Electromechanical and elastic isotropy in the (011) plane of 0.7 Pb(Mg 1/3 Nb 2/3) O 3 - 0.3 PbTiO 3 crystals: Inhomogeneous shearing of polarization

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Electromechanical and elastic isotropy in the (011) plane of $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$ crystals: Inhomogeneous shearing of polarization

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Temperature dependent electromechanical investigations of $\langle 110 \rangle$, $\langle 001 \rangle$, and $\langle 111 \rangle$ oriented morphotropic phase boundary compositions of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ crystals have been performed. Softening of the dielectric constant, piezoelectric constant, and Young's modulus was found for all three orientations, near a ferroelectric rhombohedral to ferroelectric tetragonal transformation. However, the value of Young's modulus was an order of magnitude higher along $\langle 111 \rangle$, than either $\langle 001 \rangle$ or $\langle 110 \rangle$. An unusual electromechanical and elastic equivalence was found between the $\langle 110 \rangle$ and $\langle 001 \rangle$ directions. This result demonstrates that the enhanced electromechanical performance of oriented piezocrystals is not constrained to the $\langle 001 \rangle$ orientation, but rather to the (011) plane. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1486051]

I. INTRODUCTION

$(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$(x)PbTiO_3$ (PMN-PT) $(1\text{-}x)/x$ and $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ PZN-PT $(1\text{-}x)/x$ single crystals are currently under development for use in transducer and projector applications.[1,2] Investigations have focused on compositions in these crystalline solutions close to the morphotropic phase boundary (MPB) between rhombohedral and tetragonal ferroelectric states, which occurs at $x = 0.32$ for PMN-PT.

High electromechanical performance coefficients in mixed B-site cation perovskites was first reported nearly 20 years ago by Kuwata, Uchino, and Nomura.[3,4] In poled $\langle 001 \rangle$-oriented single crystals of $0.91Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.09PbTiO_3$ (PZN-PT 91/9), longitudinal piezoelectric (d_{33}) and electromechanical coupling (k_{33}) coefficients of 1500 pC/N and 0.92 were reported, respectively. These investigations were performed by a standard resonance-antiresonance method under relatively low-field drive level conditions, which were significantly below that required to induce saturation in the electrically-induced strain response (ϵ-E). Recently, Shrout and coworkers[1,2] have investigated the high-field behavior of $\langle 001 \rangle$-oriented PZN-PT 92/8 and $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$ (PMN-PT 70/30) crystals. Strain levels of up to 1.2% were reported at field levels of ~ 30 kV/cm. Accordingly, anomalously high values of d_{33} (>4000 pC/N) can be estimated from the slope of the ϵ-E curves (i.e., $d_{33} = \delta\epsilon/\delta E$).

The origin of the high electromechanical behavior has been attributed to an electrically-induced rhombohedral ferroelectric (FE_r) to tetragonal ferroelectric (FE_t) phase transformation.[1,2,5–7] The FE_r phase has a much smaller c/a ratio than the FE_t one; accordingly under field the large c/a ratio change results in enhanced electrically-induced strains. For PMN-PT and PZN-PT, investigations have also demonstrated the presence of monoclinic (FE_m) and orthorhombic (FE_o) ferroelectric states in between the FE_r and FE_t phases.[8–10] These results open an interesting possibility that intermediate states may be responsible for the high electromechanical performance. In PMN-PT and PZN-PT, first-principles calculations have shown that these intermediate states can only be stabilized in the presence of randomly-quenched disorder.[5,6] Furthermore, first-principles simulations have indicated that the transformation under electric field between FE_r and FE_t proceeds by a rotation of the polarization between $\langle 111 \rangle$ and $\langle 001 \rangle$.[5,7]

