Anisotropy in Domain Engineered $0.92Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.08PbTiO_3$ Single Crystal and Analysis of Its Property Fluctuations

Rui Zhang, Bei Jiang, Wenhua Jiang, and Wenwu Cao

Abstract—The orientation dependence of slowness and electromechanical coupling coefficients of $0.92Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.08PbTiO_3$ (PZN-8%PT) domain engineered single crystal was analyzed based on the measured complete set of elastic, piezoelectric, and dielectric constants. There exist one quasi-longitudinal, one quasi-shear, and one pure shear wave in each of the [100]–[010], [010]–[001], and [001]–[110] planes. The slowness of the quasi-shear wave exhibits strong anisotropy in all three planes, and the coupling coefficient k_{33} and k_{31} reach their maximum in [001] and [110] directions of cubic axis, respectively. Because the composition of PMN-8%PT system is very close to the morphotropic phase boundary, the extraordinary large piezoelectric coefficients d_{31} and d_{33}, and high coupling coefficient k_{33} are very sensitive to compositional variation. We have performed error analysis and proposed an improved characterization scheme to derive a complete data set with best consistency.

I. Introduction

Recently, several relaxor-based $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) domain engineered single-crystal systems with different compositions near and away from the morphotropic phase boundary (MPB) have been successfully measured and reported [1], [2]. These data have greatly facilitated the designs of large displacement piezoelectric actuators, medical ultrasonic transducers with more accurate and expedited modeling, and further understanding on the physical mechanism of these crystal systems with different compositions.

The PMN-33%PT system has been proven to have much higher piezoelectric constant d_{33}, dielectric permittivity ϵ_{33}^T, and electromechanical coupling coefficient k_{33} compared to those of PMN-PT systems away from the MPB composition. For the $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) system, only the $0.955Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.045PbTiO_3$ (PZN-4.5%PT) single-crystal system has been characterized so far [3], which is away from the MPB composition (PZN-9%PT). Therefore, the data may not represent the maximum electromechanical capability of the solid solution PZN-PT single-crystal system [4]–[7]. However, it is very difficult to control the property of PZN-9%PT because the property will be drastically reduced if the structure becomes tetragonal [7]. The PZN-8%PT is almost at the MPB on the rhombohedral phase side, which can provide the best properties among the PZN-PT systems. After poled along the [001] direction of the original cubic axis, the multidomain PZN-8%PT single crystal has a pseudo-tetragonal symmetry.

In this paper, we report the measured complete material constants for the PZN-8%PT and use them to calculate the orientation dependence of slowness and electromechanical coupling coefficients. In addition, issues regarding self-consistency of the whole data set and reasons for property fluctuation of PZN-8%PT system are analyzed.

II. Experimental Procedure

The PZN-8%PT single crystals were grown using the high temperature flux technique [8]. The crystals were oriented using a back reflection Laue camera with an accuracy of ±0.5°, then were cut into rectangular parallelepiped shape with one pair of surfaces in [001]. Gold electrodes were sputtered onto the [001] and $[00\bar{1}]$ surfaces, and an external electric field of 1.0~1.5 MV/m was applied at room temperature to pole the sample into a multidomain state. The final dimensions of the finished samples used for the ultrasonic measurement were 5 mm × 5 mm squares with a thickness of 2–3 mm. For the length extensional and the thickness resonance measurements, the aspect ratio of the sample exceeded 5:1 in order to yield nearly pure resonance modes [9].

In the ferroelectric phase, the dipole in each unit cell of the PZN-8%PT crystal is along one of the eight <111> directions. It has been shown experimentally that the crystal can hold a macroscopic polarization only when the poling field is applied along one of the six <100> directions. Four remaining degenerate dipole orientations are left after poling, creating a multidomain structure with strong elastic interaction among the existing domains. Statistically, the four remaining domains have an equal probability to form so that the global macroscopic symmetry has been assumed as $4mm$ in all the published literature [1]–[3].

