

## Temperature stability of the piezoelectric and elastic response of dc biased [001] and [110] oriented Pb ( Zn 1/3 Nb 2/3 ) O 3 - PbTiO 3 single crystals

Ahmed Amin and Dwight Viehland

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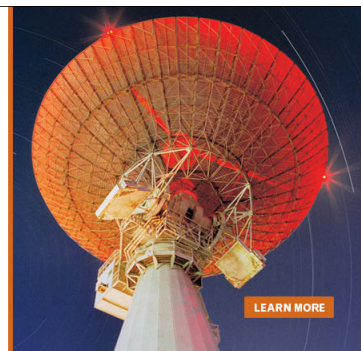
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# Temperature stability of the piezoelectric and elastic response of dc biased [001] and [110] oriented $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ single crystals

Ahmed Amin

Naval Sea Systems Command, Newport, Rhode Island 02841

Dwight Viehland

Department of Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia 24061

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Temperature and field dependent investigations of the longitudinal electromechanical properties of [001]- and [110]-oriented  $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.045\text{PbTiO}_3$  single crystals have been performed. Electromechanical equivalence was found between [001] and [110] orientations in the ferroelectric rhombohedral  $\text{FE}_r$  phase region, but not in the ferroelectric tetragonal  $\text{FE}_t$  one. A dc bias of 0.4 MV/m did not affect this equivalence. Softening of the dielectric constant ( $K$ ), piezoelectric coefficient ( $d_{33}$ ), and Young's modulus ( $Y$ ) were observed along both the [001] and [110] orientations in the  $\text{FE}_r$  phase region on heating towards the  $\text{FE}_t$  one. Above the  $\text{FE}_r\text{-FE}_t$  phase transition, a significant anisotropy was observed in the electromechanical and elastic coefficients. These results demonstrate that the enhanced length extensional (33-mode) electromechanical coupling  $k_{33}$  of rhombohedral crystals far from the morphotropic phase boundary is not constrained to the  $\langle 001 \rangle$  orientation, but rather to the (110) plane. © 2004 American Institute of Physics. [DOI: 10.1063/1.1789271]

## I. INTRODUCTION

Single crystals of lead zinc niobate–lead titanate PZN- $x\%$ PT and lead magnesium niobate–lead titanate PMN- $x\%$ PT are currently under development.<sup>1,2</sup> Investigations have focused on compositions close to the morphotropic phase boundary (MPB) between rhombohedral and tetragonal ferroelectric states. Their extremely high electromechanical coupling  $k_{33} > 0.90$  offers the potential for both broadband and high acoustic energy density when compared to standard lead zirconate titanate (PZT) ceramics. They show great promise in underwater sonar projectors, receiving arrays, and medical ultrasound imaging systems. A vast improvement in axial resolution and contrast of sonar and ultrasound systems will occur as a result of the single crystal broadband capabilities.

The high electromechanical properties of morphotropic ferroelectric PZN-PT single crystals were first reported nearly 20 years ago by Kuwata, Uchino, and Nomura.<sup>3,4</sup> In poled  $\langle 001 \rangle$ -oriented single crystals of  $0.91\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.09\text{PbTiO}_3$  longitudinal piezoelectric ( $d_{33}$ ) and electromechanical coupling ( $k_{33}$ ) coefficients of 1500 pC/N and 0.92 were reported, respectively. No length extensional results were reported for rhombohedral crystals far from the MPB. These investigations were performed by a standard resonance-antiresonance method under relatively low-field drive conditions, which were significantly below that required to induce saturation in the electrically-induced strain response ( $\epsilon\text{-}E$ ). Recently, the high-field behavior of  $\langle 001 \rangle$ -oriented PZN-PT 92/8 and  $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.3\text{PbTiO}_3$  (PMN-PT 70/30) crystals has been investigated by Shroud and co-workers.<sup>1,2</sup> Strain levels of up to 1.2% were reported at field levels of  $\sim 3$  MV/m. Accordingly, anomalously high values of  $d_{33} (> 4000 \text{ pC/N})$  can be estimated from the slope of the strain ( $\epsilon$ )-field ( $E$ ) curves (i.e.,  $d_{33} = \partial\epsilon/\partial E$ ).

