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Temperature dependent electromechanical investigations of (110), (001), and (111) oriented morphotropic phase boundary compositions of \(\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3\) 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 (111), than either (001) or (110). An unusual electromechanical and elastic equivalence was found between the (110) and (001) directions. This result demonstrates that the enhanced electromechanical performance of oriented piezocrystals is not constrained to the (001) orientation, but rather to the (011) plane. © 2002 American Institute of Physics. [DOI: 10.1063/1.1486051]

I. INTRODUCTION

\((1-x)\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-(x)\text{PbTiO}_3\) (PMN-PT) \((1-x)/x\) and \(\text{Pb(Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3\) PZN-PT \((1-x)/x\) single crystals are currently under development for use in transducer and projector applications. 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. In poled \(\langle 001\rangle\)-oriented single crystals of \(0.91\text{Pb(Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.09\text{PbTiO}_3\) (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-antis resonance method under relatively low-field drive level conditions, which were significantly below that required to induce saturation in the electrically-induced strain response \((e-E)\). Recently, Shrot and coworkers have investigated the high-field behavior of \(\langle 001\rangle\)-oriented PZN-PT 92/8 and \(0.7\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.3\text{PbTiO}_3\) (PMN-PT 70/30) crystals. Strain levels of up to 1.2% were reported at field levels of \(\sim30\) kV/cm. Accordingly, anomalously high values of \(d_{33}\) (>4000 pC/N) can be estimated from the slope of the \(e-E\) curves (i.e., \(d_{33} = \delta E/\delta E\)).

The origin of the high electromechanical behavior has been attributed to an electrically-induced rhombohedral ferroelectric \((\text{FE}_r)\) to tetragonal ferroelectric \((\text{FE}_t)\) phase transformation. The \(\text{FE}_t\) phase has a much smaller \(c/a\) ratio than the \(\text{FE}_r\) 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 \((\text{FE}_m)\) and orthorhombic \((\text{FE}_o)\) ferroelectric states in between the \(\text{FE}_r\) and \(\text{FE}_t\) phases. 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. Furthermore, first-principles simulations have indicated that the transformation under electric field between \(\text{FE}_r\) and \(\text{FE}_t\) proceeds by a rotation of the polarization between (111) and (001).

Recent dielectric investigations by Lu et al. have demonstrated a complex transformation sequence in piezocrystals that is dependent upon orientation and electrical history. An intermediate \(\text{FE}_o\) state was shown to exist between the \(\text{FE}_r\) and \(\text{FE}_o\) ones, whose temperature range of existence varied, suggesting metastability. Furthermore, the results indicated that the margin of stability in the \(\text{FE}_r\), \(\text{FE}_o\), and \(\text{FE}_t\) phases 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 \(\text{FE}_o\) state does not exhibit enhanced piezoelectricity. However, a \(\langle 110\rangle\)-oriented \(\text{FE}_o\) polydomain state exhibited very significant enhancements with a longitudinal piezoelectric constant \((d_{33})\) of \(\sim1500\) 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
investigations have shown that the temperature dependent properties along the (001) and (110) orientations are nearly identical. Also, an unusual piezoelectric instability between two ferroelectric states in (011) and (001) 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

(011), (001), and (111)-oriented crystals of 0.7Pb(Mg1/3Nb2/3)O3-0.3PbTiO3 grown by a flux method have been obtained from HC Materials (Urbana, IL). The crystals were of dimensions 0.3×0.3×0.9 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 digital multimeter. All measurements were computer automated.

III. RESULTS

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

At ~80 °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 °C, the value of $d_{33}$ was nearly equivalent along the (001) and (111) orientations, having a value of ~1500 pC/N. However, the value of $d_{33}$ for the (011) oriented specimen decreased to ~600 pC/N. In fact, the temperature dependence of $d_{33}$ for the (011) in this temperature range was seemingly an extrapolation of that of the (111) oriented crystal in the temperature range of T<80 °C. At T>110 °C, a secondary transition occurred for the (011) and (111) oriented crystals. In this temperature range, the values of $d_{33}$ were close for both orientations and decreased with increasing temperature. However, for the (111) 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 (001), (111) and (011) 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 (001) and (011) were nearly equivalent over the temperature range of 25$<T<$80 °C, similar to that for $d_{33}$. In both cases, $K_{33}$ increased from ~5000 to ~15 000 over this temperature range. However,
the value for the (111) oriented crystal was dramatically lower, increasing from ~500 to ~1000 with increasing temperature for 25<T<80 °C. Data taken using an LCR meter for a (001) oriented specimen that was previously published\textsuperscript{12} is also shown in Fig. 2. This data can be seen to be in agreement with the results of this investigation.

