Orientation dependence of piezoelectric properties of single domain $0.67Pb(Mg_{1/3}Nb_{2/3})O_3-0.33PbTiO_3$ crystals

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The orientation dependence of piezoelectric properties has been calculated for $0.67Pb(Mg_{1/3}Nb_{2/3})O_3-0.33PbTiO_3$ (PMN–33%PT) single-domain crystals based on the measured full matrix properties. It is found that the maximum $d_{33}^{*}=2411$ pC/N and $k_{33}^{*}=0.94$ occur, respectively, in directions 63.0° and 70.8° from the spontaneous polarization direction. In [001] of the cubic coordinate, the rotated properties are $d_{33}^{*}=2316$ pC/N and $k_{33}^{*}=0.93$, respectively, comparable to the measured multidomain properties. The results revealed the origin of the superior electromechanical properties in [001] poled PMN–33%PT multidomain crystals as from the large d_{15} of the single-domain property. © *2003 American Institute of Physics.*
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The quality of relaxor based $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PZN–PT) and $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMN–PT) ferroelectric single crystals has improved drastically since 1996,[1–4] and several complete data sets of PZN–PT and PMN–PT single crystals have been measured for different compositions.[5–9] As shown in the measured data sets, the effective electromechanical coupling coefficient k_{33}^{eff} could be as large as 0.94 for $0.67Pb(Mg_{1/3}Nb_{2/3})O_3-0.33PbTiO_3$ (PMN–33%PT) multidomain single crystal, and its piezoelectric coefficient d_{33}^{eff} could reach 2820 pC/N; while for $0.92Pb(Zn_{1/3}Nb_{2/3})O_3-0.08PbTiO_3$ (PZN–8%PT) crystals, the d_{33}^{eff} could even reach 2900 pC/N. Such values are more than four times of that of the best modified $Pb(Zr_xTi_{1-x})O_3$ ceramics, which have been dominating piezoelectric applications for more than 40 years. In order to understand the origin of these high electromechanical properties, intensive research has been conducted on these crystals.[10–18] It is conceivable that the orientation dependence would play a key role in these multidomain systems, but one cannot evaluate it quantitatively because of the lack of a complete data set for the single domain state. Recently, we have successfully obtained such a complete data set for the PMN–33%PT by applying a bias field to maintain the unstable single domain configuration.[19] This letter is to calculate the orientation dependence based on our measured complete data sets for the single domain state.

Above 160 °C, the PMN–33%PT single crystal has a cubic perovskite structure with crystal symmetry $m\bar{3}m$. It transforms to ferroelectric rhombohedral phase with $3m$ symmetry when cooled below 160 °C. However, the single domain state is proved to be rather unstable at room temperature, which makes the characterization of the single domain data rather difficult. When an electric poling field along [001] of the original cubic coordinates is applied to the crystal, a multidomain configuration can be produced, which consists of four degenerate states and two sets of perpendicular charged domain walls. The interlocking of many domains and the presence of charged defects makes the multidomain structure much more stable than the single domain state. Statistically, the multidomain crystal has a pseudotetragonal $4mm$ macroscopic symmetry, although the microscopic crys-

