Rapid piezoelectric response and origin in (001) $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})_{0.70}\text{Ti}_{0.30}\text{O}_3$ crystal

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Rapid piezoelectric response and origin in (001) $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})_{0.70}\text{Ti}_{0.30}\text{O}_3$ crystal

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Normal piezoelectric coefficient d_{33} , domain structure, and x-ray diffraction of a (001)-cut $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})_{0.70}\text{Ti}_{0.30}\text{O}_3$ (PIN-30%PT) single crystal have been investigated as a function of poling electric (E) field. E -field-dependent domain structures were observed by using a polarizing microscope. Piezoelectric coefficient d_{33} exhibits a rapid increase at $E=1-3$ kV/cm and reaches a maximum of about 1200 pC/N near $E=6$ kV/cm. Structural d spacing and domain structure results suggest that polarization rotation from rhombohedral to monoclinic M_A phases causes the high piezoelectric response. Overpoling phenomenon associated with a sudden reduction of d_{33} with increasing field was not evidenced. © 2009 American Institute of Physics.

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The most attractive feature of relaxor-based ferroelectrics $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PMN-PT) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PZN-PT) is that they have high piezoelectric coefficients compared with PZT ceramics.¹ Ferroelectric (FE) and piezoelectric properties of these high-strain crystals 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 To reduce thermal instability caused by overheating, it has been a goal to find crystals with high Curie (T_C) or depolarization temperatures. Among high-strain FE materials, $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})_{1-x}\text{Ti}_x\text{O}_3$ (PIN-PT) crystals have drawn attention because of their high- T_C feature.³ For instance, the depolarization temperature $T_d \cong 122$ °C of (001) PIN-30%PT crystal is about 20–40 °C higher than PMN-24%PT and PMN-30%PT crystals.⁴

From E -field-dependent domain observation, micron-size orientational percolation was induced in a (001) PIN-30%PT crystal with an E field along [001].³ Under $E=40$ kV/cm at room temperature, [001] tetragonal domains randomly appeared in the matrix,³ suggesting two components (spherical glassy matrix and polar nanoclusters) as proposed for PMN.⁵ The (001) PIN-34–35%PT crystals have piezoelectric coefficient $d_{33} \cong 2000$ pC/N and electromechanical coupling factor $k_{33} \cong 94\%$ with $T_C \cong 270$ °C.^{6,7} A diffuse E -field-induced R - T transition was evidenced in a (001) PIN-28%PT crystal.⁸

In this crystal and other high-strain relaxor FE crystals,^{9–11} the piezoelectric coefficient often shows a rapid increase at the low-poling E fields, perhaps followed by an

overpoling reduction with increasing field. No one had observed and explained before with experimental evidence of this rapidly E -field-dependent piezoresponse for the PIN-PT crystals. In this report, we propose that R - M_A polarization rotation is responsible for the rapid growth of piezoresponse at $E=1-3$ kV/cm in the (001) PIN-30%PT crystal.

The single crystal PIN-30%PT (starting composition) was grown using a modified Bridgman method with an allomeric PMN-29%PT seed crystal to restrain the pyrochlore phase. The sample was cut perpendicular to a (001) direction. The normal (or direct) piezoelectric coefficient d_{33} was measured by using a model ZJ-6B quasistatic piezometer. d_{33} was obtained by measuring the surface charge density (P) under a stress (X) along [001], i.e., $d_{33} = P_3/X_3$. Before each d_{33} measurement, the sample was poled along [001] by a dc voltage at room temperature.

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 12.

A Rigaku model MultiFlex x-ray diffractometer with $\text{Cu } K\alpha_1$ and $\text{Cu } K\alpha_2$ radiations was used for E -field-dependent x-ray diffraction (XRD), in which the crystal was poled along [001] at room temperature for about 30 min and then the XRD scan was performed without an E field. The basal surfaces were coated with thin gold films (thickness $\cong 30$ nm) as electrodes. The intensity ratio of $K\alpha_1$ and $K\alpha_2$ radiations is about 2:1.¹³ The XRD spectra were fitted with a sum of Gaussian and Lorentzian terms. The 2θ -reflection and d spacing obey the Bragg's law, $2d \sin \theta = n\lambda$.

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FIG. 1. (Color online) E -field-dependent piezoelectric coefficient d_{33} of (001) PIN-30%PT.

