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# Non-180 Degree Domain Contribution in the Dielectric and Piezoelectric Properties of $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ Single Crystals

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In order to elucidate the non-180° domain contribution to the properties of $0.91Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.9PbTiO_3$ (PZN-PT) single crystals, [001] crystal plates with uniform domain structures, 110° (010) type domains and 70° type (011) domains, were cut from a large wafer, and electric and piezoelectric properties were measured for these crystal plates. The experimental results of dielectric constants, P-E hysteresis curves, electric-field-induced strains and their frequency dependence indicated that the domain contribution to these properties was larger in the 70° domains than in the 110° domains. This difference in the domain contribution of the two domain structures was considered by the relation between the directions of spontaneous polarization and domain walls and possibility of the domain reversal by electric field.

## 1. INTRODUCTION

A giant piezoelectric effect ($k_{33}$=0.92 and $d_{33}$=1500pC/N) of $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) single crystals was first discovered by Kuwata et al.[1]. Park and Shrout [2-4] recently found that [001] oriented rhombohedral PZN-PT single crystals showed an electric-field-induced strain of 1.7% at 120kV/cm, $d_{33}$ over 2500pC/N and hysteresis-free strain vs. electric field behavior. They pointed out that a very stable domain structure was formed in [001] wafer of PZN-PT crystal under DC-bias and the domain wall motion was not detectable up to 20kV/cm. The large and hysteresis-minimized strain of PZN-PT crystals was due to this domain situation, called engineered domains.

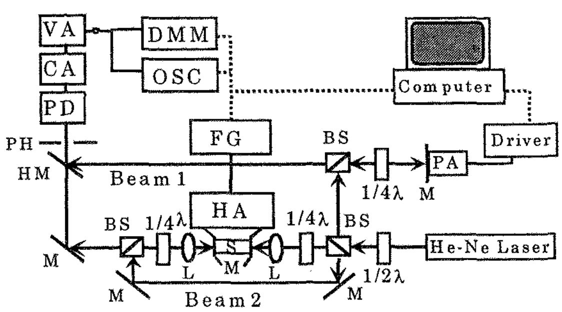
However, the relation between the domain structures and electric or piezoelectric properties is still ambiguous in PZN-PT crystals because of the lack of experimental results on the dependence of these properties on the domain structures. Yamashita et al. [5-6] have been trying to make large PZN-PT crystals, and recently they have grown crystal ingots with 40mmϕ by Bridgeman method. Wafers with 20 - 40mmϕ can be obtained from the ingots, which enable us to select crystal plates with a uniform domain structure. In this study, we have measured electric and piezoelectric properties of PZN-PT crystals with specified domain structures and found a marked dependence of properties on domain structures.

## 2. EXPERIMENTAL PROCEDURE

[001] wafers of PZN-PT crystals with the composition of 0.91PZN-0.9PT were provided from Toshiba Corp. Domain structures in the wafers were identified with an optical microscope. Crystal plates ($2x2mm^2$, [001]) with uniform domain structures were cut from the wafer and used for the following measurements.

Dielectric constants of the crystal plates were measured by an impedance analyzer (hp4192A) as a function of frequency. P-E hysteresis curves were measured by a ferroelectric test system (Radiant Tech. RT66A) at 5Hz.

The electric-field-induced strains of PZN-PT crystal plates were measured by a laser-fiber type non-contact dilatometer (resolution: 0.025μm) and a Mach-Zehnder type laser interferometer shown in Fig.1 [7]. In this interferometer system, He-Ne laser beam is sprit into two directions (beam1 and beam2) by a polarized beam splitter. The beam1 is a reference beam. The beam2 is reflected by the two mirrors attached on the surfaces of a PZN-PT crystal plate. The beam1 and beam2 are joined at a half mirror to make interference fringes. The piezoelectric displacement of the crystal moves the fringes, which can be detected as a change of light intensity. The signal of the photo-detector is amplified and stored in a digital oscilloscope with the signal applied to the crystal. The displacement of the crystal can be calculated from the change in the signal of photo-detector.




VA:Voltage amp., OSC:Storage oscilloscope, HA:High voltage amp., M:Mirror, L:Lens, HM:Harf mirror, BS:Beam splitter, PH:Pin hole, DMM:Digital multi meter, FG:Function generator,PD:Photo diode, CA:Current amp., PA:piezo-actuator, S:Sample

Fig.1 Schematic diagram of Mach-Zehnder interferometer

## 3. RESULTS AND DISCUSSION

### 3.1 Identification of Domain Structure

A photograph of a wafer of PZN-PT crystal is shown in four kinds of different regions. Inclusions of PbO were observed in one region. Three different domain structures, two with stripe domain walls and one with randomly oriented domains, were observed in other regions.