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For the $4mm$ symmetry, there are 11 independent material constants: 6 elastic, 3 piezoelectric, and 2 dielectric constants. In order to determine them unambiguously, a hybrid method combining both the ultrasonic pulse-echo and resonance methods was used. The elastic stiffness constants c_{11}^E, c_{33}^D, c_{44}^E, c_{66}^E, c_{12}^E, and c_{44}^D could be directly determined from the measurements of phase velocities of ultrasonic waves propagating along appropriate pure mode directions [10]. The elastic compliances s_{11}^E, s_{33}^E, and the electromechanical coupling coefficients, k_{33}, k_{31}, and k_t, were determined from the measured resonance and antiresonance frequencies of the length-extensional vibration bars and thickness-extensional vibration plates, respectively. Also, the piezoelectric strain constants d_{33} could be directly measured by using the quasi-static method. The dielectric constants ε_{11}^T and ε_{33}^T were obtained from the low frequency capacitances using the parallel plate capacitor approximation.

In order to check the self-consistency of these 14 measured constants, we need to explicitly provide 6 independent elastic constants c_{ij}^E or s_{ij}^D, 3 independent piezoelectric constants e_{ij} or d_{ij}, and 2 independent dielectric permittivity ϵ_{ij}^T or ϵ_{ij}^S. For this purpose, some relevant constitutive relations and conversion formula were used. Errors are unavoidable in every measurement, and they will propagate to all derived constants. Based on detailed error analysis, an improved characterization scheme is formulated to minimize the error propagation to allow us getting a self-consistent complete data set of domain engineered PZN-8%PT single crystal. Details of the technique could be found in [1]–[3], [11].

III. Results and Discussion

A complete set of elastic, piezoelectric, and dielectric constants of PZN-8%PT is listed in Table I. Material constants marked with an "*" were determined directly by measurements, and the others were indirectly derived quantities. The relevant constants of PZN-4.5%PT also are listed in Table I for comparison. It is seen that the difference in elastic stiffness constants under constant electric field is very small between the two systems. Therefore, we conclude that the PT composition in the PZN-PT system has little influence to the elastic stiffness under constant electric field. The most pronounced differences between the two systems listed in Table I are in s_{33}^E, d_{33}, and ε_{33}^T. The values of these constants of PZN-8%PT are, respectively, 1.34, 1.45, and 1.48 times of the corresponding values of PZN-4.5%PT. Our results seem to confirm the previously reported phenomena that larger d_{33} is associated with larger s_{33}^E [1], [2].

As indicated in Table I, the values of some constants are derived indirectly. There are usually several relationships available to derive a given constant. We selected the relationships based on the least error criterion. Our error analysis also showed that data inconsistency mainly comes from property variation from sample to sample. The situation is more serious for the PZN-8%PT system because its extraordinary large piezoelectric coefficients d_{31} and d_{33}, and high coupling coefficient k_{33} are very sensitive to compositional variations. For example, the piezoelectric coefficient e_{31} and e_{33} were usually derived from the measured c_{11}^E, c_{12}^E, c_{13}^E, c_{33}^E, d_{31}, and d_{33} by using the following equations:

$$e_{31} = d_{31}\left(c_{11}^E + c_{12}^E\right) + d_{33}c_{13}^E \tag{1}$$

$$e_{33} = 2d_{31}c_{13}^E + d_{33}c_{33}^E. \tag{2}$$

From the standard error analysis, we found that even very small variations in the values of c_{12}^E and c_{13}^E will cause large variations in the calculated values of e_{31} and e_{33} when the amplitudes of d_{31} and d_{33} are very large. For comparison, error analysis was performed for PZN-4.5%PT, PZN-8%PT, and $BaTiO_3$, respectively, and the results are listed in Table II. The d_{31} and d_{33} values also are shown in Table II. In general, the larger the amplitudes of d_{31} and d_{33} are, the greater are the uncertainties of calculated values of e_{31} and e_{33}. In fact, those formulas became unstable when used for PZN-PT single crystals, especially for composition near the MPB. However, one can see that there is no problem when (1) and (2) were used for $BaTiO_3$ because its relatively small piezoelectric coefficients do not introduce large error amplification. In order to reduce this uncertainty, we have made 16 different measurements for the 11 independent unknown constants. Those additional independent measurements provide consistency checks and were built into our computer program.

Because the growth method and the nature of the crystal, Pb loss is extremely difficult to control. Usually, 5–10% compositional variation is common in a large crystal boule. This will greatly affect the consistency of the measured data set, particularly for composition near the MPB, for which the properties can change drastically with slight variation of composition. For samples cut from different parts of the same crystal boule, the measured values of d_{33} range from 1800 to 3000 (pC/N) and ε_{33}^T could vary between 5000 and 8000. In order to examine the exact PT composition in each sample, the temperature dependence of dielectric permittivity was measured. It was found that the PT composition could change as much as 8% in the same crystal boule, as shown in Fig. 1. The data given in Table I was obtained from those samples with almost the same 8%PT composition.

