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D. Viehland and J. F. Li

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Anhysteretic field-induced rhombhohedral to orthorhombic transformation in ⟨110⟩-oriented $0.7Pb(Mg_{1/3}Nb_{2/3})O_3-0.3PbTiO_3$ crystals

D. Viehland[a] and J. F. Li
Department of Materials Science and Engineering, Virginia Tech, Blacksburg, Virginia 24061

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The electric-field induced polarization ($P-E$) and strain ($\epsilon-E$) characteristics of $\langle 110\rangle_c$-oriented $0.7Pb(Mg_{1/3}Nb_{2/3})O_3-0.3PbTiO_3$ crystals have been investigated, under both unipolar and bipolar drive. A field-induced transformation was observed below saturation. Under unipolar drive, the $P-E$ and $\epsilon-E$ loops were anhysteretic even at the transformation point, demonstrating complete reversibility between ferroelectric rhombohedral and orthorhombic phases. The results show that ''polarization rotation'' can occur between $\langle 111\rangle_c$ and $\langle 110\rangle_c$, where the polarization is confined to the $(100)_c$ in a monoclinic M_b type symmetry.
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$(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-(x)PbTiO_3$ [designated as PMN–PT $(1-x)/x$ here forward] and $Pb(Zn_{1/3}Nb_{2/3})O_3-PbTiO_3$ [designated as PZN–PT $(1-x)/x$ here forward] single crystals are currently under development for use in transducer and projector applications.[1,2] In poled ⟨001⟩-oriented single crystals, longitudinal piezoelectric (d_{33}) and electromechanical coupling (k_{33}) coefficients of 1500 pC/N and 0.92 have been reported,[1–4] respectively. Strain levels of up to 1.2% have been reported at field levels of ~30 kV/cm.[1,2]

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] Theoretical considerations[5] have shown that a homogeneous polarization rotation (i.e., as a single domain condition) can occur between the $\langle 111\rangle_c$ (FE_r) and $\langle 001\rangle_c$ (FE_t) directions under an electric field. Two different rotation pathways were predicted, representing two possible monoclinic phases where the polarization is not constrained to a direction but rather a plane.[5–7] These two monoclinic ferroelectric (FE_m) phases were designated as M_c in which the polarization is confined to $(011)_c$ plane, and as M_a where the polarization is confined to $(010)_c$ plane, as shown in Fig. 1. Recent investigations have shown that ''rotation'' could be structurally inhomogeneous via microtwins,[8–10] rather than homogeneous.

The presence of an orthorhombic ferroelectric (FE_o) state has also been demonstrated by x-ray diffraction,[8] and by optical microscopy[11] and property measurements in $\langle 110\rangle_c$-oriented specimens that are poled.[8,11] Accordingly, a third FE_m symmetry M_b could potentially exist where the polarization is confined to the $(100)_c$. The purpose of this investigation was to perform high-field measurements of the induced polarization and strain for $\langle 110\rangle_c$-oriented piezocrystals.

$\langle 110\rangle_c$-oriented PMN–PT 70/30 [composition designated simply as PMN–PT here forward] grown by a flux method have been obtained from HC Materials (Urbana, IL). The crystals were of dimensions $0.05\times0.5\times0.5$ mm. The specimens were electroded with gold and poled. Polarization versus field ($P-E$) measurements were made using a modified Sawyer–Tower bridge. This system was computer controlled and capable of automatic determinations of standard $P-E$ measurement compensation parameters. A sinusoidal driving field was used. In addition, strain versus field ($\epsilon-E$) measurements were simultaneously performed using an inductance method. Specimen displacement was detected inductively using a linear variable differential transformer. A lock-in amplifier was used to filter random intensity fluctuations from those with the characteristic time constant of the drive, achieving small displacement resolutions. Measurements of the $P-E$ and $\epsilon-E$ characteristics were performed under both unipolar and bipolar drives. To enhance the smoothness of the data for susceptibility determination from the slopes of the curves, a sequential (25×) averaging mode was used for the unipolar measurements.