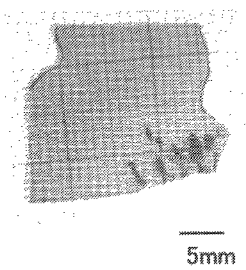



Fig.2 Photograph of a wafer

Optical micrographs of two kinds of domain structures with stripe domain walls were shown in Fig.3. Crossed nicols observation in polarizing microscope indicated that the domain walls were vertical to the crystal plates and the extinction positions of neighboring domains were approximately identical for both domain structures. By considering these information and the relation between extinction positions and the direction of domain walls, the domain structures (A) and (B) in Fig.3 were identified as 110° (010) type domains (Fig.4(A)) and 70° (011) type domains (Fig.4(B)) in rhombohedral phase. For electric measurements, Pt-sputtered electrodes were made on the surfaces with gray color in Fig.4.

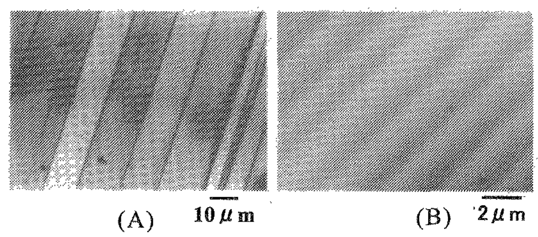
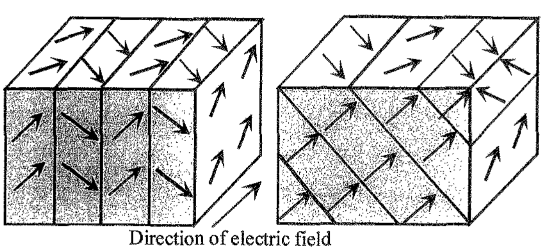



Fig.3 Two domain structures observed in PZN-PT crystals




(A) (B)

Fig.4 Two domain structures corresponding to the optical micrographs in Fig.3(A) and Fig.3 (B). (A) 110° (010) type domains and (B) 70° (011) type domains. Arrows denote projections of the polarization vector into the corresponding plane.

3.2 Electric Properties

Figure 5 shows the frequency dependence of relative dielectric constant of the crystal plates with the domain structures in Fig.4 (A) and (B). Dielectric constants decrease with increasing frequency for both crystals. It is important that the dielectric constant of 70° domains is larger that that of 110° domains. Arlt et al.[8] pointed out that the non-180° domain wall motion increased the dielectric constant. The non-180° domain contribution to the dielectric constant was also observed in PT single crystals [9]. The results in Fig.5 indicate that the non-180° domains affects the dielectric constants in PZN-PT crystals, and the domain contribution of 70° domains are larger than that of 110° domains if the electric field is applied to the direction shown in Fig.4.

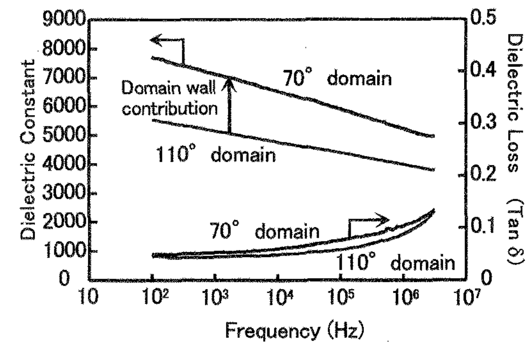



Fig.5 Dielectric properties of PZN-PT crystals with different domain structures.

Figure 6 shows the P-E hysteresis curves of PZN-PT crystals with different domain structures. Spontaneous polarization of the 70° domain crystal is about 28μC/cm$^2$ and that of 110° domain crystal is about 22μC/cm$^2$. Coercive field of the two crystals is about 650V/mm and independent of domain structure. It should be noted that the shape of the P-E hysteresis curves depends on the domain structures, i.e.: the 110° domain crystal shows a hysteresis curve with a rectangular shape, indicating the digital domain switching mainly due to the 180° domain reversal. The gradual polarization reversal in the 70° domain crystal shows the contribution of non-180° domains. The P-E hysteresis curves indicate that the contribution of 70° domains is larger than that of 110° domains.

