Superior $d_{32}^*$ and $k_{32}^*$ coefficients in 0.95Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$–0.045PbTiO$_3$ and 0.92Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$–0.08PbTiO$_3$ single crystals poled along [011]

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Abstract

The elastic, piezoelectric and dielectric constants of [011] poled [100] cut length extension bars made of 0.95Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$–0.045PbTiO$_3$ (PZN–4.5%PT) and 0.92Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$–0.08PbTiO$_3$ (PZN–8%PT) single crystals were fabricated and measured. The absolute value of piezoelectric coefficient $d_{33}$ of PZN–8%PT single 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 0.78 and 0.86, respectively, showing great application potential for transverse mode sensors, actuators and other electromagnetic devices.

Keywords: Single crystal; Ferroelectric; Electromechanical property

1. Introduction

Earlier work on (1–$x$)Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$–$x$PbTiO$_3$ (PZN–PT) and (1–$x$)Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–$x$PbTiO$_3$ (PMN–PT) solid solution system 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 Morphotropc Phase Boundary (MPB) composition exhibits extraordinary large electromechanical coupling coefficient $k_{33}$ (>90%) and piezoelectric coefficient $d_{33}$ (>2000 pC/N) at room temperature after being poled in [001] of the cubic coordinates [3,4]. Considering that the best piezoelectric materials used today, the modified Pb(Zr$_{0.52}$Ti$_{0.48}$)$_3$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 electromagnetic 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 0.67Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–0.33PbTiO$_3$ (PMN–33%PT) crystal [11] explains us 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 $d_{32}^*$ of 0.95Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$–0.045PbTiO$_3$ (PZN–4.5%PT) measured by employing a strain gage [23]. In this paper, we report some measured results of 0.92Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$–0.08PbTiO$_3$ (PZN–8%PT) and PZN–4.5%PT poled along...
[011] by the resonance method. Similar $d_{32}$ value as Ref. [23] was found in PZN–4.5%PT and a much larger $d_{32}$ value was found in the PZN–8%PT [011] poled 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.

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 (111) 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 inter-action among different domains. Statistical, the remaining two types of domains have an equal possibility to form so that the global macroscopic symmetry is orthorhombic mnm2. In this work, the poling direction is taken as the Z-direction, which is along [011] of the cubic phase. The [011] 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 ±0.5°. Then, 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 on to [011] and [011] faces of each sample, then an external electric field ~0.4 MV/m was applied at room temperature to fully pole the sample. For the 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 $4.0 \times 8.0 \times 0.8 \ mm[011] \times 0.8 \ mm[011]^T$.

For the length-extensional resonance measurements, an HP 4194A Impedance/Gain-phase Analyzer was employed. The 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 mnm2 symmetry assumption, we have the following constitutive relations [25]:

\[ S_2 = s_{32}^{E} T_2 + d_{32}^{E} E_3, \quad (1a) \]
\[ D_3 = d_{32}^{E} T_2 + s_{33}^{E} E_1, \quad (1b) \]

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

\[ \frac{k_{32}^*}{k_{32}^0} = \frac{\tan((\pi/2)(f_r/f_a))}{(\pi/2)(f_r/f_a)} \quad (2) \]
\[ s_{32}^{E} = \frac{1}{4\pi E L^2} \quad (3) \]

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

\[ d_{32}^* = k_{32}^* s_{32}^{E}/k_{33} \quad (4) \]

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

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 Y-cut PZN–4.5%PT and PZN–8%PT single crystals in the [011] direction.
[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 compositions 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 value of $d'_{32}$ 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 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 0.78 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

![Amplitude and phase spectra measured from Y-cut extensional bars of PZN–4.5%PT crystal poled along [011].](image1)

![Amplitude and phase spectra measured from Y-cut extensional bars of PZN–8%PT crystal poled along [011].](image2)
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.

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