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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.<sup>1,2</sup> The  $\text{FE}_r$  phase has a much smaller  $c/a$  ratio than the  $\text{FE}_t$ , accordingly under field the large  $c/a$  ratio change results in enhanced electrically-induced strains. Recent studies on PMN-PT and PZN-PT 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.<sup>5-9</sup> These results open an interesting possibility that intermediate states may be responsible for the high electromechanical performance.

Dielectric investigations<sup>7,8</sup> 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  $\text{FE}_t$  phases. The 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  $\text{FE}_t$  states might be sufficiently fragile so that changes in orientation, electrical history, or mechanical constraints may change the free energy balance. Piezoelectric studies on poled [110] crystals showed that a monodomain  $\text{FE}_o$  state does not exhibit enhanced piezoelectricity. However, a  $\langle 110 \rangle$ -oriented  $\text{FE}_r$  polydomain state exhibited very significant enhancements with a longitudinal piezoelectric constant ( $d_{33}$ ) of  $\sim 1500 \text{ pC/N}$ . Recent studies<sup>9</sup> by Viehland, Li, and Amin have demonstrated that the enhanced electromechanical performance of oriented  $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.3\text{PbTiO}_3$  single crystals is not con-

strained to the [001] orientation, but rather to the (110) plane, with the longitudinal coupling coefficient along [001] and [110] being equivalent.

Unfortunately, a thorough investigation of the anisotropy of the electromechanical properties as a function of dc bias and temperature has not yet been reported for any single composition in either the PMN-*x*% PT or PZN-*x*% PT crystalline solution. The purpose of this investigation was to determine the temperature dependence of the dc biased and unbiased longitudinal piezoelectric constant ( $d_{33}$ ), dielectric constant ( $K_{33}$ ), electromechanical coupling coefficient ( $k_{33}$ ), and Young's modulus ( $Y$ ) for (001)- and (110)-oriented 0.955Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-0.045PbTiO<sub>3</sub> (PZN-PT) crystals. Information concerning the effect of dc bias and temperature on the electromechanical properties is extremely useful, since dc biased operation will be required for applications of the crystals in sonar projectors.

In this work, we will show that the temperature dependent properties along the [001] and [110] orientations are nearly identical, and independent of bias in the FE<sub>r</sub> state. Also, an unusual piezoelectric instability between two ferroelectric states in [001] and [110] oriented crystals of PZN-PT has been found. We have observed a longitudinal piezoelectric coefficient of ~5000 pC/N along the [110] direction that is independent of bias (0.4 MV/m).

**II. EXPERIMENTAL PROCEDURE**

Ferroelectric rhombohedral [001]- and [110]-oriented 0.955Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-0.045PbTiO<sub>3</sub> crystals grown by a flux method were obtained from TRS Ceramics (State College, PA). The crystals were of dimensions 3 × 3 × 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. dc bias fields were applied using a high voltage dc source and a blocking circuit. Isothermal frequency sweeps under zero bias were first performed. This was followed by application of a dc bias of 0.4 MV/m, and subsequent repeat of the frequency sweep. The field was returned to zero bias, and the measurement process repeated at a number of stable temperatures between 20 < *T* < 130 °C.

**III. RESULTS**

The longitudinal piezoelectric coefficient ( $d_{33}$ ) versus temperature for poled [001]- and [110]-oriented PZN-PT crystals is shown in Fig. 1 for both the unbiased and dc biased conditions. An equivalence of  $d_{33}$  for the [001] and [110] directions is evident in both the FE<sub>r</sub> and FE<sub>t</sub> phase regions. The piezoelectric constant increased by a factor of 3 on heating from 20 < *T* < 100 °C, decreasing abruptly by a factor of 3 at *T* = *T*<sub>tr</sub> ~ 110 °C. In addition, the  $d_{33}$  values were not affected by dc bias in either the FE<sub>r</sub> or FE<sub>t</sub> phase