Recent dielectric investigations by Lu *et al.*[11] have demonstrated a complex transformation sequence in piezocrystals that is dependent upon orientation and electrical history. An intermediate FE_o state was shown to exist between the FE_r and FE_t ones, whose temperature range of existence varied, suggesting metastability. Furthermore, the results indicated that the margin of stability in the FE_r, FE_o, and FE_t states may be sufficiently fragile that changes in orientation, electrical history, or mechanical constraints may change the free energy balance. Piezoelectric studies on poled $\langle 110 \rangle$ crystals showed that a monodomain FE_o state does not exhibit enhanced piezoelectricity. However, a $\langle 110 \rangle$-oriented FE_r polydomain state exhibited very significant enhancements with a longitundonal piezoelectric constant (d_{33}) of ~ 1500 pC/N.

Unfortunately, a thorough investigation of the anisotropy of the electromechanical properties has not yet been reported for a single composition. The purpose of this investigation was to measure the temperature dependence of longitudinal piezoelectric constant (d_{33}), dielectric constant (K_{33}), electromechanical coupling coefficient (k_{33}), and Young's modulus (Y) for $\langle 001 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ oriented crystals. These

FIG. 1. (Color) d_{33} as a function of temperature for $\langle 001 \rangle$, $\langle 011 \rangle$, and $\langle 111 \rangle$ oriented PMN-PT crystals.
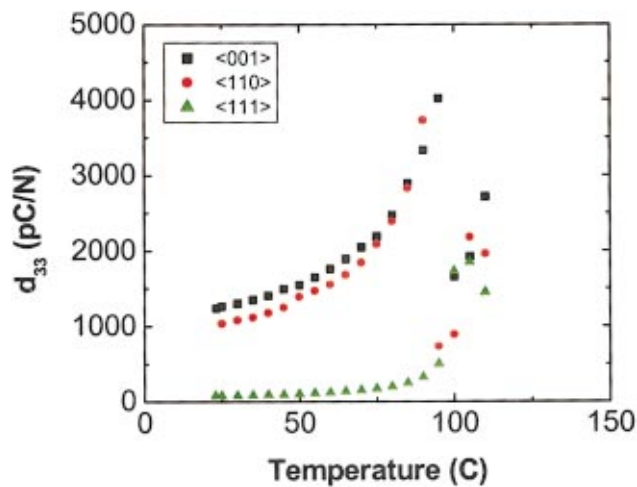

FIG. 2. (Color) K_{33} as a function of temperature for $\langle 001 \rangle$, $\langle 011 \rangle$, and $\langle 111 \rangle$ oriented PMN-PT crystals. These data were calculated from the resonance-antiresonance measurements. Data taken using an LCR meter which was previously published in Ref. 12 for an $\langle 001 \rangle$ oriented crystal of similar composition is also shown.

investigations have shown that the temperature dependent properties along the $\langle 001 \rangle$ and $\langle 110 \rangle$ orientations are nearly identical. Also, an unusual piezoelectric instability between two ferroelectric states in $\langle 011 \rangle$ and $\langle 001 \rangle$ oriented crystals of MPB compositions of PMN-PT and PZN-PT has been found. We have observed piezoelectric constants as high as ~ 5000 pC/N.

II. EXPERIMENTAL PROCEDURE

$\langle 011 \rangle$, $\langle 001 \rangle$, and $\langle 111 \rangle$-oriented crystals of $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$-$0.3\text{PbTiO}_3$ grown by a flux method have been obtained from HC Materials (Urbana, IL). The crystals were of dimensions $0.3 \times 0.3 \times 0.9$ mm. The specimens were electroded with gold and poled. The piezoelectric response was measured using a HP 4194 impedance analyzer. The piezoelectric constant, electromechanical coupling coefficient, dielectric constant, and Young's modulus were calculated from the resonance-antiresonance curves using a standard IEEE method. Temperature dependent measurements were performed in conjunction with a Delta Design environmental chamber and a HP digitial multimeter. All measurements were computer automated.