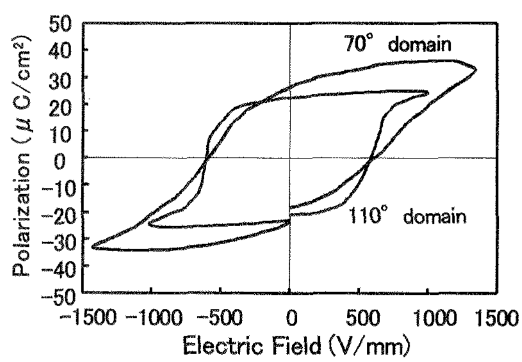



Fig.6 P-E hysteresis curves of PZN-PT crystals with different domain structures.

3.3 Electric-Field-Induced Strains

Figure 7 shows the electric-field-induced strain vs. electric field curve of PZN-PT crystals measured by the laser-fiber type dilatometer. The frequency was about 0.02Hz. Before the measurements, the poling procedure was carried out at 1.5kV/mm for 30 min at room temperature. It was found that the strain vs. electric field curve changes markedly with the domain structures.

In the 70° domain crystal, a large hysteresis is observed in the strain curve. This hysteresis is due to the contribution of domain wall motion in 70° domain structure. The strain of the 70° domain crystal is larger than that of the 110° domain crystal. In the first measurement of the 110° domain crystal, a large residual strain was observed (dotted line in Fig.7) but the residual strain was reduced in the successive measurements. This seems to indicate that the poling of the crystal is proceeded during the first measurement. After the full poling, the residual strain and hysteresis were not observed in the 110° domain crystal, showing that the non-180° domain contribution is small [7]. The results in Fig.7 indicate that the domain contribution to the electric-field-induced strain is larger in the 70° domain crystal than in the 110° domain crystals.

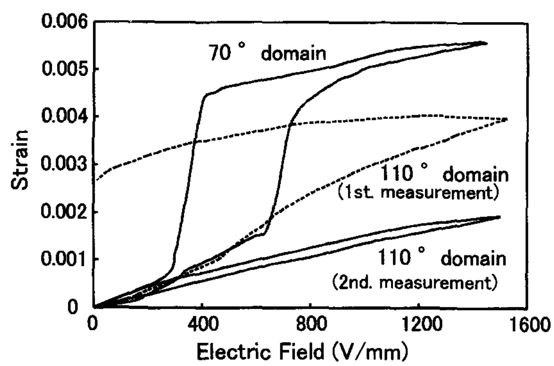



Fig.7 Electric-field-strain vs. electric field curves of PZN-PT crystals.

The apparent piezoelectric constants, determined from the slope of the strain vs. electric curve, are shown in Fig.8 as a function of frequency. The strains at high frequencies were measured by the interferometer shown in Fig.1. Large dispersion of piezoelectric constant is observed in the 70° domain crystal. The similar dispersion was observed in PZT ceramics [7] but the relaxation frequency of PZT ceramics (100- 400Hz) was much higher than PZN-PT crystals (~0.1Hz). The dispersion of piezoelectric constant is caused by the non-180° domain wall motion (extrinsic piezoelectric effect)

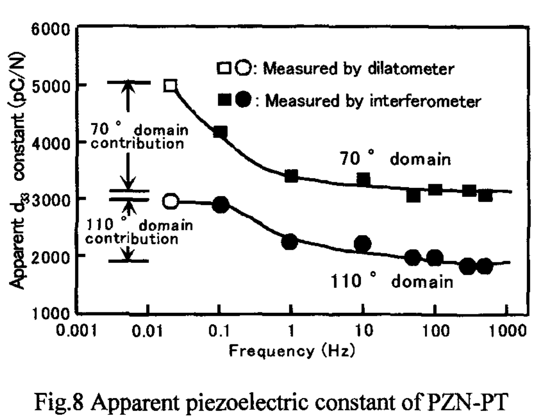



Fig.8 Apparent piezoelectric constant of PZN-PT crystals as a function of frequency.

because the velocity of the ferroelastic domain wall motion is restricted in the crystal. In the 110° domain crystal, the dispersion of piezoelectric constant is also observed but its degree is less than the 70° domain crystal. This result also indicates that the domain contribution to the apparent piezoelectric constant is larger in the 70° domain crystal than in the 110° domain crystal.

