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Piezoelectric response and origin in (001) $Pb(Mg_{1/3}Nb_{2/3})_{0.70}Ti_{0.30}O_3$ crystal

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Converse and direct piezoelectric coefficients (d_{33}^C and d_{33}^D) of (001)-cut $Pb(Mg_{1/3}Nb_{2/3})_{0.70}Ti_{0.30}O_3$ (PMN-30%PT) single crystals have been investigated as a function of poling electric (E) field. E-field-dependent domain structures were observed by using a polarizing microscope. Both d_{33}^C and d_{33}^D exhibit a rapid increase at $E=1-2$ kV/cm and reach maxima at $E=2.5-4$ kV/cm. This study suggests that polarization rotation from rhombohedral to monoclinic M_A phases plays an important role while the high piezoelectric response builds up. Overpoling phenomenon evidenced by a sudden reduction in piezoelectric coefficient with increasing field is very sensitive to Ti content. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3012384]

The most attractive feature of relaxor-based ferroelectrics $Pb(Mg_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$ (PMN-PT) is that they have high piezoelectric coefficients compared with lead zirconic titanate ceramics.[1] Ferroelectric (FE) and piezoelectric properties of PMN-PT are sensitive to Ti content, poling E field, and crystallographic orientation.[1] The ultrahigh piezoelectric response (piezoresponse) has been theoretically attributed to polarization rotations between rhombohedral (R) and tetragonal (T) phases through monoclinic (M) or orthorhombic (O) symmetries.[2]

From E-field-dependent domain observation, a polarization rotation via an $R-M_A-T_{001}$ transition sequence was evidenced in a (001) PMN-24%PT crystal.[3] Randomly distributed [001] T domains were observed under $E=38$ kV/cm in a (001) PMN-30%PT crystal[4] and suggested that the domain matrix consists of dipole glass and FE nanoclusters as proposed for PMN.[5] From synchrotron x-ray diffraction (XRD), an M_A phase was observed in a (001) PMN-35%PT crystal after poling at $E=43$ kV/cm, but if only weakly poled the sample exhibits an average R symmetry.[6] An overpoling was observed in piezoelectric coefficients of flux-grown PMN-(31–32)%PT crystals.[7] No overpoling was seen in PMN-28%PT and PMN-30%PT crystals.[7] A recent E-field-dependent d_{33} measurement in a (001) PMN-30%PT crystal showed a dramatic overpoling for $E\geq 2$ kV/cm due to the appearance of M_C phase.[8]

The equality of "direct piezoelectric effect ($P_i=d_{ij}X_j$)" (the production of surface charge when an external stress is applied) and "converse piezoelectric effect ($S_j=d_{ij}E_i$)" (the production of strain when an external E field is applied) is self-evident.[9] In other words, the piezoelectric coefficient $d_{ij}=(P_i/X_j)_E=(S_j/E_i)_T$ can be obtained by measuring surface charge density or strain under external stress or E field, respectively. Here P, E, X, and S represent charge density (C/m^2), E field (V/m), mechanical stress (N/m^2), and strain, respectively.

In this crystal and other relaxor FE crystals,[7,8] the piezoelectric coefficient often shows a rapid increase with field in the low-field region, followed by a reduction due to overpoling. No one had explained before with experimental evidence of this rapid piezoresponse increase with E field in PMN-PT crystals, which is crucial for applications. In this report, we propose that $R-M_A$ polarization rotation is responsible for this high piezoresponse in the (001) PMN-30%PT crystal. No significant overpoling was observed with increasing field. However, a moderate overpoling was observed in a crystal with a slightly smaller Ti content.

The PMN-30%PT crystal was grown using a modified Bridgman method. The sample was cut perpendicular to a ⟨001⟩ direction. The Ti content (x) was determined by using the zero-field-heated[4] dielectric maximum temperature $T_m=414.75$ K at $f=10$ kHz, i.e., $x=[T_m(°C)+10](\%)/5\cong 30.4\%$.[10] For measurement of the converse piezoelectric coefficient (d_{33}^C), a Rigaku Model MultiFlex x-ray diffractometer with Cu $K\alpha_1$ and Cu $K\alpha_2$ radiations was used for determination of d spacing. The widths of divergence and scattering slits are 0.5° and the cross section of the x-ray beam on the sample is greater than 4×4 mm^2. The sample dimensions are $5.7\times 4.0\times 0.6$ mm^3 and the basal surfaces were coated with thin gold electrodes (thickness $\cong 30$ nm). The intensity ratio of $K\alpha_1$ and $K\alpha_2$ radiations is about 2:1.[11] The conventional x-ray penetration depth is less than 10 μm.[12] The XRD spectra were fitted with a sum of Gaussian and Lorentzian terms.