Figure 2 shows the bipolar $P-E$ and $\epsilon-E$ characteristics for $\langle 110\rangle_c$-oriented PMN–PT. Hysteretic responses can be

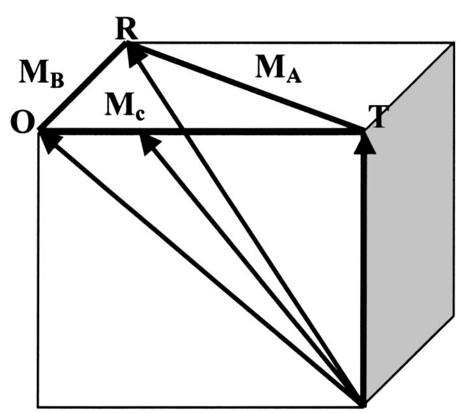

FIG. 1. Possible paths for polarization to change between the rhombohedral R and tetragonal T phases, as originally proposed by Fu and Cohen (see Ref. 5). The thick lines illustrate the planes in which the polarization is confined in the respective M_A, M_B, and M_C monoclinic states.

[a]Electronic mail: viehland@mse.vt.edu

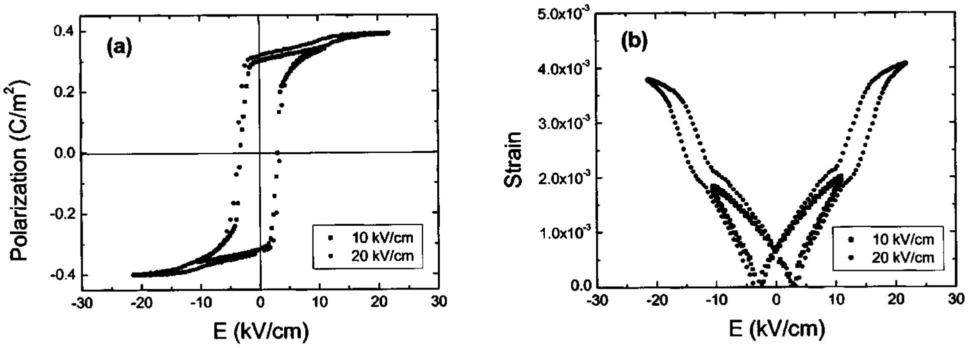

FIG. 2. Bipolar $P-E$ and $\epsilon-E$ characteristics of $\langle 110 \rangle_c$-oriented PMN–PT. (a) $P-E$ response and (b) $\epsilon-E$ response.

seen in both cases. In Fig. 2(a), the saturation polarization P_s, remanent polarization P_r, and coercive field E_c can be seen to be 0.4, 0.3 C/m^2, and 3.5 kV/cm, respectively. These results demonstrate that full saturation can be achieved along the $\langle 110 \rangle_c$. In Fig. 2(b), a typical butterfly hysteresis loop can be seen in the $\epsilon-E$ response. A high saturation strain of 4×10^{-3} and relatively low remanent strain of 6×10^{-4} can be seen. For $\langle 110 \rangle_c$-oriented specimens, it was consistently observed that the magnitude of strain on polarization switching in the tails of the hysteresis loops was quite small, resulting in a low remanent strain.

Data are shown at several different E in Fig. 2. At higher fields ($E>10$ kV/cm), an induced phase transformation was found. This induced transition is more clearly evident in the $\epsilon-E$ response, where the induced strain can be seen to increase significantly near $E=10$ kV/cm, shortly after which saturation is reached. The $P-E$ response also exhibited evidence of changes between measurements taken at 10 and 20 kV/cm. However, the difference in induced polarization between these two measurements was not large compared to the total polarization.