We found that, for a good quality PZN-8%PT single crystal, the piezoelectric strain constants d_{33} could be more than 2890 pC/N as shown in Fig. 2. Combining the results of this work and the works of Park and Shrout [7] and Kuwata *et al.* [12], the piezoelectric coefficients d_{33} as a function of composition for PZN-PT are presented in Fig. 3. It was noticed that d_{33} of the PZN-PT crystal system increase nonlinearly and very drastically near the MPB. This is why even a very small composition difference in PZN-8%PT samples could bring about larger property variations.

TABLE I

Measured and Derived Material Properties of PZN-8%PT and PZN-4.5%PT Single Crystal Poled Along [001].**

Elastic Stiffness Constants: c_{ij} (10^{10} N/m^2)												
PT (%)	$c_{11}^{E^*}$	$c_{12}^{E^*}$	c_{13}^{E}	c_{33}^{E}	$c_{44}^{E^*}$	$c_{66}^{E^*}$	c_{11}^{D}	c_{12}^{D}	c_{13}^{D}	$c_{33}^{D^*}$	$c_{44}^{D^*}$	c_{66}^{D}
8	11.5	10.5	10.9	11.51	6.34	6.50	11.8	10.8	10.0	14.3	6.76	6.50
4.5†	11.1	10.2	10.1	10.5	6.4	6.3	11.3	10.4	9.5	13.5	6.7	6.3
Elastic Compliance Constants: s_{ij} (10^{-12} m^2/N)												
PT (%)	$s_{11}^{E^*}$	s_{12}^{E}	s_{13}^{E}	s_{33}^{E}	s_{44}^{E}	s_{66}^{E}	s_{11}^{D}	s_{12}^{D}	s_{13}^{D}	$s_{33}^{D^*}$	s_{44}^{D}	s_{66}^{D}
8	87.0	−13.1	−70.0	141	15.8	15.4	55.8	−44.2	−8.2	18.5	14.8	15.4
4.5†	82.0	−28.5	−51.0	108	15.6	15.9	61.5	−49.0	−9.0	20.6	14.9	15.9
Piezoelectric Constants: $e_{i\lambda}$ (C/m^2) $d_{i\lambda}$ (10^{-12} C/N) $g_{i\lambda}$ (10^{-3} Vm/N) $h_{i\lambda}$ (10^8 V/m)												
PT (%)	e_{15}	e_{31}	e_{33}	d_{15}	d_{31}	d_{33}^{*}	g_{15}	g_{31}	g_{33}	h_{15}	h_{31}	h_{33}
8	10.1	−5.1	15.4	159	−1455	2890	6.2	−21.3	42.4	4.2	−5.8	17.7
4.5†	8.9	−3.7	15.0	140	−970	2000	5.0	−21.0	44	3.4	−4.3	17
Dielectric Constants: $\epsilon(\epsilon_0)$ $\beta(10^{-4}/\epsilon_0)$									Electromechanical Coupling Constants			
PT (%)	ϵ_{11}^{S}	ϵ_{33}^{S}	$\epsilon_{11}^{T^*}$	$\epsilon_{33}^{T^*}$	β_{11}^{S}	β_{33}^{S}	β_{11}^{T}	β_{33}^{T}	k_{15}	k_{31}^{*}	k_{33}^{*}	k_{t}^{*}
8	2720	984	2900	7700	3.68	10.2	3.45	1.30	0.25	0.60	0.94	0.45
4.5†	3000	1000	3100	5200	3.4	10.0	3.2	1.9	0.23	0.50	0.91	0.50

*Measure properties.

**Density: $\rho = 8315$kg/m^3 (PZN-8%PT),
$\rho = 8310$kg/m^3 (PZN-4.5%PT)

†The complete set of constants of PZN-4.5%PT single crystal are from [3].

TABLE II

Error Amplifications of Derived Piezoelectric Coefficients e_{31} and e_{33} Caused by the Relative Error of Some Elastic Constants.

