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Journal of Physics and Chemistry of Solids 65 (2004) 1083–1086

JOURNAL OF
PHYSICS AND CHEMISTRY
OF SOLIDS

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Superior d_{32}^* and k_{32}^* coefficients in $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$ and $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.08\text{PbTiO}_3$ single crystals poled along [011]

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Received 14 August 2003; accepted 29 October 2003; available online 7 February 2004

Abstract

The elastic, piezoelectric and dielectric constants of [011] poled Y cut length extension bars made of $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$ (PZN–4.5%PT) and $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.08\text{PbTiO}_3$ (PZN–8%PT) single crystals were fabricated and measured. The absolute value of piezoelectric coefficient d_{32}^* of PZN–8%PT crystal poled along [011] reaches as high as 1887 pC/N, which is almost twice as its d_{33}^* value. The electromechanical coupling coefficient k_{32}^* of PZN–4.5%PT and PZN–8%PT crystals poled along [011] are 0.73 and 0.86, respectively, showing great application potential for transverse mode sensors, actuators and other electromechanical devices.
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Keywords: D. Ferroelectricity; D. Electromechanical properties

1. Introduction

Earlier work on $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PZN–PT) and $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN–PT) solid solution systems can be dated back to the 1960s [1,2]; however, it was not until recently that the relaxor-based ferroelectric single crystal systems have generated a great deal of attention. It was found that the single crystal systems near the Morphotropic Phase Boundary (MPB) composition exhibit extraordinary large electromechanical coupling coefficient k_{32}^* (>90%) and piezoelectric coefficient d_{32}^* (>2000 pC/N) at room temperature after being poled along [001] of the cubic coordinates [3,4]. Considering the best piezoelectric materials used today, the modified $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT), only has k_{33} of 75% and d_{33} of 700 pC/N, the new systems show a promising potential to produce higher sensitivity ultrasonic transducers with superior broadband characteristics, large strain actuators, and other more efficient electromechanical devices.

The mechanism that causes the domain engineered single crystal systems to have such large electromechanical properties is still not well understood. The lack of complete physical property data is the main hindrance for further

theoretical studies. A few complete sets of elastic, piezoelectric and dielectric constants for [001] poled domain-engineered PZN–PT and PMN–PT ferroelectric single crystals with compositions near MPB have been measured in the past few years [5–10]. One can see from those measured data that the largest effective d_{33}^* and k_{33}^* constants are always obtained from samples poled along [001] of the cubic prototype phase, and the properties of the multi-domain samples strongly depend on both domain patterns generated during the poling process and the effective symmetry associated with these domain patterns.

The small values of d_{33} and k_{33} for single-domain $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.33\text{PbTiO}_3$ (PMN–33%PT) crystal [11] imply that the large effective d_{33} and k_{33} values of multi-domain PZN–PT crystals poled along [001] are due to the orientation effect. For single-domain PMN–33%PT crystals poled along [111], the d_{15} value can reach as high as 4100 pC/N even under electrical bias [11]. Trying to improve specific material properties using the domain engineering methodology has become a new trend in material research community. Some limited successes have been reported in the literature [12–22].

Recently, Liu and Lynch reported a large d_{32}^* value of $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$ (PZN–4.5%PT) measured by employing a strain gage [23]. In this paper, we report some measured results of $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.08\text{PbTiO}_3$ (PZN–8%PT) and PZN–4.5%PT poled along

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[011] by the resonance method. Similar d_{32}^* value as in Ref. [23] was found in PZN–4.5%PT and a much larger d_{32} value was found in the [011] poled PZN–8%PT crystal. In addition, we found that the electromechanical coupling coefficient k_{32}^* can reach as high as 86% for the PZN–8%PT, making it an excellent candidate for transverse mode electromechanical devices. We have labelled the effective quantities with a “*” to indicate that they are measured in their intrinsic coordinates, such as the orthorhombic XYZ-coordinates for crystals poled along [011], while the poling directions are labeled using the cubic coordinates following literature convention.