Two processes were used in the XRD scans. The first is called "prior poled before zero-field" (PP-ZF), in which the crystal was poled along [001] by a dc voltage at room temperature for 20 min and then the XRD scan was performed without E field. In the "nonzero-field" (NZF) process, the crystal was poled at room temperature for 20 min and then the XRD scan was performed under the same E field. The E field was raised in steps in both PP-ZF and NZF. Hereafter, $d_{E=0}$ and $d_{E\neq 0}$ represent the d spacings obtained from the first and second processes, respectively. The 2θ reflection and d spacing obey the Bragg law $2d\sin\theta=n\lambda$. The strain (S_3) and d_{33}^C were calculated by the equations, $S_3(\%)=(d_{E\neq 0}-d_{E=0})\times 100\%/d_{E=0}$ and $d_{33}^C=E_3/S_3$.

The direct (or normal) piezoelectric coefficient (d_{33}^D) was measured by using a model ZJ-6B quasistatic piezo-d_{33}/d_{31}

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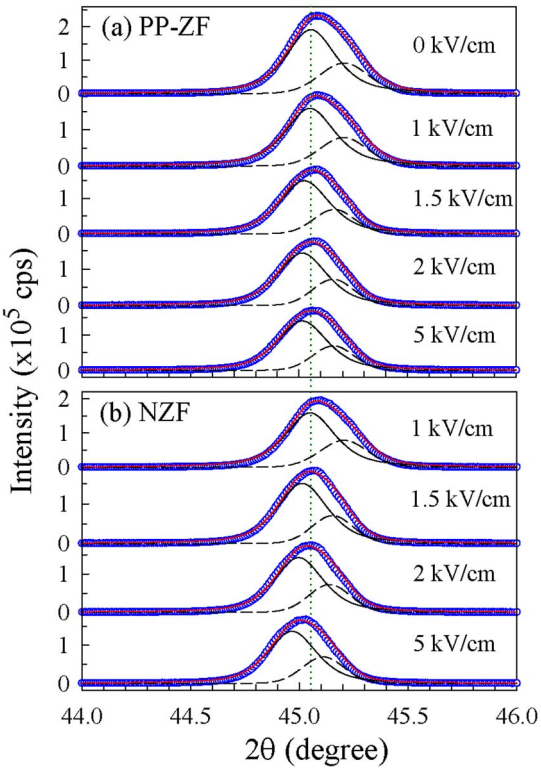

FIG. 1. (Color online) *E*-field-dependent (002) (a) PP-ZF and (b) NZF XRD spectra. The solid and dashed lines correlate to the $K\alpha_1$ and $K\alpha_2$ radiations, respectively. The red solid line is the sum of fittings. The dotted line is a guide for the XRD shifts.

meter. d_{33}^D was obtained by measuring the surface charge density (P) under a stress along [001], i.e., $d_{33}^D = P_3/X_3$. Before each d_{33}^D measurement, the sample was poled along [001] by a dc voltage at room temperature for 20 min.

E-field-dependent domain structures were observed by using a Nikon E600POL polarizing microscope with a crossed polarizer/analyzer (P/A) pair. Transparent conductive films of indium tin oxide were deposited on the (001) surfaces. The sample thickness is about 70 μm. Angles of the P/A pair measured are with regard to the [110] direction. The experiment and details for using optical extinction to determine domain phases can be found in Refs. 1 and 3.

Figure 1(a) shows the (002) PP-ZF XRD spectra at different poling *E* fields. The XRD peak shows a shift toward low-2θ positions as *E* field increases. A significant shift occurs at $E=1-2$ kV/cm, which is slightly less than the coercive field of $E_C \cong 2.2$ kV/cm measured at 46 Hz.[4] Above $E=2.0$ kV/cm, the XRD position exhibits a rather gradual change as *E* field increases. Similar *E*-field-dependent behavior was observed in the (002) NZF XRD spectra as seen in Fig. 1(b), which shows a rather significant shift at $E=1-2$ kV/cm.