	PZN-4.5%PT $d_{31} = -970$ $d_{33} = 2000$	PZN-8.0%PT $d_{31} = -1455$ $d_{33} = 2890$	BaTiO$_3$ $d_{31} = -34.5$ $d_{33} = 85.6$
$\left(\frac{\Delta e_{31}}{e_{31}}\right) \Big/ \left(\frac{\Delta c_{12}^{E}}{c_{12}^{E}}\right)$	21.5	53.0	2.3
$\left(\frac{\Delta e_{31}}{e_{31}}\right) \Big/ \left(\frac{\Delta c_{13}^{E}}{c_{13}^{E}}\right)$	43.8	109.6	4.9
$\left(\frac{\Delta e_{33}}{e_{33}}\right) \Big/ \left(\frac{\Delta c_{33}^{E}}{c_{33}^{E}}\right)$	14.9	19.2	3.9
$\left(\frac{\Delta e_{33}}{e_{33}}\right) \Big/ \left(\frac{\Delta c_{13}^{E}}{c_{13}^{E}}\right)$	28.7	36.9	7.2

The orientation dependence of the slowness and electromechanical coupling coefficient of the measured PZN-8%PT system is investigated based on the measured material constants and are plotted in Figs. 4 and 5. For a length extensional rod, the k_{33} refers to the coupling coefficient when the electrode surface is along the length of the rod. When the electrode surfaces are perpendicular to the length of the rod, the coupling coefficients are k_{31} or k'_{31} for another orientation of the rod. In the [100]–[010] plane there are one quasi-longitudinal, one quasi-shear, and one pure shear waves. In this plane the coupling coefficient k_{33} is isotropic, and k_{31} reaches its maximum in the [110] direction. For this case, there is no need to distinguish between k_{31} and k'_{31}. In the [010]–[001] plane there also are one quasi-longitudinal, one quasi-shear, and one pure shear waves. The slowness of the quasi-shear wave exhibits strong anisotropy in both planes mentioned above. In the [010]–[001] plane, the coupling coefficient k_{31} for the rod with its length in the [100] direction is different from k_{31}, for which the rod length is in the plane. The coupling coefficients k_{33} and k_t reach their maximum in [001]. In the [110]–[001] plane the situation is very similar to that in the [010]–[001] plane, in which k_{31} and k'_{31} are for the rods with the length in the [1$\bar{1}$0] direction and in the [110]–[001] plane, respectively.

IV. Summary and Conclusions

Based on the measured complete set of elastic, piezoelectric, and dielectric constants of this system, the orientation dependence of slowness and electromechanical

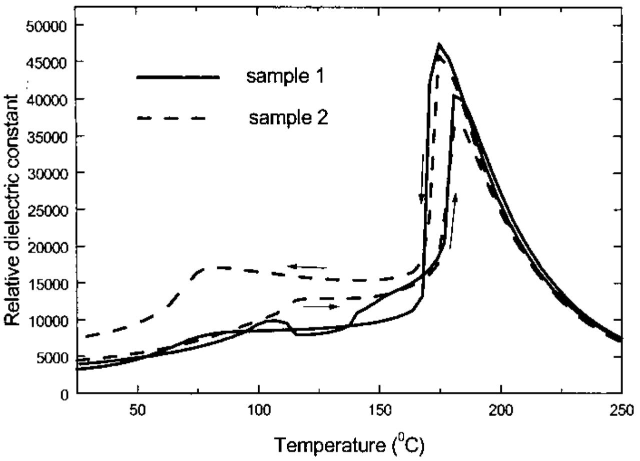


Fig. 1. Temperature dependence of the dielectric constants of PZN-8%PT single-crystal sample 1 and 2 at 1 kHz freqency.

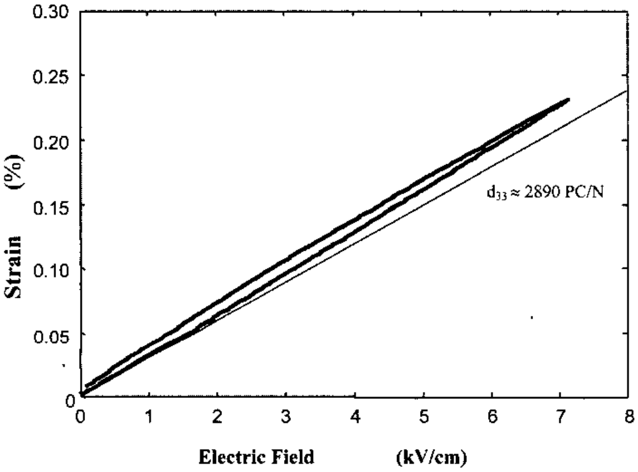


Fig. 2. A typical strain vs. E-field behavior along [001] of cubic coordinates for PZN-8%PT single-crystal samples. The thin line is a calculated curve based on d_{33} = 2890 pC/N for comparison.