III. RESULTS

Figure 1 shows the longitudinal piezoelectric constant (d_{33}) as a function temperature for poled $\langle 001 \rangle$, $\langle 111 \rangle$, and $\langle 011 \rangle$ oriented PMN-PT crystals. Inspection of the data will reveal that the values of d_{33} along the $\langle 001 \rangle$ and $\langle 011 \rangle$ were nearly equivalent over the temperature range of $25 < T < 80\,°\text{C}$. In both cases, d_{33} increased from ~ 1200 to ~ 4000 pC/N over this temperature range. However, the value of d_{33} for the $\langle 111 \rangle$ oriented crystal was dramatically lower, increasing from ~ 100 to ~ 500 pC/N with increasing temperature for $25 < T < 80\,°\text{C}$.

At $\sim 80\,°\text{C}$, a transition occurred, which is known to be between two ferroelectric states.[5,7,12] At this temperature, an abrupt change in d_{33} was found. For $90 < T < 110\,°\text{C}$, the value of d_{33} was nearly equivalent along the $\langle 001 \rangle$ and $\langle 111 \rangle$ orientations, having a value of ~ 1500 pC/N. However, the

value of d_{33} for the $\langle 011 \rangle$ oriented specimen decreased to ~ 600 pC/N. In fact, the temperature dependence of d_{33} for the $\langle 011 \rangle$ in this temperature range was seemingly an extrapolation of that of the $\langle 111 \rangle$ oriented crystal in the temperature range of $T < 80\,°\text{C}$. At $T > 110\,°\text{C}$, a secondary transition occurred for the $\langle 011 \rangle$ and $\langle 111 \rangle$ orientated crystals. In this temperature range, the values of d_{33} were close for both orientations and decreased with increasing temperature. However, for the $\langle 111 \rangle$ orientation, no secondary transition was obvious and the value of d_{33} continued to increase over the temperature range investigated.

Figure 2 shows the longitudinal dielectric constant (K_{33}) as a function of temperature for poled $\langle 001 \rangle$, $\langle 111 \rangle$ and $\langle 011 \rangle$ oriented crystals. These data were taken using the resonance-antiresonance method. Inspection of the data will reveal that the values of K_{33} along the $\langle 001 \rangle$ and $\langle 011 \rangle$ were nearly equivalent over the temperature range of $25 < T < 80\,°\text{C}$, similar to that for d_{33}. In both cases, K_{33} increased from ~ 5000 to $\sim 15\,000$ over this temperature range. However,

