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Piezoelectric properties of PZN-PT single crystals with various domain structures

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Electric field induced strains of $Pb(Zn_{1/3}Nb_{2/3})O_3$–9%$PbTiO_3$ (PZN-9%PT) single crystals were measured as a function of the domain structure in order to investigate its contribution to the piezoelectric properties. In a PZN-9%PT single crystal wafer, the rhombohedral 71° domains, the tetragonal 90° domains and the random domains were observed using a polarizing microscope. The samples with the uniform domain structure were cut from the crystal wafer, and their polarization and strain behaviors were measured using a modified Sawyer -Tower circuit and LVDT. The sample with the rhombohedral 71° domains indicated a large hysteretic strain behavior, and it was assigned to the electric field induced phase transition. On the other hand, the samples with the tetragonal 90° domains and the random domains showed a small hysteresis-free strain behavior. Therefore, it was revealed that the electric field induced strain behaviors were significantly dependent on the domain structures using the PZN-9%PT single crystals. This phenomenon was originated from the two-phase coexistence of tetragonal and rhombohedral. In order to solve this problem, the chemical composition of the PZN-PT was shifted from the morphotoric phase boundary (MPB) to the rhombohedral phase, and thus the PZN-7%PT single crystals was chosen. In a PZN-7%PT single crystal wafer, 3 kinds of the unknown domains were observed, but there was slight difference of their electric field induced strain behaviors despite of the domain structures. Therefore, it was confirmed that the homogeneous piezoelectric properties were obtained using the PZN-7%PT single crystals.

Key words: PZN-PT single crystal, giant piezoelectricity, domain structure, MPB

1. INTRODUCTION

A giant piezoelectric effect of the PZN-9%PT single crystals oriented along [001] direction was first discovered in 1982 [1]. Its piezoelectric constant over 2,500 pm/V was much larger than those (100-500pm/V) of the piezoelectric materials such as $Pb(Zr,Ti)O_3$ (PZT) and barium titanate. Moreover, it was reported that the PZN-9%PT single crystals exhibited the large electromechanical coupling factor (k_{33}) of 92%. Thus, it is expected that the PZN-9%PT single crystals can be used as the high performance medical ultrasonic transducer. In fact, Kobayashi *et al.* produced a prototype of the ultrasonic transducer using the PZN-9%PT single crystals as piezoelectric oscillator, and investigated its piezoelectric property [2]. As a result, they confirmed its high piezoelectric performance, but they also found that the piezoelectric property of one piezoelectric oscillator did not consist with that of other oscillator in ultrasonic transducer probe. It was known that the origin of the giant piezoelectric effect of the PZN-9%PT single crystals was the engineered domain structures [3]. Therefore, it is considered that the different property between each oscillator can be assigned to the dfference of the domain structures.

The PZN-9%PT single crystals have a chemical composition of the morphotoric phase boundary (MPB) between rhombohedral and tetragonal phases. Hence, the PZN-9%PT single crystals have 5 kinds of the domain structures; the rhombohedral 71° domains (rhomb71), the rhombhedral 109° domains (rhomb109), the rhombhedral 180° domains (rhomb180), the tetragonal 90° domains (tetra90) and the tetragonal 180° domains (tetra180). Figure1 shows rhomb71, rhomb109 and tetra90 domains [4]. As the above described, it is important to investigate the contribution of the domain structure of the PZN-9%PT single crystals to piezoelectric properties. For this purpose, it is necessary to prepare the sample with the uniform domain structures.

In this study, we prepared several samples with uniform domain structures from one PZN-9%PT single crystal wafer. Their electric induced strain and the P-E hysteresis curves were also measured at the same time using a new developed measurement system with the modified Sawyer -Tower circuit and LVDT displacementmeter. Finally, we proposed the solution to obtain homogeneous piezoelectric properties in the whole of one PZN-PT single crystal wafer.

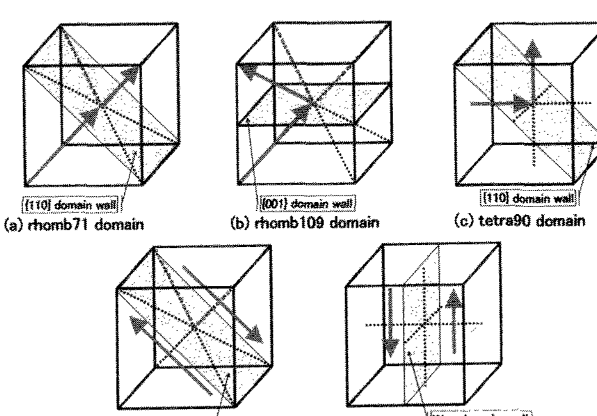

Fig.1 the 5 kind of Domain structures expected for PZN-9%PT single crystals

2. EXPERIMENT

The PZN-9%PT and PZN-7%PT single crystals with the high quality were grown using the Bridgeman method from Toshiba Co. A detail process using the PbO flux was reported elsewhere [5]. The [100], [010], and [001] directions were identified by the back reflection Laue method..

