\langle 001 \rangle$ direction. It is expected that the latter direction would experience the larger thermal and chemical gradient during crystal growth, and this could be the reason for the anomalous anisotropy in thermal expansion behavior observed, even though all the

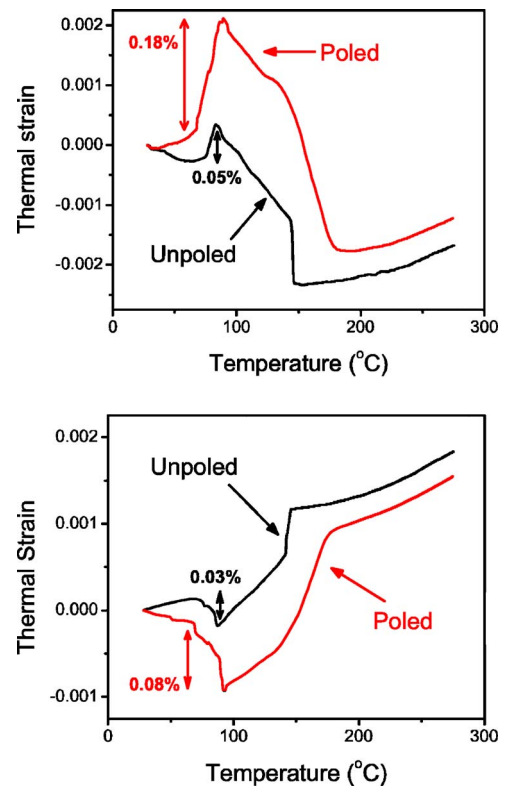


FIG. 3. (Color online) (a) Thermal strain for both unpoled and poled crystals along the poling direction (for poling along the unique direction), and (b) thermal strain for both unpoled and poled crystals normal to the poling direction (for poling along the unique direction).

three $\langle 001 \rangle$ directions were *indistinguishable* by XRD. This scenario could also be expected for $\langle 001 \rangle$ seeded crystal growth.

B. Poled crystal

The crystals were electrically *poled* at room temperature and 6 kV/cm dc. The piezoelectric d_{33} coefficient was 3700 pC/N for a composition close to the MPB. Bipolar ferroelectric measurements determined a coercive field of 2 kV/cm and saturation of P_S before 6 kV/cm . When the poling was carried out along the unique direction, the signs for the changes in thermal strains during the $R \rightarrow T$ phase transformation remained the same, and the magnitudes increased [Figs. 3(a) and 3(b)]. The amount of expansion along the unique direction during the $R \rightarrow T$ phase transformation increased from 0.05% in the unpoled state to 0.18% in the poled state. The latter is a large tensile strain for an oxide material, close to the strain-of-fracture. The amount of contraction normal to the unique direction increased from 0.03% to 0.08% . That is, the *poled* material expanded further in the unique direction and contracted more in the other two orthogonal directions at the $R \rightarrow T$ phase transformation, indicating an enhanced alignment of domains along the poling direction, in this case the unique direction. The phase transformations in a poled crystal also appeared to be more gradual than for the same crystal starting in the unpoled

state, with the temperature increasing from 156 °C to 183 °C for completion of the $T \rightarrow C$ phase transformation. The effect on the lower temperature $R \rightarrow T$ transformation was less pronounced, 85–92 °C. After heating a poled crystal above the $R \rightarrow T$ transformation temperature, the values for the d_{33} coefficient measured at room temperature were found to decrease with increasing heat treatment temperature. For example, an approximate decrease of 50 % by heating 5 °C above the transformation temperature.

Another important effect of room-temperature poling was that the thermal expansion coefficients of crystals in the rhombohedral phase changed their sign upon poling. In *poled* specimens, the crystals now expanded along the unique direction and contracted along the other two orthogonal directions as temperature increased. Poling in the $\langle 001 \rangle$ direction was in accordance with domain state $4mm$ (tetragonal) macroscopic property symmetry, with the fourfold rotation along the poling axis. As the temperature approached the $R \rightarrow T$ phase transformation temperature, the crystal expanded along the unique direction of the macroscopic tetragonal symmetry until it transformed to that of c -textured crystallographic tetragonal symmetry. The other two orthogonal directions acted in accordance with this behavior, as the crystal initially contracted along these directions with increasing temperature.