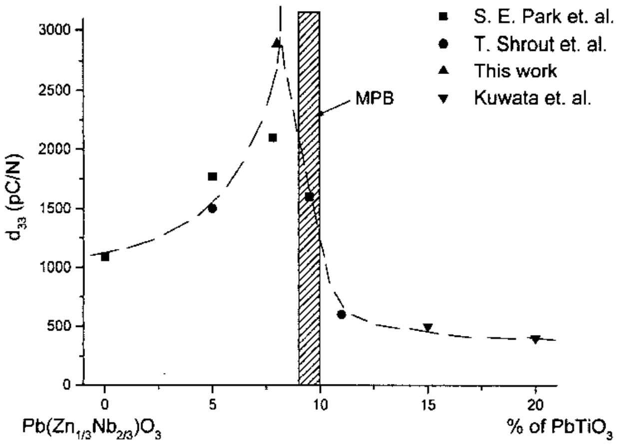


Fig. 3. Piezoelectric coefficients d_{33} as a function of composition of domain engineered PZN-PT single crystals.

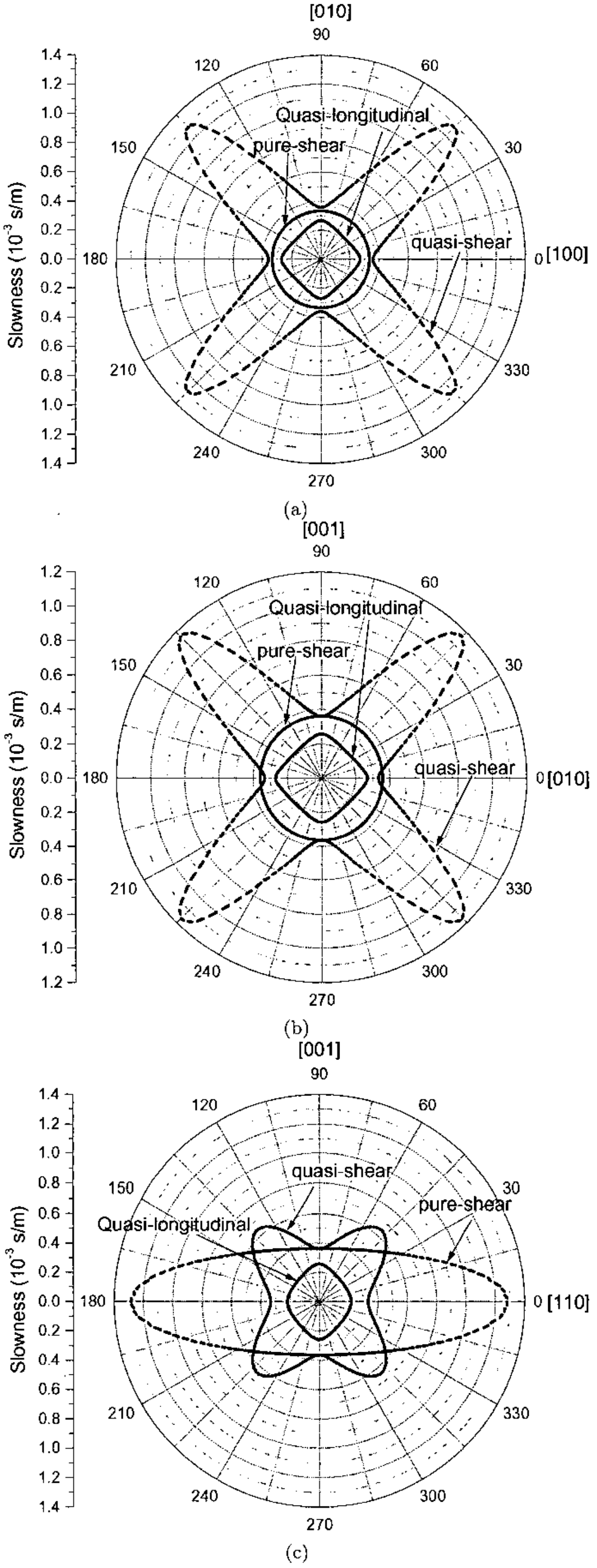
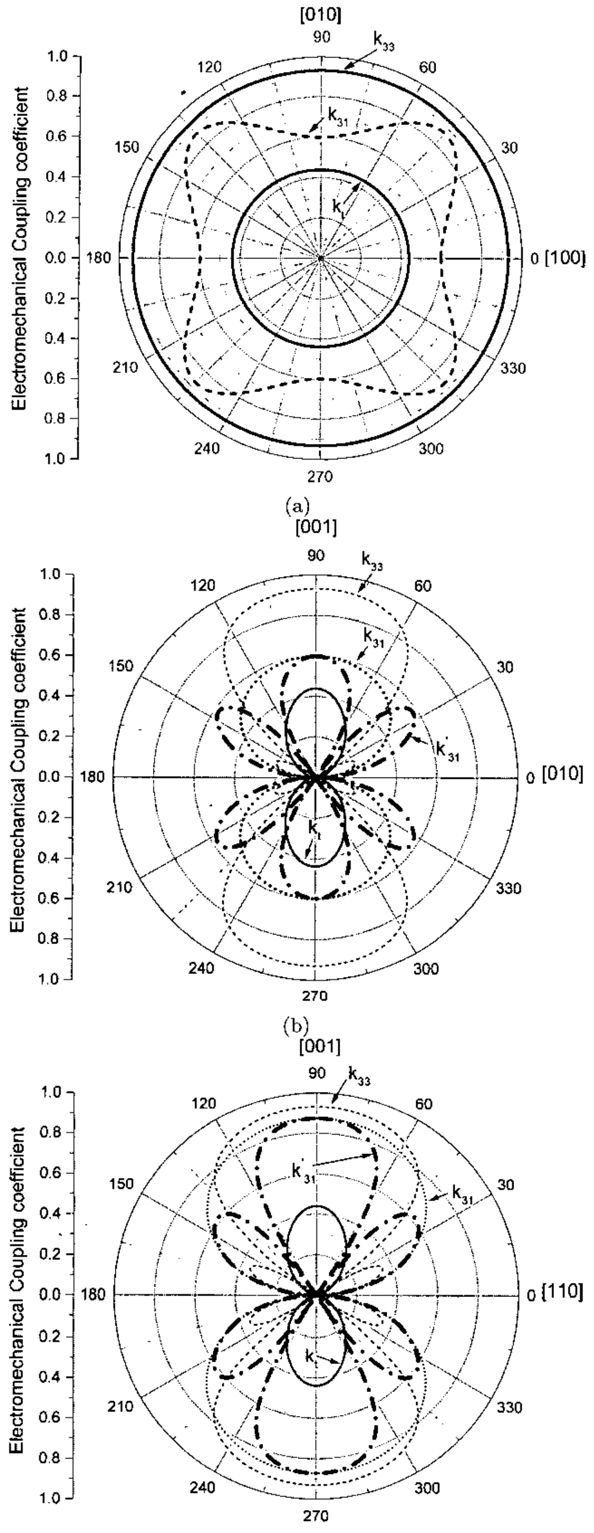