FIG. 3. (Color) $(K_{33})^{-1}$ as a function of temperature for $\langle 001 \rangle$, $\langle 011 \rangle$, and $\langle 111 \rangle$ oriented PMN-PT crystals.
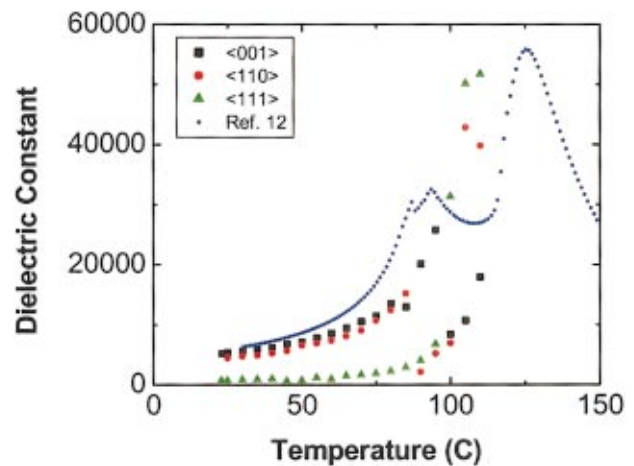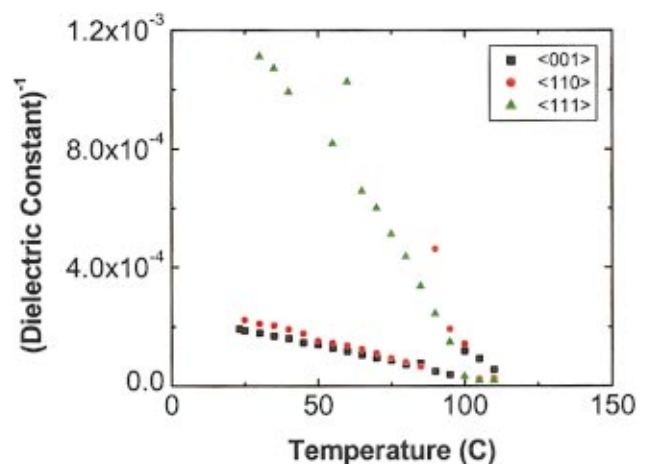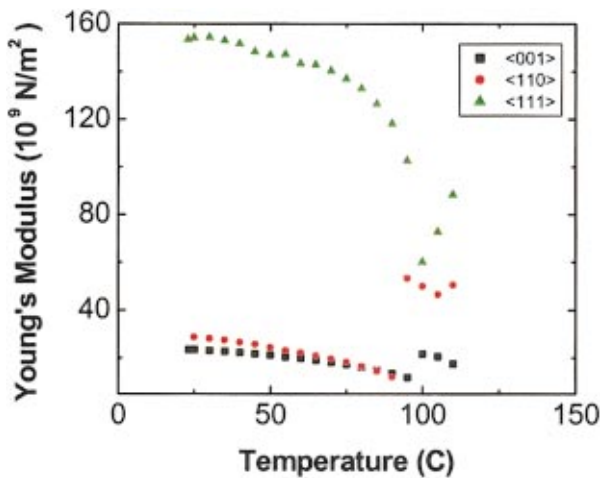
FIG. 4. (Color) Y_1 as a function of temperature for $\langle 001 \rangle$, $\langle 011 \rangle$, and $\langle 111 \rangle$ oriented PMN-PT crystals.

the value for the $\langle 111 \rangle$ oriented crystal was dramatically lower, increasing from ~ 500 to ~ 1000 with increasing temperature for $25 < T < 80\,^{\circ}\mathrm{C}$. Data taken using an LCR meter for a $\langle 001 \rangle$ oriented specimen that was previously published[12] is also shown in Fig. 2. This data can be seen to be in agreement with the results of this investigation.

Along the $\langle 011 \rangle$, a significant decrease in K_{33} was found near $\sim 80\,^{\circ}\mathrm{C}$. For $80 < T < 100\,^{\circ}\mathrm{C}$, the values of K_{33} were nearly equivalent along the $\langle 011 \rangle$ and $\langle 111 \rangle$ orientations, both following an extrapolation of the temperature dependence of K_{33} for the $\langle 111 \rangle$ orientation observed in the temperature range of $25 < T < 80\,^{\circ}\mathrm{C}$. At $\sim 100\,^{\circ}\mathrm{C}$, abrupt changes in K_{33} were observed for all three orientations. Near this temperature, the value of K_{33} decreased dramatically for the $\langle 001 \rangle$ orientation, but increased dramatically for the $\langle 011 \rangle$ and $\langle 111 \rangle$ orientations. In the temperature range of $100 < T < 120\,^{\circ}\mathrm{C}$, the value of K_{33} for the $\langle 001 \rangle$ orientation seemingly followed an extrapolation of that observed at lower temperatures for the $\langle 111 \rangle$ ($25 < T < 80\,^{\circ}\mathrm{C}$) and for the $\langle 111 \rangle$ and $\langle 011 \rangle$ ($80 < T < 100\,^{\circ}\mathrm{C}$). Correspondingly, the value of

K_{33} for the $\langle 011 \rangle$ and $\langle 111 \rangle$ orientations seemingly followed an extrapolation of that observed at lower temperatures for the $\langle 001 \rangle$ ($25 < T < 100\,^{\circ}\mathrm{C}$).