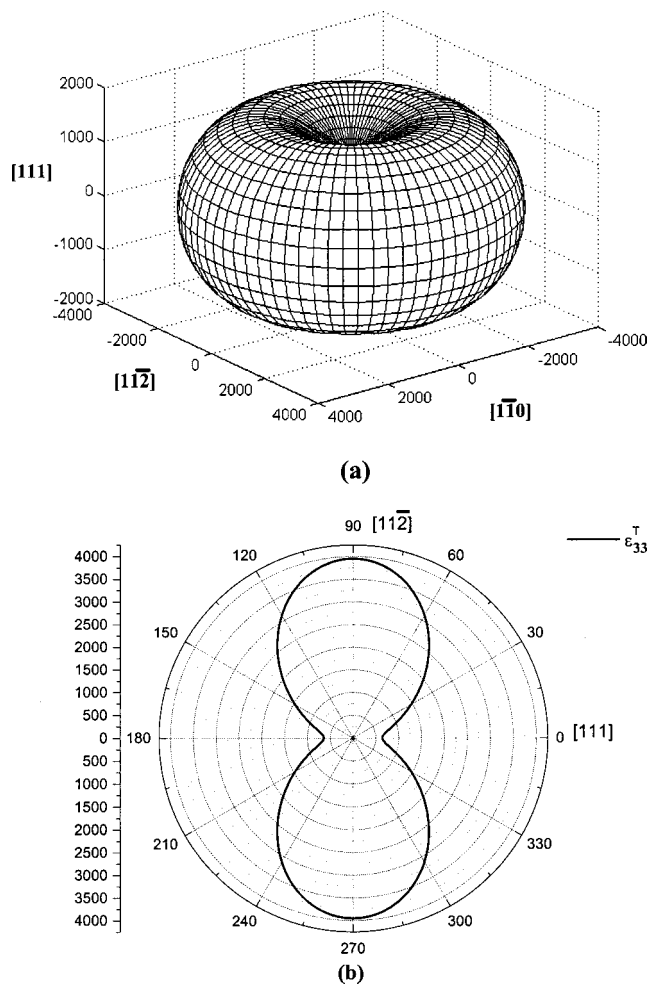

FIG. 1. (a) Orientation dependence of dielectric constant of PMN–33%PT single crystal with single domain. (b) Cross section plot of (a) in $[111]-[11\bar{2}]$ plane.

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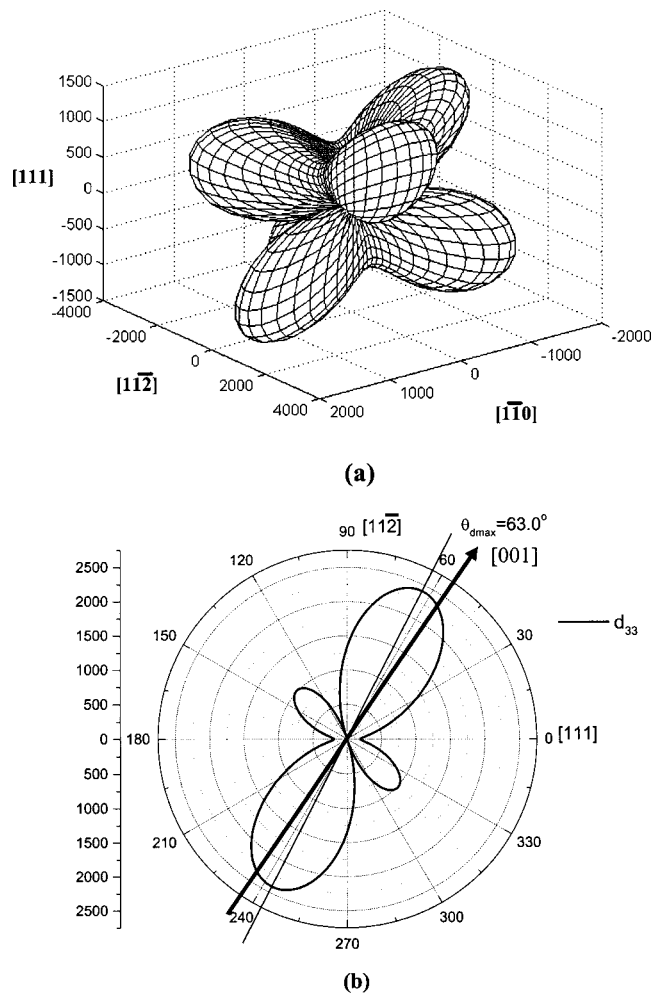

FIG. 2. (a) Orientation dependence of piezoelectric constant d_{33} of PMN–33%PT single crystal with single domain. (b) Cross section plot of (a) in $[111]$–$[112]$ plane.