Figure 1 shows E -field-dependent direct piezoelectric coefficient d_{33} , which exhibits a rapid increase at $E = 1\text{--}3$ kV/cm and reaches a maximum of about 1200 pC/N near $E = 6$ kV/cm. The d_{33} shows a very slight reduction for $E > 10$ kV/cm. Note that the coercive field (E_C) at room temperature is about 4.5 kV/cm measured at 46 Hz.³ A similar but more dramatic increase in piezoresponse at $E = 1\text{--}2$ kV/cm was observed in the (001) PMN-30%PT crystal.¹¹

To understand what causes the rapid piezoresponse at $E = 1\text{--}3$ kV/cm, E -field-dependent domain structures were observed at room temperature as given in Fig. 2. Most of the domain matrix at $E = 0$ has an extinction angle at $P/A = 0^\circ$, indicating that the major phase is rhombohedral. There is no obvious change in the extinction angle at $E \leq 4$ kV/cm in which range the d_{33} increases rapidly. For poling field $E \geq 5$ kV/cm, percolating microdomains of approximately 10–200 μm sizes were induced with the green-blue regions seen at $P/A = 45^\circ$ and the extinction at $P/A = 0^\circ$. The field-induced micrometric percolations were possibly caused by rotating much smaller microdomains or nanocluster polarizations into alignment so that the boundaries disappear.

FIG. 2. (Color online) E -field-dependent domain structures observed at $P/A = 45^\circ$ and 0° .

FIG. 3. (Color online) E -field-dependent (002) XRD spectra at $E = 0\text{--}7$ kV/cm taken at room temperature. 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 2θ -shift.

Figure 3 shows E -field-dependent (002) XRD spectra taken after poling at room temperature. The (002) XRD suggests a coexistence of R phase (the high- 2θ strong peak) and M phase (the low- 2θ broad shoulder) at room temperature. The high- 2θ strong peak (as indicated by “I”) shows a significant shift between 1.5 and 3 kV/cm, which is consistent with the rapid response in d_{33} at $E = 1\text{--}3$ kV/cm. Above $E = 3.0$ kV/cm, the d_1 spacing exhibits a rather slight change as E field increases.

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 these vectors has been considered 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 XRD result (Fig. 3) shows d spacing increasing with field from $d_1 = 2.0211$ Å ($E = 0$) to about $d_1 = 2.0232$ Å ($E = 7$ kV/cm). Conversion of an oppositely oriented domain, such as $[\bar{1}, \bar{1}, \bar{1}]$ to its opposite polarization direction $[1, 1, 1]$, does not require any change in the unit cell shape. The third hypothesis is that after reducing the number of domain types from eight to four, the field perhaps changes the four R domain types to $4M_A$ domain types with similar polarization directions.

According to the optical extinction principle for the (001) orientation, these M_A domain types have the same extinction angle as the R phase.^{1,12} As shown in Fig. 3, the high- 2θ peak (as indicated by I) exhibits an obvious shift at $E = 1.5\text{--}3.0$ kV/cm, and remains at almost the same shifted

value for larger fields. The broad low- 2θ peak (as indicated by “II”) does not exhibit obvious change with E field. If the shift was caused by a field-induced strain that does not completely relax when the field is removed, one would expect d to increase with E for $E > 3$ kV/cm. On the contrary, the shift is independent of the prior E magnitude. It is consistent with the third hypothesis because once the field is large enough to induce the M_A phase, the d spacing stays at the equilibrium value for that phase and is not affected by the increasing E field. These results suggest that the dramatic piezoresponse at $E = 1\text{--}3$ 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 $\langle 111 \rangle$ to $\langle 001 \rangle$ is the M_A phase.

In conclusion, the direct piezoelectric coefficient d_{33} of the (001) PIN-30%PT crystal exhibits a rapid increase at $E = 1\text{--}3$ kV/cm and then reaches a maximum of about 1200 pC/N near $E = 6$ kV/cm. This rapid increase in piezoresponse with the increasing field is attributed to polarization rotation through the R - M_A phase transformation. A similar rapid piezoresponse was evidenced at $E = 1\text{--}2$ kV/cm in a (001) PMN-30%PT crystal.¹¹ These studies suggest that polarization rotation between R and M_A phases plays a crucial role for the rapidly E -field-dependent piezoresponse in high-

strain relaxor FE crystals.¹¹ Overpoling phenomenon of d_{33} was not observed in this (001) PIN-30%PT crystal.

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