By using the Bragg law from the $K\alpha_1$ radiation, both *d* spacing and full width at half maxima (δ_{FWHM}) are plotted in Fig. 2 as a function of *E* field. The accuracy of *d* spacing is better than 0.1%. Both *d* spacing and δ_{FWHM} exhibit a significant response at $E=1-2$ kV/cm, especially for the NZF XRD spectra. $d_{E\neq 0}$ and $d_{E=0}$ spacings exhibit an approximately linear response at $E \geq 2.0$ kV/cm. A small but obvious reduction in δ_{FWHM} that occurs at $E \geq 2.0$ kV/cm in both PP-ZF and NZF XRD spectra suggests a sudden increase in domain size, especially in the NZF.

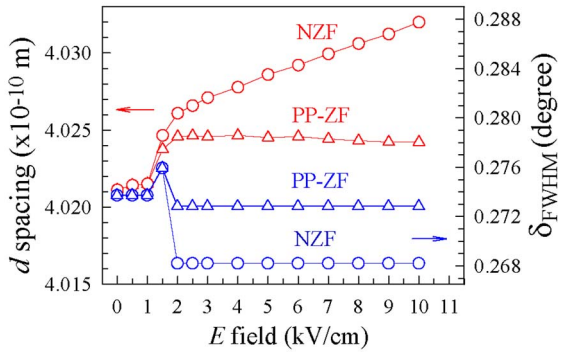

FIG. 2. (Color online) *E*-field-dependent *d* spacing and δ_{FWHM}.

Figure 3 shows *E*-field-dependent d_{33}^C and d_{33}^D. Both d_{33}^C and d_{33}^D exhibit a rapid and large growth at $E=1-2$ kV/cm and reach maxima of about 2100 and 1600 pC/N, respectively. The d_{33}^D is the average value measured from positions near the center of the sample. An obvious variation of about 50% in d_{33}^D was observed at different positions on the sample surface. A significant variation (>80%) in d_{33}^D was reported in a (001) PMN-30%PT crystal.[8] The reason why d_{33}^C is about 30% larger than d_{33}^D at $E \geq 3$ kV/cm is possibly a spatial variation in Ti content. In addition, surface current leakage may occur in the d_{33}^D measurement and causes a reduction below the true value.

To understand what causes the rapid piezoresponse at $E=1-2$ kV/cm, *E*-field-dependent domain structures were observed as given in Fig. 4. Most of the domain matrix at zero field has an extinction angle at P/A=0°, indicating that the major phase is rhombohedral. There is no obvious change in the extinction angle at $E=0-2$ kV/cm in which the piezoelectric coefficient increases rapidly.

To explain the above results, we examine their consistency with three hypotheses. The first hypothesis is that the field induces a *T* domain polarized along [001]. This would require that the extinction angle changes from 0° to 45°, which does not occur. The second hypothesis is that the field applied along [001] favors the four *R* domains with a polarization component along [001]. Field-induced rotation of

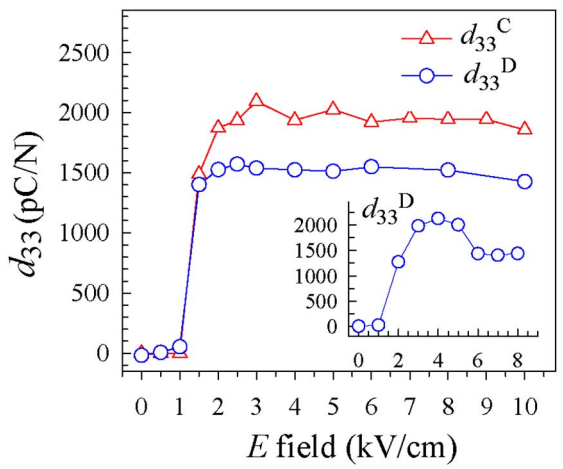

FIG. 3. (Color online) *E*-field-dependent piezoelectric coefficients d_{33}^D (circle symbol) and d_{33}^C (triangle symbol). The inset is the maximum d_{33}^D obtained from another (001) PMN-30%PT crystal with 29.6% Ti content.