2. Experimental procedure

In the ferroelectric phase, the dipole in each unit cell of both PZN–4.5%PT and PZN–8%PT crystals is along one of the eight $\langle 111 \rangle$ directions of the cubic phase (Fig. 1a). The coordinates used are also shown in Fig. 1, which is based on the cubic phase. There are two remaining energetic degenerate dipole orientations left after the application of a poling electric field along [011] (Fig. 1b). Such a poling field creates a multi-domain structure with strong elastic interaction among different domains. Statistically, the remaining two types of domains have an equal possibility to form so that the global macroscopic symmetry is orthorhombic $mm2$. In this work, the poling direction is taken as the Z-direction,

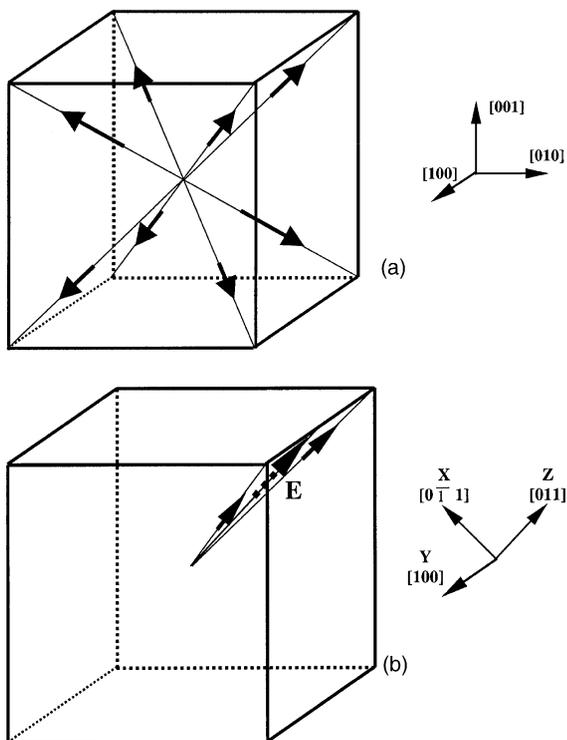


Fig. 1. (a) The eight polarization directions in PZN–4.5%PT and PZN–8%PT single crystals before poling. (b) Possible domain configurations and associated polarization orientations in PZN–4.5%PT and PZN–8%PT single crystals after being poled along [011].

which is along [011] of the cubic phase. The $[0\bar{1}1]$ and [100] are then defined as the X and Y axes, respectively, for the orthorhombic structure.

The single crystals used in this work were grown by a modified Bridgman Method using a Pt crucible supported at the bottom by a conical insulator stand [13]. The crystals were orientated using Laue method with an accuracy of $\pm 0.5^\circ$. Each sample was cut and polished into a rectangular parallelepiped shape with three pairs of parallel surfaces perpendicular to each other. Gold electrodes were sputtered onto [011] and $[0\bar{1}\bar{1}]$ faces of each sample, then an external electric field ~ 0.4 MV/m was applied at room temperature to fully pole the sample. For length extensional resonance measurements, the aspect ratio of the sample should exceed 5:1 [24] in order to yield nearly pure resonance modes. The final dimensions of the samples used for k_{32}^* and d_{32}^* measurements are about $4.0 \text{ mm}[100]^L \times 0.8 \text{ mm}[0\bar{1}\bar{1}]^W \times 0.8 \text{ mm}[011]^T$.

By using an HP 4194A Impedance/Gain-phase Analyzer, resonance and anti-resonance frequencies, corresponding to the minimum and maximum values of the impedance–frequency spectrum, were obtained and used to calculate the electromechanical coupling coefficients and elastic compliance. The dielectric measurements were carried out at 1 kHz using a Stanford Research System SR715 LCR Meter. Also, the piezoelectric strain constants d_{33}^* can be directly measured using the quasi-static method.