Poling *normal* to the unique direction resulted in behavior similar to poling along the unique direction, i.e., uniaxial thermal strain behavior along the poling direction [Figs. 4(a) and 4(b)]. The c -oriented tetragonal domains were aligned in the poling direction, which in this case was perpendicular to the direction that had been unique prior to poling. Poling normal to the unique direction also resulted in a more gradual phase transformation. The ability to reorient the uniaxial direction indicated the observed phenomenon was consistent with the domain structure. Upon *thermal depoling* of the crystal at the $T \rightarrow C$ transformation, the thermal strain behavior reverted to its original unpoled state [Fig. 4(a)], with the unique direction in its original direction, regardless of the previous poling conditions, i.e., the crystal remembered the unique direction.

C. Boundary conditions

When the thermal strain was measured under *short-circuit* conditions (Fig. 5), the phase transformations for both poled and unpoled crystals were found to be sharper than when measured under the previous open-circuit conditions (Figs. 2–4). Although the temperature at which the cubic phase completely formed could be as much as 20 °C different between the poled and unpoled states for *open-circuit* conditions ($T \rightarrow C$), it did not change with poling for short-circuit boundary conditions. This is consistent with domains persisting along the poling direction in the tetragonal phase under open-circuit conditions, aiding the stabilization of the tetragonal phase up to higher temperatures than in a completely random multidomain state. A c -oriented but unpoled tetragonal domain structure, with a unique thermal expansion direction but with no net spontaneous polarization, could still form under the short-circuit boundary conditions for 180° domain alignment.

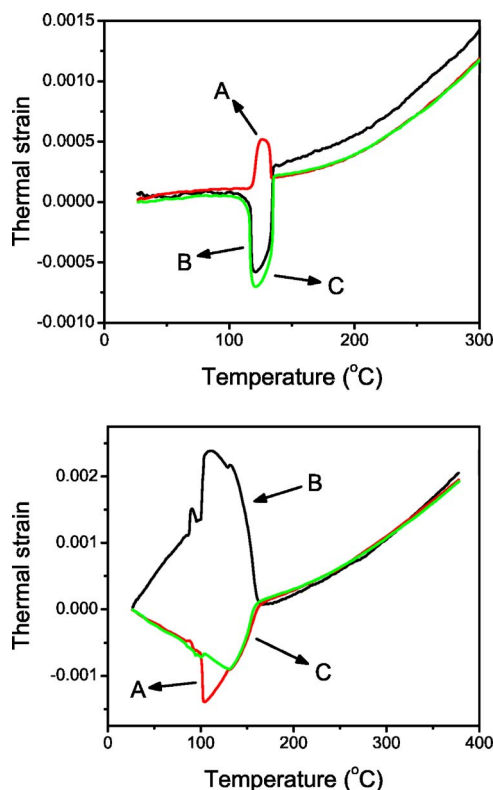


FIG. 4. (Color online) (a) Thermal strain for each $\langle 001 \rangle$ direction for an unpoled crystal, and (b) thermal strain for each $\langle 001 \rangle$ direction for a crystal poled normal to the unique axis.

Dielectric constant values for PMN-PT crystals as a function of temperature are reported in Fig. 6, together with $\tan \delta$ data. Note the crystals were of high quality, with $\tan \delta < 10^{-4}$ in the cubic phase, and even less than 10^{-3} at 225 °C. There was no significant dispersion in K with increasing frequency. Measurements in poled and unpoled states showed that the $R \rightarrow T$ phase transformation was dependent on the poling state of the crystal (similar to the observations for thermal expansion measurements). It should be noted that the dielectric constant was greatest for the *poled* state at room temperature, but greater in the *unpoled* state in the tetragonal

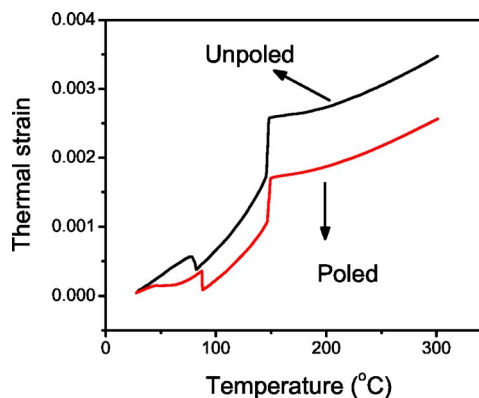


FIG. 5. (Color online) Thermal strain for unpoled and poled crystals along one of the $\langle 001 \rangle$ directions measured under short-circuit boundary conditions.