The extrapolation of the temperature dependent K_{33} data between the various orientations is better illustrated in Curie–Weiss plots. Figure 3 shows the inverse dielectric constant $(K_{33})^{-1}$ as a function of temperature for poled $\langle 001 \rangle$, $\langle 111 \rangle$, and $\langle 011 \rangle$ orientations. In this figure, $(K_{33})^{-1}$ can be seen to have a linear relationship with T in the poled condition for $T < 100\,^{\circ}\mathrm{C}$, along all three orientations. Inspection of this figure will reveal two linear relationships: one an extrapolation of the low temperature data for the $\langle 001 \rangle$ and $\langle 011 \rangle$ orientations, and the other an extrapolation of low temperature data for the $\langle 111 \rangle$ orientation. Various transitions occur for all three orientations between these two linear extrapolations, but no significant deviations were observed from either extrapolation in the temperature range investigated ($T < 120\,^{\circ}\mathrm{C}$).

Figure 4 shows the Young's modulus (Y_1) as a function of temperature for poled $\langle 001 \rangle$, $\langle 111 \rangle$ and $\langle 011 \rangle$ oriented crystals. Inspection of the data will reveal that the values of Y_1 along the $\langle 001 \rangle$ and $\langle 011 \rangle$ were nearly equivalent over the temperature range of $25 < T < 80\,^{\circ}\mathrm{C}$. In both cases, Y_1 decreased from $\sim 2.5 \times 10^{10}$ to $\sim 5 \times 10^9\,\mathrm{N/m^2}$ over this temperature range. However, the value for the $\langle 111 \rangle$ oriented crystal was dramatically higher. At room temperature, Y_1 was found to be equal to $\sim 1.6 \times 10^{11}\,\mathrm{N/m^2}$ along the $\langle 111 \rangle$, softening occurred with increasing T for $T < 100\,^{\circ}\mathrm{C}$, however, the value of Y_1 remained significantly higher along the $\langle 111 \rangle$ relative to either the $\langle 001 \rangle$ or $\langle 011 \rangle$. Interestingly, evidence of only one phase transition was observed in the temperature dependence of Y_1, which occurred at $\sim 90\,^{\circ}\mathrm{C}$. On heating about this temperature, Y_1 softened along the $\langle 001 \rangle$ and $\langle 011 \rangle$ orientations, but stiffened along the $\langle 111 \rangle$. In this temperature range, no equivalence was observed in Y_1 between any of the three orientations.

Figure 5 shows the longitudinal electromechanical coupling coefficient (k_{33}) as a function of temperature for poled $\langle 001 \rangle$, $\langle 111 \rangle$, and $\langle 011 \rangle$ orientations. Inspection of the data will reveal that the values of k_{33} along the $\langle 001 \rangle$ and $\langle 011 \rangle$ were nearly equivalent ($k_{33} \sim 0.92$) over the temperature range of $25 < T < 80\,^{\circ}\mathrm{C}$, and temperature independent. However, the value for the $\langle 111 \rangle$ orientation was significantly lower. At room temperature k_{33} was found to be equal to ~ 0.38 along the $\langle 111 \rangle$, which subsequently increased with increasing T approaching a maximum value of ~ 0.8 at $\sim 100\,^{\circ}\mathrm{C}$. For $T > 100\,^{\circ}\mathrm{C}$, the value of k_{33} decreased with increasing T for both the $\langle 111 \rangle$ and $\langle 011 \rangle$ orientations, but was relatively temperature independent for the $\langle 001 \rangle$ direction over the temperature range investigated.