Since the cross-section dimensions of our samples are much smaller compared to their length dimension, it is convenient to choose stress T and electric field E as independent variables. Under the orthorhombic $mm2$ symmetry assumption, we have the following constitutive relations [25]:

$$S_2 = s_{22}^{E^*} T_2 + d_{32}^* E_3, \quad (1a)$$

$$D_2 = d_{32}^* T_2 + \epsilon_{33}^{T^*} E_3. \quad (1b)$$

and the electromechanical coupling coefficient k_{32}^* and elastic compliance constant $s_{22}^{E^*}$ can be linked to the resonance (f_r) and anti-resonance (f_a) frequencies as follows [24]:

$$\frac{k_{32}^{*2} - 1}{k_{32}^{*2}} = \frac{\tan[(\pi/2)(f_a/f_r)]}{(\pi/2)(f_a/f_r)} \quad (2)$$

$$s_{22}^{E^*} = \frac{1}{4\rho f_r^2 L^2} \quad (3)$$

where ρ denotes the density of the sample. Then, d_{32}^* can be calculated by

$$d_{32}^* = k_{32}^* \sqrt{s_{22}^{E^*} \epsilon_{33}^{T^*}} \quad (4)$$

where $\epsilon_{33}^{T^*}$ is the dielectric permittivity under zero stress measured along the poling direction [011], which is calculated directly from the capacitance measurements.

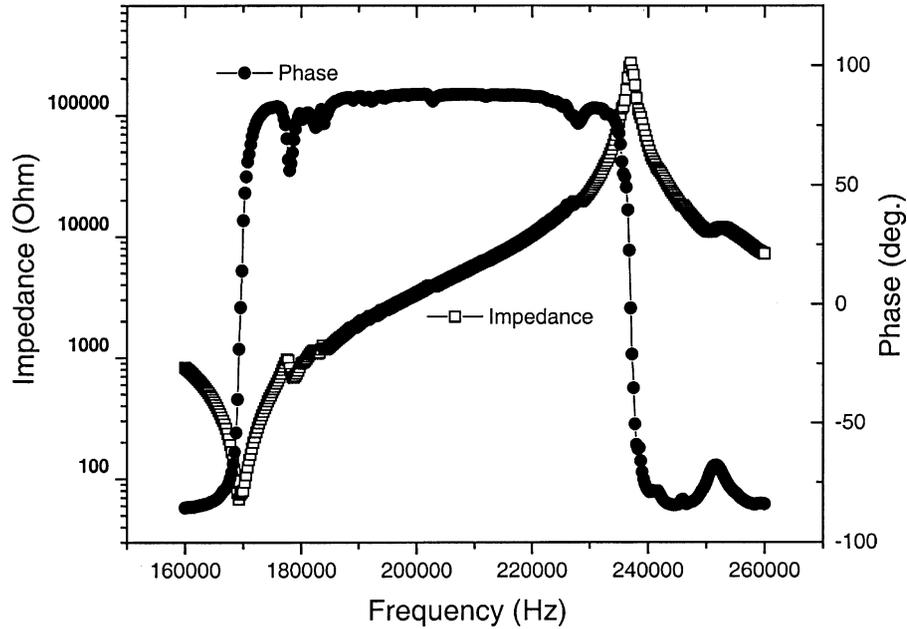


Fig. 2. Amplitude and phase spectra measured from Y-cut extensional bars of PZN–4.5%PT crystal poled along [011].

3. Results and discussion

Figs. 2 and 3 show the characteristics of the resonance and anti-resonance frequencies and the phase spectrum for Y-cut PZN–4.5%PT and PZN–8%PT single crystals in the length expansion mode at room temperature. Using these resonance and anti-resonance frequencies and the equations listed above, the related material properties of PZN–4.5%PT and PZN–8%PT single crystals poled along [011] are derived and are listed in Table 1. The corresponding material properties of PZN–4.5%PT and PZN–8%PT single crystals poled along [001] are also listed

in the same table for comparison. It can be seen that the values of d_{32}^* for both PZN–4.5%PT and PZN–8%PT systems poled along [011] are larger than their d_{33}^* values, which is in contrast to the crystals of the same composition poled along [001]. The difference between d_{32}^* and d_{33}^* of PZN–8%PT crystal poled along [011] is much larger than the corresponding difference in PZN–4.5%PT crystal. The absolute d_{32}^* value of PZN–4.5%PT is similar to what have been reported in Ref. [23], while the d_{32}^* of PZN–8%PT crystal poled along [011] could reach 1887 pC/N, which is twice as its d_{33}^* value. In fact, this value becomes comparable to the effective d_{33}^* value of PZN–4.5%PT