Figures 3(a) and 3(b) show the corresponding unipolar $P-E$ and $\epsilon-E$ characteristics, respectively. These data are pronouncedly anhysteretic, over the entire range of E investigated all the way to saturation. In particular, the integrated area of the hysteresis loop in the $P-E$ response was nearly zero, at least within the limits of instrumentation error. Data are shown for three different E. The data demonstrate an induced phase transformation near 10 kV/cm, reaching saturation near 12 kV/cm. It is important to notice that this induced phase transformation was also anhysteretic. The magnitude of ΔP and ϵ at 12 kV/cm was 0.07 C/m^2 and 3×10^{-3}, respectively, which is a relatively high induced strain for a small ΔP. Accordingly, the piezoelectric (d_{33}) and electromechanical coupling (k_{33}) coefficients are high along the $\langle 110 \rangle_c$. Resonance-antiresonance investigations of $\langle 110 \rangle_c$-oriented PMN–PT crystals demonstrated equally high values of the d_{33} (1500 pC/N) and k_{33} (0.94) coefficients, as that found along the $\langle 001 \rangle_c$. This dismisses the notion that the high electromechanical performance can only be due to an induced FE$_t$ phase and/or polarization rotation towards $\langle 001 \rangle_c$.

These results are in contrast to the induced phase transition observed in $\langle 001 \rangle$-oriented crystals, where significant

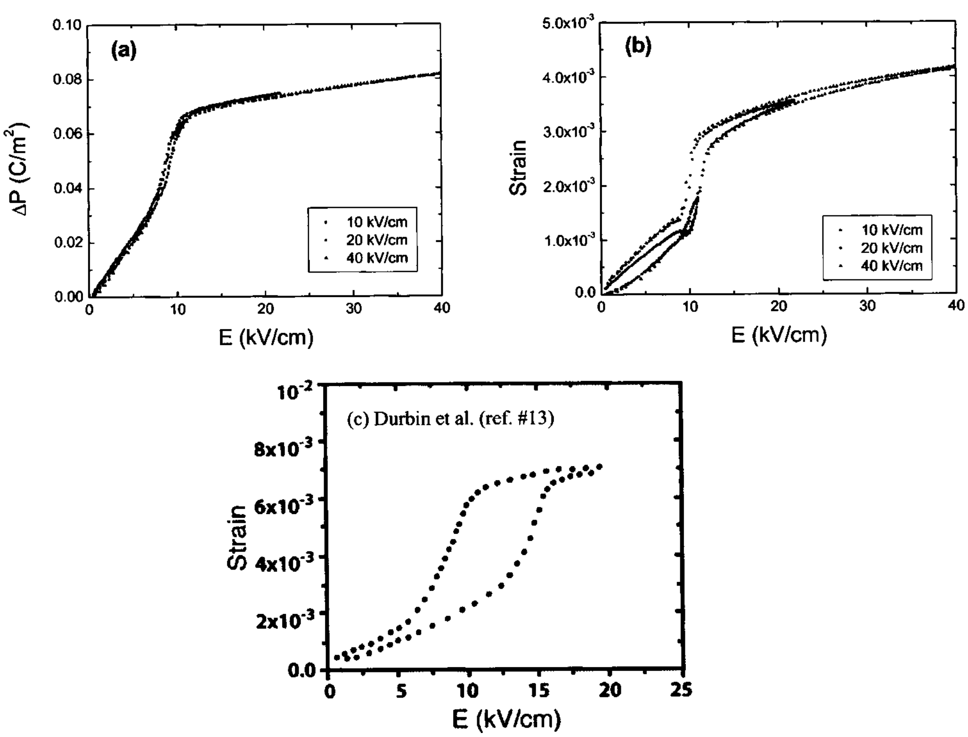

FIG. 3. Unipolar $P-E$ and $\epsilon-E$ characteristics of $\langle 110 \rangle_c$-oriented PMN–PT. (a) $P-E$ response and (b) $\epsilon-E$ response. (c) Unipolar $\epsilon-E$ characteristics of $\langle 001 \rangle_c$ PZN–PT for comparisons (see Ref. 13).