Along the (011), a significant decrease in $K_{33}$ was found near ~80 °C. For 80<T<100 °C, the values of $K_{33}$ were nearly equivalent along the (011) and (111) orientations, both following an extrapolation of the temperature dependence of $K_{33}$ for the (111) orientation observed in the temperature range of 25<T<80 °C. At ~100 °C, abrupt changes in $K_{33}$ were observed for all three orientations. Near this temperature, the value of $K_{33}$ decreased dramatically for the (001) orientation, but increased dramatically for the (011) and (111) orientations. In the temperature range of 100<T<120 °C, the value of $K_{33}$ for the (001) orientation seemingly followed an extrapolation of that observed at lower temperatures for the (111) (25<T<80 °C) and for the (111) and (011) (80<T<100 °C). Correspondingly, the value of $K_{33}$ for the (011) and (111) orientations seemingly followed an extrapolation of that observed at lower temperatures for the (001) (25<T<100 °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 ($K_{33}$)\textsuperscript{-1} as a function of temperature for poled (001), (111), and (011) orientations. In this figure, ($K_{33}$)\textsuperscript{-1} can be seen to have a linear relationship with $T$ in the poled condition for $T$<100 °C, along all three orientations. Inspection of this figure will reveal two linear relationships: one an extrapolation of the low temperature data for the (001) and (011) orientations, and the other an extrapolation of low temperature data for the (111) 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 °C).

Figure 4 shows the Young’s modulus ($Y_1$) as a function of temperature for poled (001), (111) and (011) oriented crystals. Inspection of the data will reveal that the values of $Y_1$ along the (001) and (011) were nearly equivalent over the temperature range of 25<T<80 °C. In both cases, $Y_1$ decreased from ~2.5×10\textsuperscript{10} to ~5×10\textsuperscript{9} N/m\textsuperscript{2} over this temperature range. However, the value for the (111) oriented crystal was dramatically higher. At room temperature, $Y_1$ was found to be equal to ~1.6×10\textsuperscript{11} N/m\textsuperscript{2} along the (111), softening occurred with increasing $T$ for $T$<100 °C, however, the value of $Y_1$ remained significantly higher along the (111) relative to either the (001) or (011). Interestingly, evidence of only one phase transition was observed in the temperature dependence of $Y_1$, which occurred at ~90 °C. On heating about this temperature, $Y_1$ softened along the (001) and (011) orientations, but stiffened along the (111). 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 (001), (111), and (011) orientations. Inspection of the data will reveal that the values of $k_{33}$ along the (001) and (011) were nearly equivalent ($k_{33}$~0.92) over the temperature range of 25<T<80 °C, and temperature independent. However, the value for the (111) orientation was significantly lower. At room temperature $k_{33}$ was found to be equal to ~0.38 along the (111), which subsequently increased with increasing $T$ approaching a maximum value of ~0.8 at ~100 °C. For $T$>100 °C, the value of $k_{33}$ decreased with increasing $T$ for both the (111) and (011) orientations, but was relatively temperature independent for the (001) 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\textsubscript{v} to FE\textsubscript{o} to FE\textsubscript{r} on heating.\textsuperscript{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...
study: FE$_t$ for $T<80$ °C, FE$_o$ for $80<T<100$ °C, and FE$_r$ 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. 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 (001) and (011) 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 (111) 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 (111).

Elastic isotropy in the (011) plane has previously been reported in martensitic transformations, and artensitic phenomena are well-known to be a transformational region between pseudocubic and tetragonal ferroelastic phases in the presence of static quenched disorder. Symmetry adaptivity occurs in this region due to strain accommodation, resulting in metastable intermediate orthorhombic and monoclinic states. Symmetry adaptivity in martensitic transformations results from a lattice shearing from the pseudocubic towards the (001), via the (011). Consequently, an instability in $\frac{1}{2}[C_{111} - C_{112}]$ is observed in the transformation, and the effective elastic stiffness along the (001) plane is isotropic.

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 (111) and (001), via the (011), as in premartensite. Accordingly, equivalence of the elastic properties would be expected between the (001) and (011) 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 of polarization rotation have been based on 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, oriented along the (110). 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. Furthermore, in a poled condition, oriented PMN-PT crystals of a similar composition have been shown to be in a monodomain FE$_t$ state at room temperature, however, in an annealed condition a relaxor ferroelectric condition is known to exist instead. 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$_t$, FE$_o$, and metastable FE$_m$ monoclinic and FE$_r$ states. Polarization rotation would effectively occur, but it would be an inhomogeneous shearing. In consideration of the presence of a metastable intermediate FE$_r$ state, polarization rotation from the (111) to the (001) would occur in two steps. These steps are rotation from (111) towards (011), followed by a rotation from (011) towards (001). Accordingly, different types of FE$_m$ states would serve as bridges. One whose polarization is confined to the (0kl) plane that bridges FE$_t$ and FE$_r$, and a second whose polarization is confined to the (hkk) plane which bridges FE$_r$ and FE$_o$.

The presence of two bridging monoclinic states allows for the polarization in anyone of the three FE phases (FE$_t$, FE$_o$, or FE$_r$) 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 (011) towards either the (111) [via the (0kl) plane] or the (001) [via the (hkk) plane]. Consequently, in the FE$_r$ state, the values of $K_{33}$ and $d_{33}$ will be low along the (011), whereas along the (111) and (001) 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 (001) and (011) orientations in PMN-PT crystals. This isotropy has been explained based upon an inhomogenous shearing of the polarization from the pseudocubic (111) towards the (001), via the (011). 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 (111) compared to (100) and (011) suggests a large force constant anisotropy with extrema in the (011) plane.

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