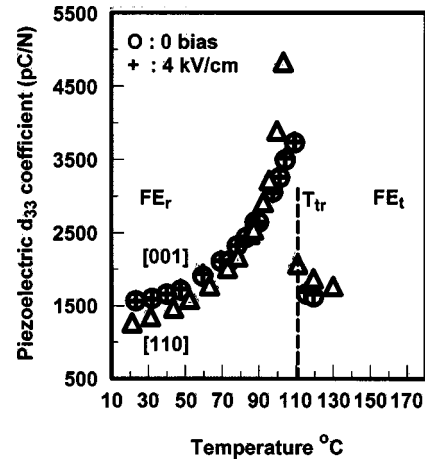


FIG. 1. Piezoelectric  $d_{33}$  coefficient as a function of temperature at 0 and 0.4 MV/m dc bias for [100]- and [110]-oriented PZN-PT crystals. dc field data points for the [110] orientation were omitted in all figures for clarity.

regions as one would expect for stable domain states. The application of dc bias did not cause any discernable change in the dielectric constant. Therefore, one should not expect any change in the piezoelectric coefficient due to intrinsic contributions ( $d = \epsilon_0 KQP$ , where  $\epsilon_0$  is the free space permittivity,  $K$  is the dielectric constant,  $Q$  is the electrostriction, and  $P$  is the polarization). This is consistent with the experimental observations.

Figure 2 shows the short circuit Young's modulus  $Y_1$  as a function of temperature for poled [001]- and [110]-oriented crystals at dc biases of 0 and 0.4 MV/m. Inspection of the data reveals that  $Y_1[110]$  is slightly larger than  $Y_1[001]$ , and that both coefficients are bias independent for 20 < *T* < 130 °C. Softening of  $Y_1[110]$  and  $Y_1[001]$  occurred upon approaching *T*<sub>tr</sub> (110 °C) from below. The values  $Y_1[110]$  and  $Y_1[001]$  decreased from 12 and 20 GPa, respectively at *T* = 25 °C, to ~8 GPa at 90 °C. The values of  $Y_1[110]$  and  $Y_1[001]$  were equivalent over the limited temperature range of 90 < *T* < 110 °C. In the FE<sub>t</sub> phase region for *T* > 110 °C, both  $Y_1[110]$  and  $Y_1[001]$  stiffened with increasing temperature. In addition, the anisotropy constant  $Y_1[110]/Y_1[001]$  was ~4.

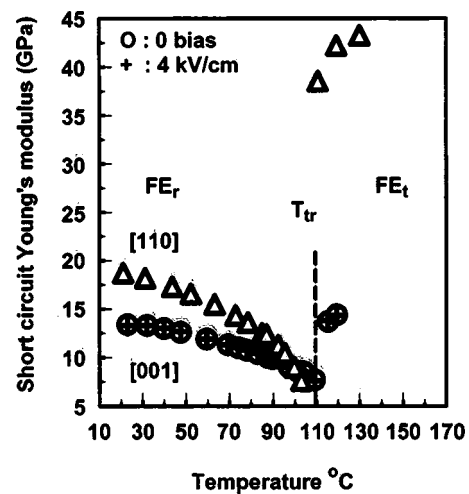


FIG. 2. Short circuit Young's modulus as a function of temperature at 0 and 0.4 MV/m dc bias for [100]- and [110]-oriented PZN-PT crystals.

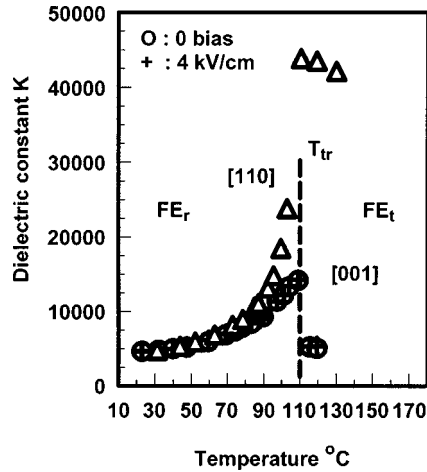


FIG. 3. Dielectric constant  $K$  as a function of temperature at 0 and 0.4 MV/m dc bias for [100]- and [110]-oriented PZN-PT crystals.