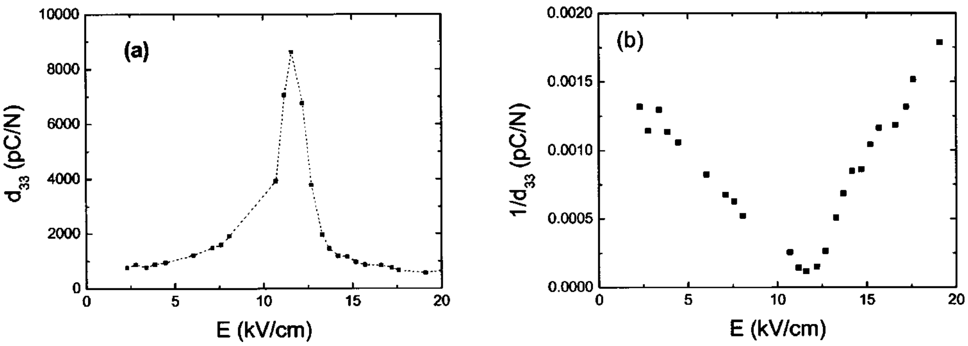

FIG. 4. d_{33} and $(d_{33})^{-1}$ as a function of E of $\langle 110\rangle_c$-oriented PMN–PT, calculated from the slope of Fig. 3(b). (a) d_{33} and (b) $(d_{33})^{-1}$.

hysteresis occurs,[1,2,12,13] as shown in Fig. 3(c). For an electric field applied along the $\langle 001\rangle_c$ in PMN–PT, first principles calculations[7] have shown that polarization rotation occurs first from $(111)_c$ towards $(001)_c$ via M_c, transforming to M_a at a critical field above which point rotation occurs from $(110)_c$ towards $(001)_c$. This transformation results in hysteresis in the unipolar $P-E$ and $\epsilon-E$ responses.[12,13] For $\langle 110\rangle_c$-oriented PMN–PT, the results in Fig. 3 give evidence of a polarization rotation from $(111)_c$ towards $(110)_c$ via M_b. With increasing *E*, rotation occurs towards $(110)_c$, but reaches a critical point at which it undergoes a transformation to the FE_o phase. This FE_o phase has been observed by x-ray diffraction,[8] optical microscopy,[9] and by full saturation in the polarization in $\langle 110\rangle_c$-oriented crystals. There is no intermediate step in the transformation sequence, such as observed for $\langle 001\rangle_c$-oriented specimen, and thus significantly reduced hysteretic effects are found.

Figure 4(a) shows d_{33} as a function of E, which was calculated from the slope (increasing E side) of the $\epsilon-E$ response. These data demonstrate a strong increase in d_{33} with E near 10 kV, approaching a maximum value of 9000 pC/N. This instability demonstrates a field-induced transformation. A Curie–Weiss-type plot of $(d_{33})^{-1}$ as a function of E is shown in Fig. 4(b). Linear behavior both above and below the transformation point can be seen, where the ratio of the slopes was 2:1. This is consistent with a near-second order transformation. It is interesting that the susceptibility in the elastic strain with E follows Curie–Weiss type behavior, such results would not necessarily require polarization rotation via an intermediate FE_m phase sandwiched between the FE_r and FE_o phases. Rather, a simple mean-field approach could explain some of the attributes of the enhanced piezoelectric response.

In summary, the results of this investigation demonstrate a near completely reversible transformation between a FE_r and FE_o phases in $\langle 110\rangle_c$-oriented PMN–PT crystals, where the polarization is confined to the $(100)_c$ in a monoclinic M_b type symmetry. This induced transformation results in equally high electromechanical coefficients, as that observed for $\langle 001\rangle_c$ oriented crystals. In PMN–PT, various induced transformations can occur at relatively low fields, depending upon specimen orientation.

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