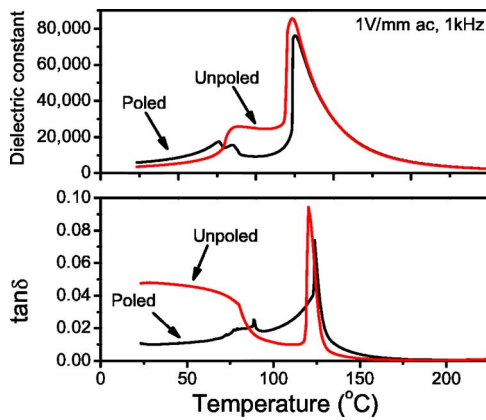


FIG. 6. (Color online) Weak-field dielectric constant as a function of temperature for both unpoled and poled crystals along the poling direction.

region. At 25 °C, the dielectric constant for the rhombohedral phase increased from $K=3680$ to $K=6050$ on poling, i.e., there was a *positive* voltage coefficient of capacitance; whereas at 100 °C, the dielectric constant for the tetragonal phase decreased from $K=24\,840$ to $K=9250$ on poling, i.e., a *negative* voltage coefficient of capacitance. Frequency measurements at room temperature on poled crystals determined a piezoelectric resonance around 200 KHz where the K value decreased to the equivalent K value for the unpoled state, indicating an elastic clamping contribution to the poled K . The $T \rightarrow C$ phase transformation, however, did not show any significant difference in temperature between poled and unpoled states (124 °C), and the peak value of dielectric constant remained essentially the same ($K \approx 80\,000$ at 124 °C). Thus, the $T \rightarrow C$ phase transformation observed by capacitance measurements was similar to that measured by dilatometry under short-circuit conditions, indicating the crystal was completely unpoled on reaching the $T \rightarrow C$ phase transformation temperature independent of the initial poling condition.

IV. CONCLUSIONS

Thermal expansion measurements on PMN-PT single crystals revealed that not all of the $\langle 001 \rangle$ directions were macroscopically equivalent even though they were *indistin-*

guishable by XRD. This result was unexpected from considerations of prototypic symmetry, and the anomaly may be attributable to the method of seeded crystal growth. The presence of a unique direction, with different thermal strain characteristics than the other two equivalent crystallographic directions was observed. The unique direction was related to the domain structure of the crystal and could be reoriented by room temperature poling in a direction normal to the unique direction. Poling promoted the formation of c -oriented tetragonal domains along the poling direction. When the crystal was poled along the unique direction, along which there was a higher percentage of c -oriented domains even in the unpoled state, domains aligned further, resulting in the maximum change in thermal strain at the $R \rightarrow T$ phase transformation. Poling normal to the unique direction reversed the sign of the change in thermal strain at the $R \rightarrow T$ transformation. The low-temperature rhombohedral phase displayed uniaxial behavior consistent with tetragonal macroscopic symmetry after poling, and the phase transformations were sharper under short-circuit boundary conditions. The presence of a preferred alignment of domains in unpoled crystals resulted in different thermal expansion properties along the equivalent crystallographic $\langle 001 \rangle$ directions. The effect of such preferred domain alignments should be considered for the understanding of properties in cut crystals, in both poled and unpoled states. For example, the dielectric constant at room temperature increased from 3680 to 6050 on poling, and the thermal expansion coefficient reversed sign. The thermal expansion characteristics that are reported for the first time may prove helpful for the successful poling and use of PMN-PT piezoelectric crystals.

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¹S. E. Park and T. R. Shrout, J. Appl. Phys. **82**(4), 1804 (1997).
²P. Han, W. Yan, J. Tian, X. Huang, and H. Pan, Appl. Phys. Lett. **86**, 052902 (2005).
³A. J. Moulson and J. M. Herbert, *Electroceramics* (Wiley, New York, 2003), Chap. 6, p. 380.
⁴T. R. Shrout, Z. P. Chang, N. Kim, and S. Markgraf, Ferroelectr., Lett. Sect. **12**, 63 (1990).
⁵Z.-G. Ye, B. Noheda, M. Dong, D. Cox, and G. Shirane, Phys. Rev. B **64**, 184114 (2001).
⁶A. K. Singh and D. Pandey, J. Phys.: Condens. Matter **13**, L931

(2001).

⁷T. R. Gururaja, Am. Ceram. Soc. Bull. **73**, 50 (1994).
⁸T. R. Gururaja, R. K. Panda, J. Chen, and H. Beck, Proc.-IEEE Ultrason. Symp. **2**, 969 (1999).
⁹D. Viehland and J. F. Li, J. Appl. Phys. **92**(12), 7690 (2002).
¹⁰J. Fousek, D. B. Litvin, and L. E. Cross, J. Phys.: Condens. Matter **13**, L33 (2001).
¹¹F. Bai, N. Wang, J. Li, D. Viehland, P. M. Gehring, G. Xu, and G. Shirane, J. Appl. Phys. **96**(3), 1620 (2004).