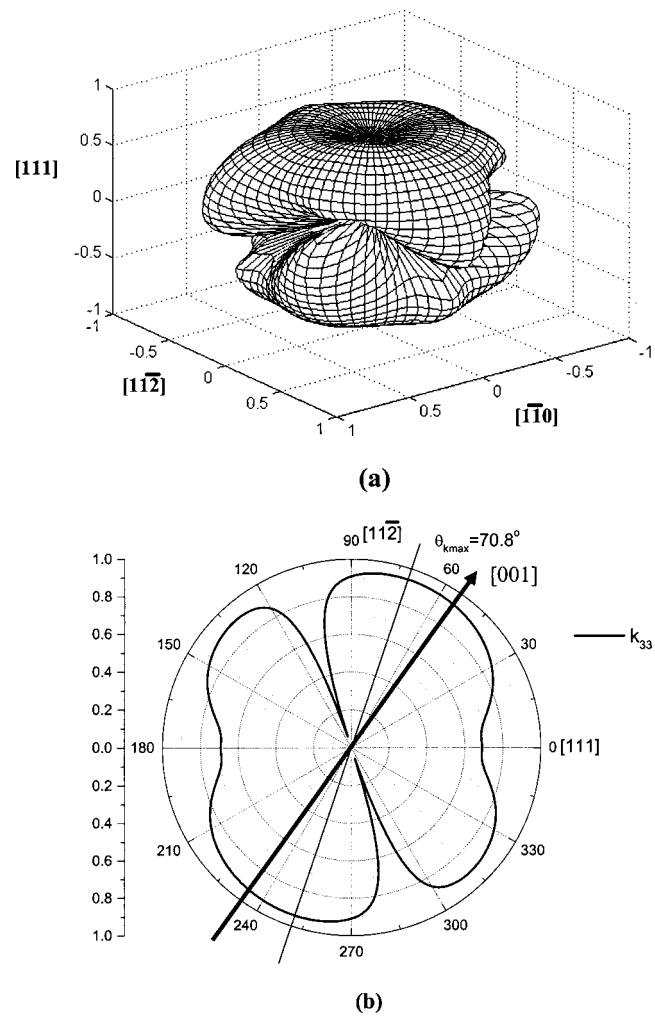

FIG. 3. (a) Orientation dependence of electromechanical coupling factor k_{33} of PMN–33%PT single crystal with single domain. (b) Cross section plot of (a) in $[111]$–$[112]$ plane.

tal symmetry of the system is rhombohedral $3m$. From our measured data sets for both the multidomain and single domain states, one can clearly see the importance of property anisotropy in the single domain state. The piezoelectric constant d_{33} of the single domain PMN–33%PT is only about 190 pC/N,[19] much smaller than that of the multidomain state. On the other hand, the shear piezoelectric constant d_{15} of the single domain PMN–33%PT was found to be 28 times of that of multidomain PMN–33%PT crystals. Obviously, the effective properties of the PMN–33%PT multidomain single crystal must have originated from the strong anisotropy of the single domain properties. This can be verified from the direct rotation of the single domain data set.

Let $\{a_i\}$ and $\{a_i^*\}$ be orthonormal bases representing the original and a new coordinates, respectively. The transformation of dielectric constant ε_{33}^T, piezoelectric constant d_{33}, and electromechanical coupling factor k_{33} to the new coordinates is performed based on the method given in Ref. 20.

To illustrate the orientation dependence of ε_{33}^T, d_{33}, and k_{33}, the axis a_3^* was rotated in three-dimensional space and the corresponding ε_{33}^{T*}, d_{33}^*, and k_{33}^* were calculated. The electromechanical coupling factor k_{33} in the new orientation is then calculated by

$$k_{33}^* = \frac{d_{33}^*}{\sqrt{s_{33}^* \varepsilon_{33}^*}}. \tag{1}$$

The results are shown in Figs. 1(a), 2(a), and 3(a), when a_3^* is rotated along the longitude and latitude line in 5° steps. A cross section is plotted for each of the above cases and is given, respectively, in Figs. 1(b), 2(b), and 3(b). The cross section data were calculated at a smaller step of 0.1° in order to accurately locate the optimal directions.