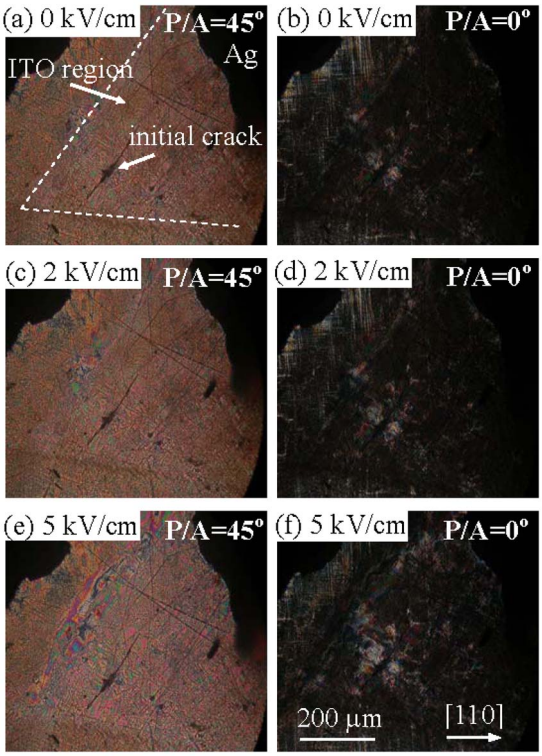

FIG. 4. (Color online) *E*-field-dependent domain structures observed at P/A=45° and 0°.

these vectors and the accompanying structure has been thought according to the principles of "domain engineering" to account for the large d_{33} once the field has succeeded in reducing the number of domain types from eight to four. The major drawback of this hypothesis is that the PP-ZF XRD result in Fig. 2 shows *d* spacing increasing with field from 4.021 to about 4.025 Å. Conversion of an antialigned domain such as $[\bar{1},\bar{1},\bar{1}]$ to its aligned [1,1,1] opposite polarization direction does not require any change in the unit cell shape or orientation; only the internal ionic configuration changes. Accordingly, there should be no change in *d* once the field is removed in the PP-ZF. The third hypothesis is that the field, perhaps after reducing the number of domain types from eight to four, changes these $4R$ domain types to the $4M_A$ domain types with similar polarization directions.

According to the optical extinction principles for the (001) orientation,[3] these M_A domain types have the same 0° extinction angle as the *R* phase. As shown in Figs. 1 and 2, the XRD peak exhibits a dramatic shift at $E=1-2$ kV/cm and remains at the same shifted value for larger fields in the PP-ZF experiment. If the shift was caused by field-induced strain that does not completely relax when the field is removed, one would expect *d* to increase with *E* for $E>2$ kV/cm. On the contrary, this independence of shift from prior *E* magnitude is consistent with the third hypothesis because once the field is large enough to induce the M_A phase, for PP-ZF the *d* spacing stays at the equilibrium value for that phase and is not affected by how large the field was. These results suggest that the dramatic piezoresponse at $E=1-2$ kV/cm is caused by polarization rotation from *R* to M_A phases. This is consistent with the first-principles calculation of $BaTiO_3$,[2] which predicts that the minimum energy path (with a rapid increase in strain) of polarization rotation from ⟨111⟩ to ⟨001⟩ is the M_A phase. At $E>2$ kV/cm as shown in Figs. 4(e) and 4(f), more domains have extinctions at $P/A\neq 0°$, implying a gradual expansion of *M* phase (possible M_A) in the matrix.[4] Of the 24 types of M_A domains, only eight have extinction angle at 0°.

The inset in Fig. 3 shows the d_{33}^D (which is the maximum value) obtained from another (001) PMN-30%PT crystal whose zero-field-heated dielectric maximum temperature is $T_m=410.81$ K at $f=10$ kHz, i.e., $x\cong 29.6\%$. The d_{33}^D reaches a maximum of about 2100 pC/N near $E=4$ kV/cm and then a moderate overpoling appears at $E\geq 6$ kV/cm. A dramatic overpoling was reported in a (001) PMN-30%PT and was attributed to the M_C phase.[8] The main reason to cause the diversity among (001) PMN-30%PT crystals seen in Fig. 3 and Ref. 8 is composition segregation, especially for $x\cong 30\%$ which locates at the morphotropic phase boundary.[13]

In conclusion, the (001) PMN-30%PT crystal exhibits a rapid increase in both d_{33}^C and d_{33}^D at $E=1-2$ kV/cm. The origin of this rapid increase in piezoresponse is polarization rotation through the $R-M_A$ transformation. This study suggests that polarization rotation, which is consistent with first-principles calculations,[2] plays a crucial role in providing the high piezoresponse. No significant overpoling was observed in the (001) PMN-30.4%PT crystal. However, a moderate overpoling was observed in the crystal with 29.6% Ti content.

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