The apparent piezoelectric constants of the two crystals asymptotically approach to certain values with increasing frequency (Fig.8). The piezoelectric constant at high frequencies can be regarded as an intrinsic piezoelectric effect without the domain contribution. However, it is important that the piezoelectric constants at high frequencies are different in the two domain structures. This means that the domain contribution still exists in the piezoelectric constants at high frequencies because the averaged crystallographic orientation is the same in the two crystals. We have not understood the origin of the non-180° domain contribution to the piezoelectric constant at higher frequencies than the observed relaxation, but it may be a vibration of domain walls rather than the shift of domain wall which contributes to the electric-field-strain at low frequencies. The variation of the piezoelectric properties in the crystal plates cut from the same wafer is a serious problem for practical applications such as ultrasonic transducers. In order to understand the domain contribution in piezoelectric property, it seems to be necessary to measure the piezoelectric dispersion in a wide frequency region.

### 3.4. 70° and 100° Domains and Their Contributions to the Properties

All experimental results mentioned above indicated that the contribution to the properties was larger in the 70° domains than in the 110° domains. The reason was considered as follow.

Figure 9 shows the directions of spontaneous polarization and the domain walls in 70° (010) type domains and 110° (011) type domains. From the consistency of spontaneous strains in neighboring domains, the following equation should be satisfied [10]:

$$(S_{ij} - S'_{ij})x_i x_j = 0 \qquad (1)$$

where $S_{ij}$, $S'_{ij}$ are spontaneous strains in neighboring domains, and $x_i$, $x_j$ are coordinates on the domain wall between two neighboring domains. In the 110° (010) type domain, the directions of spontaneous polarization in the neighboring domains (a1 and a2) are 3 and 2 (Fig.9(A)) and the equation of domain wall becomes $y$ = 0 to satisfy the eq.(1). In the 70° (011) type domain, the directions of spontaneous polarization in the neighboring domains (b1 and b2) are 1 and 3 (Fig.9(B)) and the equation of domain wall becomes $y = -z$.

The electric field was applied along the [100] direction in this study as shown in Fig.9. In the 110° domains, the spontaneous polarization along the 2-direction (a2 domain) has to switch to the 4'-direction by the electric field. However, this switching does not likely to occur because it requires the change in direction of domain walls. After switching, the equation of domain wall separating the neighboring domains with the polarization direction of 3 and 4' is $y = -x$, therefore, the switching of spontaneous polarization from 2 to 4' direction in the a2 domain requires the rotation of whole domain walls. On the other hand, the spontaneous polarization in the 70° domains easily change its direction by the electric field (1 to 3 direction in b1 domain in Fig.9(B)) without the change of the equation of domain wall. This means the shift of domain walls easily occurs in the 70° domains by the application of electric field along [100]. We think this difference in the 110° and 70° domains give the differences in the domain contribution to the properties observed for the two domain structures.

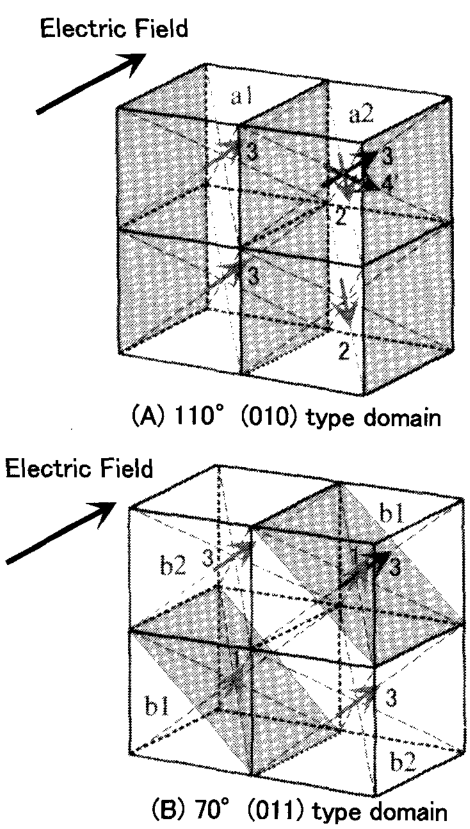



Fig.9 Directions of spontaneous polarization and domain walls in (A) 110° domain and (B)70° domain structures in rhombohedral phase.

4. SUMMARY

PZN-PT crystal plates with uniform domain structures, 110° (010) type domains and 70° (001) type domains, were cut from a [001] wafer, and electric and piezoelectric properties were measured for the crystal plates with the two domain structures. All experimental results indicated that the domain contribution to the properties was larger in 70° domains than in 110° domains. The reason of this difference was considered by the relation between the directions of spontaneous polarization and domain walls in the two domain structures.

Acknowledgements

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