The calculated orientation dependence of the physical properties of PMN–33%PT single crystal based on the single domain data set are shown in Figs. 1–3. The distance between the origin and a point on the curve represents the absolute value of the constant in the corresponding direction. Figure 1 shows the orientation dependence of the dielectric constant. The maximum dielectric constant is in the direction perpendicular to the polarization direction, while the dielectric constant minimum is along the polarization direction. Figures 2 and 3 show the orientation dependence of the longitudinal piezoelectric constants d_{33}^* and electromechanical coupling factor k_{33}^*, respectively. The maximum values of d_{33}^* and k_{33}^* can be obtained in the directions of 63.0° and 70.8°, respectively, from the polarization direction. The maximum values for the effective piezoelectric constant d_{33}^*

TABLE I. Comparison of the rotated single domain properties in [001] and the measured data for multidomain state of PMN–33%PT single crystals. Elastic compliance constants: s_{ij} (10^{-12} m^2/N), dielectric constants; $\varepsilon(\varepsilon_0)$, and piezoelectric constants: $d_{i\lambda}$ (10^{-12} C/N).

	Measured data for multidomain state	Measured data for single domain state	Rotated single domain properties in [001]
s_{11}^E	70.2	62.2	71.6
s_{12}^E	−13.1	−53.8	/
s_{13}^E	−56.0	−5.6	/
s_{14}^E	0	−166.2	/
s_{33}^E	119.4	13.3	244.6
s_{44}^E	14.5	511.0	/
s_{66}^E	15.2	232.0	/
ε_{11}^T	1600	3950	1531
ε_{33}^T	8250	640	3497
d_{15}	146	4100	134
d_{22}	0	1340	0
d_{31}	−1338	−90	−1149
d_{33}	2820	190	2316
k_{33}	0.94	0.69	0.93
k_{31}	0.59	0.15	0.77

and electromechanical coupling factor k_{33}^* of PMN–33%PT could reach 2411 pC/N and 0.94 in the corresponding orientations. These values are very close to the corresponding values of the multidomain PMN–33%PT poled in [001]. In fact, if we use the single domain data set to directly calculate the properties along [001] of the cubic coordinate (54.74° from the poling direction), we found that $d_{33}^* = 2316$ pC/N and $k_{33}^* = 0.93$, respectively, which are about the same as those directly measured in multidomain PMN–33%PT crystals. Some other calculated elastic compliance constants, dielectric constants, and piezoelectric constants along [001] of the cubic coordinate are also shown in Table I for comparison. It is shown that d_{15}^* along [001] direction decreases to 134 pC/N, much smaller than the values of d_{15} for the single domain state, while it is close to the effective d_{15}^{eff} in the multidomain state. The other interesting phenomenon is that ε_{33}^* along [001] direction is now larger than ε_{11}^*, which is similar to the relationship between the effective $\varepsilon_{33}^{\text{eff}}$ and $\varepsilon_{11}^{\text{eff}}$ in the multidomain state. Not all the rotated constants are listed here because quantities along directions other than the z direction need to be averaged. Proper average scheme has to be developed to address that problem.[21]

The calculated results from the coordinate rotation show that the material properties of PMN–33%PT single domain crystal are highly anisotropic and the maximum values of d_{33}^* and k_{33}^* should occur in directions 63.0° and 70.8°, respectively, from the polarization direction. However, these two quantities do not change much near their maximum and are almost the same as in [001] of the cubic coordinates, which is 54.74° from the poling direction. On the other hand, the values of d_{33} and k_{33} for the single domain state are relatively small, only 190 pC/N and 69%, respectively.[19] This implies that large portion of the effective d_{33}^{eff} in the multidomain state comes from the contribution of the super large shear piezoelectric constant d_{15} of the single domain property. Our calculated results given in this letter conclusively point out this correlation.

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