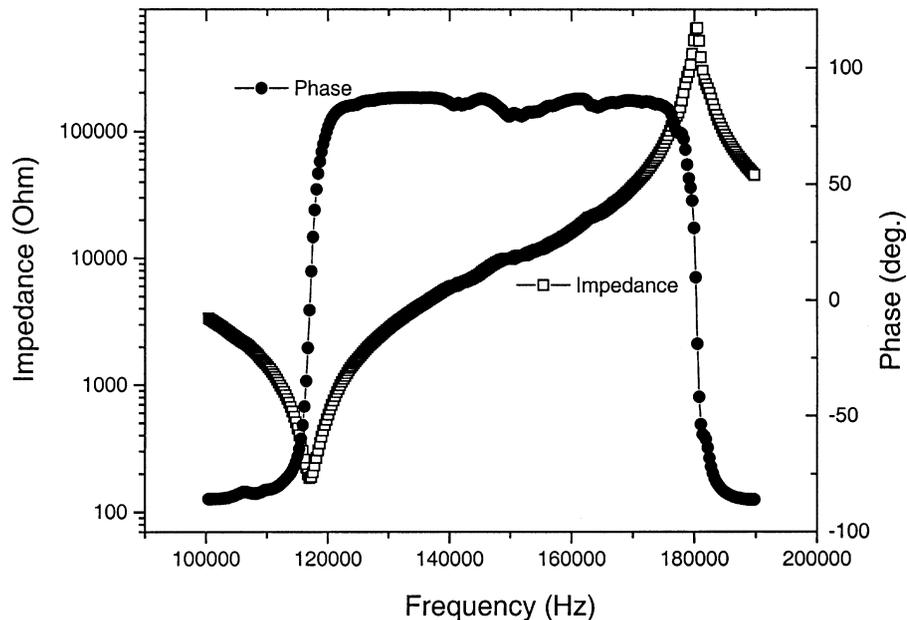


Fig. 3. Amplitude and phase spectra measured from Y-cut extensional bars of PZN–8%PT crystal poled along [011].

Table 1

Comparison of material properties of PZN–4.5%PT and PZN–8%PT single crystals poled along [001] and [011]

	Poling direction	d_{31}^* (pC/N)	d_{32}^* (pC/N)	d_{33}^* (pC/N)	k_{31}^*	k_{32}^*	ϵ_{33}^{T*} (ϵ_0)	S_{22}^{E*} (10^{-12} m ² /N)	ρ (kg/m ³)
PZN–4.5%PT	[001]	–966	–966	2000	0.50	0.50	5200	81.6	8310
	[011]	611	–1324	900	0.56	0.73	2675	140.7	8310
PZN–8%PT	[001]	–1455	–1455	2890	0.60	0.60	7700	86.9	8315
	[011]	331	–1887	580	0.31	0.86	3745	144.4	8315

system poled along [001]. On the other hand, d_{31}^* values obtained from X-cut crystals are much smaller than the corresponding d_{32}^* values in both systems, as shown in Table 1, and also have opposite sign to that of d_{32}^* . The effective electromechanical coupling coefficient k_{32}^* for the [011] poled PZN–4.5%PT and PMN–8%PT systems are 0.73 and 0.86, respectively. We can also see from the table that the k_{32}^* values obtained in both crystals poled along [011] are much larger than the k_{32}^* of [001] poled crystals. These superior k_{32}^* and d_{32}^* values make the [011] poled PZN–8%PT and PZN–4.5%PT single crystals promising candidates for sensor and actuator applications operated in lateral mode. They can also be used in other piezoelectric devices, which require electric field to be applied perpendicular to their elastic wave propagation direction.

Acknowledgements

This research was sponsored by the ONR under Grant No. N00014-98-1-0527 and NIH under Grant No. P41-RR11795.

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