IV. DISCUSSION

Previous investigations have shown that PMN-PT crystals with compositions close to that used in this study undergo a sequence of transformations from FE$_r$ to FE$_o$ to FE$_t$ on heating.[11,12] The d_{33} and K_{33} data shown in Figs. 1 and 2 are consistent with this report. Accordingly, the FE stability would be as follows with respect to the data in the present
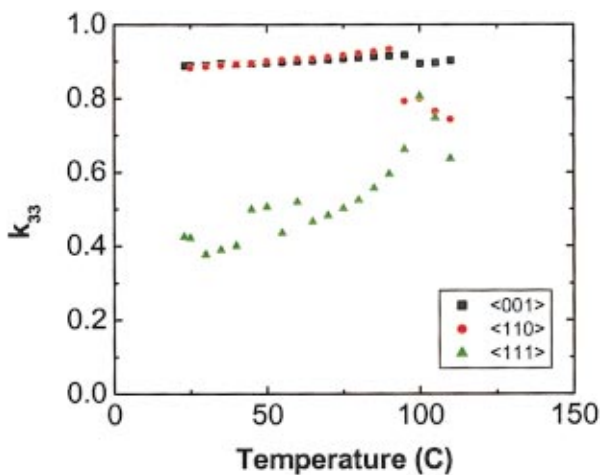

FIG. 5. (Color) k_{33} as a function of temperature for $\langle 001 \rangle$, $\langle 011 \rangle$, and $\langle 111 \rangle$ oriented PMN-PT crystals.

study: FE_r for $T < 80\,°C$, FE_o for $80 < T < 100\,°C$, and FE_t for $T > 100\,°C$. The existence of a metastable orthorhombic state has been previously discussed in a similar MPB system. For instance, Amin et al.[13] have developed an energy function that generates a near vertical MPB between two ferroelectric states, i.e., the rhombohedral and tetragonal states at Zr:Ti ratio ~1:1 in the PZT system. The orthorhombic state was always very close to but metastable with respect to the overlapping tetragonal and rhombohedral stability curves.

The results in Sec. III demonstrated a near electromechanical equivalence between the $\langle 001 \rangle$ and $\langle 011 \rangle$ orientations over the temperature range of $25 < T < 90\,°C$. In this temperature range, the values of d_{33}, K_{33}, Y_1, and k_{33} were found to be equal along these two directions. However, the values along the $\langle 111 \rangle$ orientation were found to be significantly different. Clearly, the data show an unusual isotropy in the electromechanical properties in the (011) plane, although the properties along this plane are clearly anisotropic with respect to the $\langle 111 \rangle$.

Elastic isotropy in the (011) plane has previously been reported in martensitic transformations,[14,15] and artensitic phenomena are well-known to be a transformational region between pseudocubic and tetragonal ferroelastic phases in the presence of static quenched disorder.[16–18] Symmetry adaptivity occurs in this region due to strain accommodation,[19] resulting in metastable intermediate orthorhombic and monoclinic states. Symmetry adaptivity in martensitic transformations results from a lattice shearing from the pseudocubic $\langle 111 \rangle$ towards the $\langle 001 \rangle$, via the $\langle 011 \rangle$. Consequently, an instability in $\frac{1}{2}[C_{11} - C_{12}]$ is observed in the transformation,[15] and the effective elastic stiffness along the $\langle 001 \rangle$-$\langle 011 \rangle$ plane is isotropic.[14,15]

Premartensitic-like phenomena could also occur during a transformation between a pseudocubic (i.e., rhombohedral) FE and a FE_t transition in the presence of quenched disorder. In this case, an additional instability, which is unrelated to the ferroelectric one, would not be required. An intermediate "bridging" monoclinic and/or orthorhombic condition would naturally exist as a transformational pathway between $\langle 111 \rangle$ and $\langle 001 \rangle$, via the $\langle 011 \rangle$, as in premartensite.[19] Accordingly, equivalence of the elastic properties would be expected between the $\langle 001 \rangle$ and $\langle 011 \rangle$ orientations, due to an inhomogeneous polarization shearing. Considering that the elastic strain is coupled to the square of the polarization via electrostriction, the complete electromechanical response would be anticipated to be equivalent between these two directions.

