

Phenomenological Analysis of Piezoelectric Properties in 0.88Pb (Zn_{1/3}Nb_{2/3})O₃-0.12PbTiO₃ Single Crystals with an Engineering Domain Configuration

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ABSTRACT

The piezoelectric properties of tetragonal 0.88Pb(Zn_{1/3}Nb_{2/3})O₃-0.12PbTiO₃ single crystals are characterized along the <111> direction, which composed the engineering domain configuration in the tetragonal phase. The <111>-oriented crystal possessed smaller d_{33} values compared to the crystal along the <001> spontaneous polarization direction. Based on phenomenological theory, it is shown that the engineering domain configuration does not enhance the piezoelectric constant in tetragonal 0.88Pb(Zn_{1/3}Nb_{2/3})O₃-0.12PbTiO₃ single crystals. In addition, the electrostrictive coefficients of $Q_{12} = -0.03706 \text{ m}^4/\text{C}^2$, $Q_{11} = 0.10765 \text{ m}^4/\text{C}^2$, and $Q_{44} = 0.02020 \text{ m}^4/\text{C}^2$ of tetragonal 0.88PZN-0.12PT single crystals were calculated.

Key words : PZN-PT, Electrostrictive coefficients, Single crystal, Engineering domain

1. Introduction

Relaxor ferroelectric single crystals such as Pb(Zn_{1/3}Nb_{2/3})O₃-PbTiO₃ (PZN-PT) and Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) near the morphotropic phase boundary (MPB) composition have attracted great interest due to their high electromechanical coupling factors, piezoelectric coefficients, electro-optical properties, and acousto-optical properties.¹⁻⁶ In ferroelectric single crystals, as high performance can be obtained in the single domain state or in a carefully engineered domain state, the study of the domain is of interest to many researchers.⁷⁻¹⁴

For rhombohedral lead zirconate titanate (PZT), PZN-PT, PMN-PT, and barium titanate (BaTiO₃), it was both theoretically calculated and experimentally measured that the piezoelectric constants along the perovskite [001] direction were much larger than those along the spontaneous polarization direction [111].^{2,3,9-14} For a tetragonal phase, unlike the rhombohedral phase, the engineered domain state does not always give larger piezoelectric constants. The calculated and measured results show that BaTiO₃ has a larger piezoelectric constant in the <111> engineered domain configuration than in the <001> single domain state.¹¹⁻¹³ However, tetragonal PZT shows a maximum piezoelectric constant in the <001> spontaneous polarization direction.^{9,10}

In the present study, the piezoelectric constants of tetragonal 0.88PZN-0.12PT single crystals both in the engineering domain configuration and in the single domain state are analyzed in terms of their thermodynamic effects. Tetragonal single crystals are oriented along the <111> and <001> directions and piezoelectric constants are measured using the interferometric method. Finally, the as-measured piezoelectric constants are analyzed and compared with the analytical piezoelectric properties.

2. Experimental Procedure

As the composition near the MPB can be characterized as a phase mixture, tetragonal 0.88PZN-0.12PT was selected for this experiment, as its composition is very different from that of MPB. The crystals used in this investigation were grown using the flux method and oriented along the pseudocubic {100}, {010}, and {001} and {01-1}, {2-1-1}, and {111} directions using a Laue camera.¹⁴ The typical sample size was 2×2×2 mm³, and Au-sputtered electrodes were used for the dielectric characterization. Single crystals were poled along the [001] and [111] directions by applying a 10 kV/cm electric field at a temperature that was approximately 50°C higher than the ferroelectric-paraelectric (FE-PE) phase transition temperature. They were then slowly cooled to room temperature under an electric field.

The dielectric constants along the poling direction (K_{33}) were measured at room temperature with a Hewlett-Packard 4263A LCR meter. To measure the dielectric constant perpendicular to the poling direction (K_{11}) in the [001] poled sample, an electrode on the (001) plane was carefully

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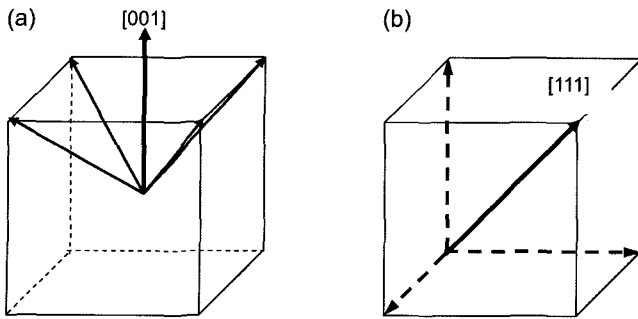


Fig. 1. Schematics of the engineered domain configuration for (a) the [001] poled rhombohedral crystal and (b) the [111] poled tetragonal crystal.

removed in a manner that did not depole the sample and an Au electrode was redeposited on the (100) plane. The piezoelectric properties were characterized using the Michelson interferometric method at a wavelength of 632.8 with a 4 Vp-p 1 kHz AC electric field.¹⁵⁾

3. Results and Discussions

In ferroelectric materials, the spontaneous polarization direction differs depending on the crystal phase. For instance, tetragonal and rhombohedral phases show spontaneous polarization along the <001> and <111> directions, respectively.¹⁶⁾ It is interesting that ferroelectric single crystals can generate ultrahigh strain when their spontaneous polarization directions differ from the crystal orientation directions.⁴⁻¹³⁾ This ultrahigh strain was explained in terms of the engineering domain configurations (see Fig. 1). For example, rhombohedral crystals (0.954PZN-0.45PT, 0.92PZN-0.8PT, rhombohedral BaTiO₃) exhibit larger strain when oriented along the <001> direction than when oriented along their spontaneous polarization direction <111>.⁷⁻¹³⁾ If the engineering domain concept is universally applicable for any phase and material, tetragonal composition 0.88PZN-0.12PT single crystals, which are oriented along the <111> direction, should have a large piezoelectric constant. However, there have been no reports or analysis regarding tetragonal PZN-PT single crystals.