Fig. 4. Orientation dependence of slowness (inverse of velocity). (a) Slowness in the [100]–[010] plane. (b) Slowness in the [010]–[001] plane. (c) Slowness in the [110]–[001] plane.



(a)

(b)

(c)

Fig. 5. Orientation dependence of electromechanical coupling coefficients. (a) Coupling coefficient in the [100]–[010] plane. (b) Coupling coefficient in the [010]–[001] plane. (c) Coupling coefficient in the [110]–[001] plane.

coupling coefficient of PZN-8%PT domain engineered single crystal was analyzed. Similar to the PZN-4.5%PT system, the slowness of the quasi-shear wave exhibits strong anisotropy in [100]–[010], [010]–[001], and [001]–[110] planes, and the coupling coefficient k_{33} and k_{31} reach their maximum in [001] and [110] directions of the cubic coordinates, respectively. Because the PZN-8%PT system is near the MPB composition, it has much larger piezoelectric and dielectric constants compared with PZN-4.5%PT. It also is observed that the PT composition has little influence to the elastic stiffness constants $c^E_{\alpha\beta}$.

The d_{33} of the PZN-PT crystal system increases nonlinearly and more drastically near the MPB, causing large property fluctuation from sample to sample because the composition is very difficult to control accurately. The extraordinary large piezoelectric coefficients d_{31} and d_{33} and high coupling coefficient k_{33} are very sensitive to compositional variation for this system, making it a real challenge for practical applications.

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