Figure 3 shows the longitudinal dielectric constant  $K_{33}$  as a function of temperature for poled [001]- and [110]-oriented crystals. The data reveal that the values of  $K_{33}[001]$  and  $K_{33}[110]$  are nearly equivalent over the temperature range of  $20 < T < 90$  °C. In both cases,  $K_{33}$  increased from  $\sim 5000$  to  $\sim 10000$  with increasing temperature over this range; however, in the range of  $90 < T < 110$  °C,  $K_{33}[110]$  increased much more rapidly than that of  $K_{33}[001]$ . For  $T > 110$  °C, abrupt changes in  $K_{33}$  were observed for both orientations, as a result of the  $FE_r$ - $FE_t$  transformation. The value of  $K_{33}[001]$  decreased dramatically, whereas that of  $K_{33}[110]$  increased. In the range of the  $FE_r$  phase ( $110 < T < 130$  °C), the anisotropy ratio  $K_{33}[110]/K_{33}[001]$  was  $\sim 10$ , which is significantly different than the value of one found in the  $FE_r$  phase. Figure 4 shows the inverse dielectric constant  $(K_{33})^{-1}$  as a function of temperature for poled [001]- and [110]-oriented crystals. In this figure,  $(K_{33})^{-1}$  can be seen to have a near-linear relationship with temperature in the poled condition for  $T < 110$  °C, along both the [001] and [110] orientations.

Figure 5 shows the longitudinal electromechanical cou-

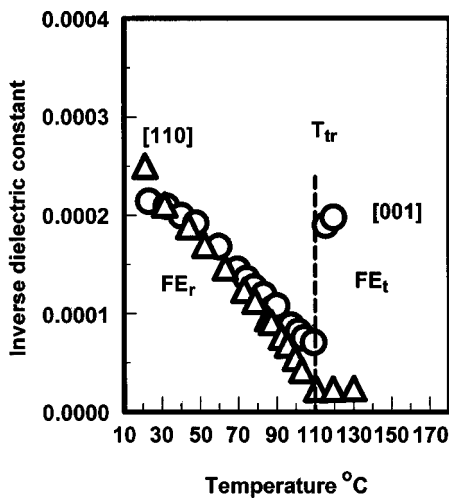


FIG. 4. Inverse  $K$  as a function of temperature at 0 dc bias for [100]- and [110]-oriented PZN-PT crystals.

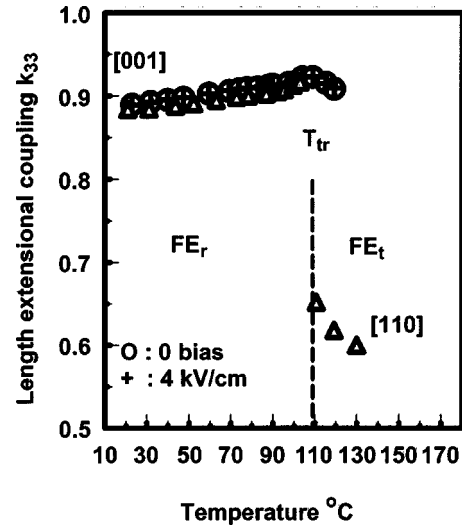


FIG. 5. Length extension coupling as a function of temperature at 0 and 0.4 MV/m dc bias for [100]- and [110]-oriented PZN-PT crystals.

pling coefficient ( $k_{33}$ ) as a function temperature for poled [001]- and [110]-oriented PZN-PT crystals. Inspection of the data reveals that the values of  $k_{33}$  along [001] and [110] are nearly equivalent and independent of dc bias over the temperature range of  $20 < T < 110$  °C. In both cases,  $k_{33}$  increased linearly from  $\sim 0.90$  to  $\sim 0.92$  over this temperature range. The temperature coefficient  $\alpha = (1/k_{33})(\partial k_{33}/\partial T)$  was determined from a linear least squares fit to the data for  $T < T_{tr}$  to be 350 and 430 ppm/°C for the [001]- and [110]-oriented crystals, respectively. For  $T > T_{tr}$ , in the  $FE_t$  phase field,  $k_{33}[110]$  was significantly smaller than that of  $k_{33}[001]$ .

#### IV. DISCUSSION

The results in this paper show an unusual isotropy of the electromechanical properties in the (110) plane for rhombohedral PZN-PT crystals far from the MPB. An electromechanical equivalence has been found between the [001] and [110] orientations in the  $FE_r$  phase field, over the temperature range of  $20 < T < 110$  °C. The short circuit Young's modulus for the two orientations is almost identical over the temperature range  $80 < T < 110$  °C. In contrast, significant anisotropy was observed in the  $FE_t$  phase field for  $T > T_{tr}$ .