Table 1 shows the measured dielectric and piezoelectric properties of 0.88PZN-0.12PT single crystals. Although the <111>-oriented crystal has an engineering domain configuration, its piezoelectric constant was smaller compared to that of the <001>-oriented crystal. This result implies that the engineering domain concept is not universal and that it

Table 1. Dielectric and Piezoelectric Properties of 0.88PZN-0.12PT Single Crystals

Composition & orientation	K_{33}	K_{11}	P_s (C/m ²)	d_{31} (pC/N)	d_{33} (pC/N)
0.88PZN-0.12PT<100>	800	8700	0.40	-210	610
<111>					479

is not applicable for tetragonal PZN-PT single crystals.

The piezoelectric effect of ferroelectrics with a centrosymmetric paraelectric phase can be considered as an electrostrictive effect that is biased by spontaneous polarization. In the tetragonal phase in the <001> orientation, the piezoelectric constant can be written as,¹⁵⁾

$$d_{31} = d_{32} = 2\varepsilon_0 K_{33}^T P_s Q_{12} \quad (1)$$

$$d_{33} = 2\varepsilon_0 K_{33}^T P_s Q_{11} \quad (2)$$

where ε_0 is the permittivity of a vacuum ($=8.854 \times 10^{-12}$ F/m), K_{33}^T is the dielectric constant of the tetragonal phase along the <001> direction, and P_s denotes the spontaneous polarization. Q_{12} ($=Q_{1122}$) and Q_{11} ($=Q_{1111}$) are the electrostrictive coefficients in cubic phase. Using the data in Table 1, $Q_{12} = -0.03706$ m⁴/C² and $Q_{11} = 0.10765$ m⁴/C² were calculated.

When the tetragonal phase is oriented along the <111> direction, the new piezoelectric constant $d_{33}^{(111)}$ can be calculated using the tensor transformation.¹⁵⁾

$$\begin{aligned} d_{33}^{(111)} &= \frac{2\sqrt{3}}{9} \varepsilon_0 K_{33}^T P_s (Q_{11} + 2Q_{12}) + \frac{4\sqrt{3}}{9} \varepsilon_0 K_{11}^T P_s Q_{44} \\ &\approx \frac{4\sqrt{3}}{9} \varepsilon_0 K_{11}^T P_s Q_{44} \end{aligned} \quad (3)$$

Here, K_{11}^T is the dielectric constant of the tetragonal phase along the <100> direction, which is located across the direction of <001> polarization. Q_{12} ($=2Q_{2323}$) represents the electrostrictive coefficients in the cubic phase. From the piezoelectric constant of the <111>-oriented crystal, $Q_{44} = 0.02020$ m⁴/C² was calculated.

From Eqs. 2 and 3, it is possible to compare the piezoelectric properties of the <001>-oriented and the <111> oriented crystals.

$$\frac{d_{33}}{d_{33}^{(111)}} = \frac{3\sqrt{3} K_{33}^T Q_{11}}{2 K_{11}^T Q_{44}} \quad (4)$$

In the perovskite structure, it is known that K_{11}^T is usually larger than K_{33}^T ; however, as Q_{11} is also larger than Q_{44} ,¹⁷⁾ the ratio cannot always be smaller than 1 and is dependent on each material. If Eq. 4 is applied for BaTiO₃, in which $K_{11}^T = 4100$, $K_{33}^T = 170$ at room temperature, $Q_{11} = 0.1107$ m⁴/C², and $Q_{44} = 0.0650$ m⁴/C², it is found that the $d_{33}/d_{33}^{(111)}$ ratio is smaller than 1. This implies that $d_{33}^{(111)}$ is larger than d_{33} , which is consistent with Wada's experimental results.¹¹⁾ The calculated $d_{33}/d_{33}^{(111)}$ ratio of the tetragonal PZN-PT is approximately 1.3, which shows that the $d_{33}^{(111)}$ value is smaller, which is consistent with Table 1. From this result, the electrostrictive coefficients of $Q_{12} = -0.03706$ m⁴/C², $Q_{11} = 0.10765$ m⁴/C², and $Q_{44} = 0.02020$ m⁴/C² of tetragonal 0.88 PZN-0.12PT single crystals can be calculated.

4. Conclusions

The piezoelectric properties of tetragonal 0.88PZN-0.12PT single crystals were characterized along the <001> and <111> directions. The <001>-oriented crystal showed a

larger piezoelectric constant of 610 pC/N compared to <111>-oriented crystal of 479 pC/N. It was demonstrated that the engineering domain concept does not apply in a <111>-oriented tetragonal 0.88PZN-0.12PT single crystal. The electrostrictive coefficients of $Q_{12} = -0.03706 \text{ m}^4/\text{C}^2$, $Q_{11} = 0.10765 \text{ m}^4/\text{C}^2$, and $Q_{44} = 0.02020 \text{ m}^4/\text{C}^2$ of tetragonal 0.88PZN-0.12PT single crystals were calculated.

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