Phenomenological descriptions[20] and first-principle simulations[8–10] of polarization rotation have been based upon a general paradigm that rotation occurs homogeneously (i.e., within a single domain condition). However, MPB compositions of PMN-PT and PZN-PT are known to contain microtwins or tweed,[21] oriented along the $\langle 110 \rangle$. Microtwins or tweed are a twinning that occurs on the 100 Å scale and result in a micro-inhomogeneous lattice. Microtwinned states are well known in ferroelastic (or martensitic) transformations involving large changes in c/a ratio between a pseudocubic (or rhombohedral) and a tetragonal state.[16–19,22,23] Furthermore, in a poled condition, oriented PMN-PT crystals of a similar composition have been shown to be in a monodomain FE_r state at room temperature, however, in an annealed condition a relaxor ferroelectric condition is known to exist instead.[11] This demonstrates that the anisotropy of the high performance piezocrystal state is only metastably locked in under application of field. Clearly, local random fields also play a crucial role upon the ferroelectric phase stability and properties of oriented piezocrystals. These systems are intrinsically poised near a relaxor ferroelectric state, in addition to a MPB.

The polarization nonuniformity due to microtwinning and symmetry adaptivity would allow the crystal structure to vary continuously between the FE_r and FE_t phases, via metastable FE_m monoclinic and FE_o states. Polarization rotation would effectively occur, but it would be an inhomogeneous shearing. In consideration of the presence of a metastable intermediate FE_o state, polarization rotation from the $\langle 111 \rangle$ to the $\langle 001 \rangle$ would occur in two steps. These steps are rotation from $\langle 111 \rangle$ towards $\langle 011 \rangle$, followed by a rotation from $\langle 011 \rangle$ towards $\langle 001 \rangle$. Accordingly, different types of FE_m states would serve as bridges. One whose polarization is confined to the $(0kl)$ plane that bridges FE_r and FE_o, and a second whose polarization is confined to the (hhk) plane which bridges FE_o and FE_t.

The presence of two bridging monoclinic states allows for the polarization in anyone of the three FE phases (FE_r, FE_t, or FE_o) to shear towards either of the other two. Accordingly, in a poled specimen, the dielectric and piezoelectric susceptibilities will be low along the direction of the spontaneous polarization as no shear contributions are possible, and will be high along the directions of the other possible polarization states that can be induced. For example, in the FE_o state, the polarization can shear away from the $\langle 011 \rangle$ towards either the $\langle 111 \rangle$ [via the $(0kl)$ plane] or the $\langle 001 \rangle$ [via the (hhk) plane]. Consequently, in the FE_o state, both the values of K_{33} and d_{33} will be low along the $\langle 011 \rangle$, whereas along the $\langle 111 \rangle$ and $\langle 001 \rangle$ both will be high. Also, the presence of only two Curie–Weiss extrapolations for the three different crystallographic axes can be understood. One linear extrapolation defines the condition in which the polarization is confined to the direction along which the field is applied. A second linear extrapolation defines the condition in which the spontaneous polarization is not confined along the direction that the field is applied. Equivalence of the dielectric and piezoelectric constants will be found in the case when the direction of the polarization and that of the applied field are not coincidental.

V. SUMMARY

Investigations have revealed an unusual electromechanical and elastic isotropy between the $\langle 001 \rangle$ and $\langle 011 \rangle$ orientations in PMN-PT crystals. This isotropy has been explained based upon an inhomogenous shearing of the polarization from the pseudocubic $\langle 111 \rangle$ towards the $\langle 001 \rangle$, via the $\langle 011 \rangle$. Analogies between this transformation and martensitic transformations are discussed, where in both cases the transformation pathway is constrained by elastic strain accommoda-

tion. The observed large elastic stiffness along the $\langle 111 \rangle$ compared to $\langle 100 \rangle$ and $\langle 011 \rangle$ suggests a large force constant anisotropy with extrema in the (011) plane.

ACKNOWLEDGMENT

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