These unusual attributes cannot be attributed to intermediate  $FE_o$  or  $FE_m$  phases, as no evidence of an intermediate ferroelectric state was found. The existence of metastable states in MPB compositions of PMN-PT crystals has previously been reported,<sup>8,9</sup> where the stability margin between states is altered by field, mechanical constraints, and electrical history.<sup>8</sup> Interestingly, the existence of a metastable  $FE_o$  state had earlier been predicted near the MPB of PZT.<sup>10</sup> Recent structural, optical and dielectric studies<sup>7,8</sup> of MPB PZN-PT crystals have demonstrated the existence of an intermediate  $FE_o$  state in-between the  $FE_r$  and  $FE_t$  phases for  $\langle 110 \rangle$  oriented crystals, but not for  $\langle 001 \rangle$  oriented ones. The width of the orthorhombic phase field depended on the poling field, temperature, and PT content ( $8.5\% < x < 11\%$  PT). The PZN-PT composition used in the present investigation is  $x=4.5\%$  PT, which lies outside this



range. A parameter space that comprises crystallographic orientation and electric boundaries (poling level) besides the usual composition and temperature coordinates has been suggested for PZN-PT phase diagrams.<sup>11</sup>

However, a parameter space that depends upon crystal cut, electrical and thermal histories is difficult to approach within a conventional Landau model. Rather, order parameter gradients and defects energy contributions will be an important part of the total energy. In fact, MPB compositions of PZN-PT and PMN-PT are known to contain microdomains or tweed.<sup>12</sup> Microdomains or tweed are a twinning that occurs on the 100 Å scale and result in a microinhomogeneous 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.<sup>13–17</sup>

Elastic isotropy in the (110) plane has previously been reported in martensitic transformations.<sup>18,19</sup> Martensitic phenomena are known to have an intermediate transformational region between pseudo-cubic and tetragonal ferroelastic phases in the presence of static quenched disorder.<sup>14,15,20</sup> Local symmetry reduction is driven by stress accommodation of microdomains,<sup>20</sup> resulting in metastable intermediate orthorhombic and monoclinic states. Symmetry adaptivity results from a lattice shearing from the pseudocubic  $\langle 111 \rangle$  towards the  $\langle 001 \rangle$ , via the  $\langle 110 \rangle$ . Consequently, an instability in  $1/2[C_{11}-C_{12}]$  is observed in the transformation,<sup>13</sup> and the effective elastic stiffness along the  $\langle 001 \rangle$ - $\langle 011 \rangle$  plane is isotropic.<sup>18,19</sup>

Premartensiticlike phenomena could also occur during a transformation between a pseudocubic (i.e., rhombohedral) FE and a FE<sub>r</sub> transition in the presence of quenched disorder. 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  $\langle 110 \rangle$ . Accordingly, equivalence of the elastic properties would be expected between the  $\langle 001 \rangle$  and  $\langle 110 \rangle$  orientations, due to an inhomogeneous polarization shearing. In consideration 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.

## V. SUMMARY

An unusual isotropy of the unbiased and dc biased longitudinal electromechanical and elastic properties has been found for [001]- and [110]-oriented PZN-PT crystals in the

FE<sub>r</sub> phase far from the morphotropic phase boundary (MPB). This isotropy has been explained based upon an inhomogeneous shearing of the polarization from the pseudocubic  $\langle 111 \rangle$  towards the  $\langle 001 \rangle$ , via the  $\langle 110 \rangle$ . Analogies between this transformation and martensitic transformations are discussed, where the transformation pathway is constrained by elastic stress accommodation. In contrast, a large anisotropy was observed in the phase region for  $T > T_{tr}$ . No discernable effect of dc bias ( $< 0.4$  MV/m) was found for the longitudinal piezoelectric, dielectric, and elastic properties of either the [001]- or [110]-oriented crystals suggesting a stable domain state and intrinsic contributions at this bias level. Unlike MPB compositions of PMN-PT crystals, no evidence of an intermediate ferroelectric orthorhombic state was observed for the PZN-PT crystal composition used in this investigation.

## ACKNOWLEDGMENT

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