First, all domains of the [001] oriented PZN-PT single crystal wafer were observed under the crossed nicols by a polarizing microscope. Next, for the investigation of piezoelectric properties, the regions with the uniform domain structures were selected and cut into the rectangular bar with a size of 3 × 1 × 0.4 mm from the [001] oriented PZN-9%PT single crystal. After, the domain structure was identified crystallographically. The Ag paste as an electrode was painted on the top and bottom surfaces with a size of 3 × 1 mm.

Figure 2 illustrated a new developed measurement system with the modified Sawyer-Tower circuit and LVDT, *i.e.*, the polarization (P) *vs.* electric field (E) hysteresis and strain (S) *vs.* E curve measurement system. The total system was controlled by the personal computer (PC) with the D/A output, A/D input and relay board. First, the triangular signal from the PC was amplified by a high-voltage amplifier (TRek 609D) and applied to the samples. The polarization was measured using the modified Sawyer-Tower circuit with the I-V converter and the following integration circuit. This circuit included the following two features; (1) the resistance in the I-V converter was variable in order to amplify a weak signal, and (2) the charge stored in standard capacitor of the integration circuit was leaked automatically in order to keep the base line of the signal. Moreover, the electric field induced strain was also measured by the contact displacementmeter with a LVDT (Millitron, Mahr). Thus, the S-E and P-E hysteresis curves at 0.1Hz were measured at the same time. This measurement was continuously repeated 5 times.

3. RESULT & DISCUSSION

3.1 PZN-9%PT

3.1.1 Domain structures As the above mentioned, the PZN-9%PT single crystals have 5 kinds of the domain structures; the rhomb71, the rhomb109, the rhomb180, the tetra90 and the tetra180. But, the rhomb180 and the tetra180 domain could

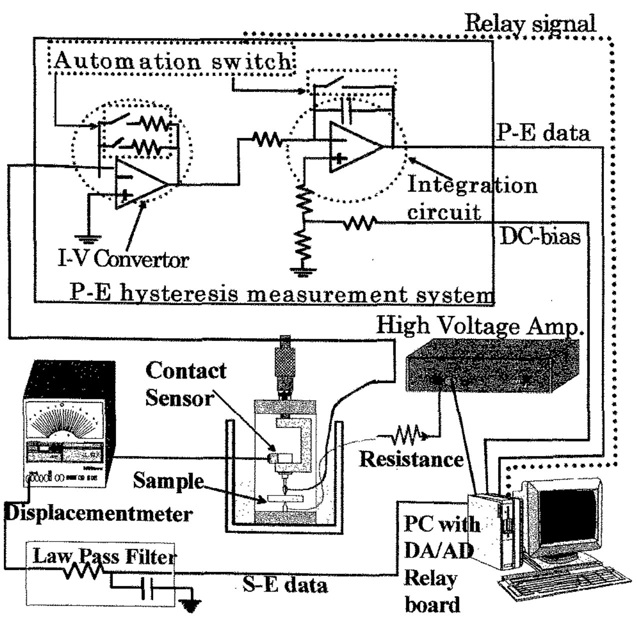

Fig.2 A schematic measurement system for S-E and P-E hysteresis curves.

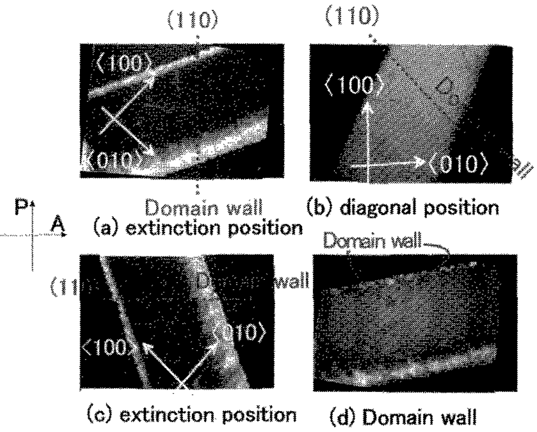

Fig.3 the rhomb71 domain structure

not be observed using the polarizing microscope because of the antiparallel spontaneous polarization between the neighboring domains. As the result of the domain observation of one PZN-9%PT single crystal wafer, the 3 kinds of the domain structures were observed. Thus these domain structures were assigned crystallographically.

Figure 3 shows the first sample of 3 kinds of the domain structures observed under crossed nicols. The domain wall of (110) plane was clearly observed as shown in Fig. 4(d), which suggested that this domain structure can be assigned to the rhomb71 or the tetra90. When the (110) plane was adjusted to the polarizer direction, the whole sample became to the extinction position (Fig. 4(a)). On the other hand, when the sample was rotated by 45°, the whole sample became to the diagonal position (Fig. 4(b)). Moreover, the sample was rotated by 45°, the whole sample returned to the extinction position again (Fig. 4(c)). This phenomenon revealed that the polar directions between the neighboring domains were normal to (110) plane. This means that this domain structure is assigned to the rhomb71 domain crystallographically.

By using the same method, the second domain structure was identified as the tetra90. Figure 4 shows the third one of 3 kinds of the domain structures observed under crossed nicols. Even if this sample was rotated, there was no extinction position, but the birefringence was observed at any angles. This suggested that there were the laminated domain structures along thickness direction. Thus we can not assign to crystallographical domain structure. So this domain (Fig. 4) was named as the random domain.

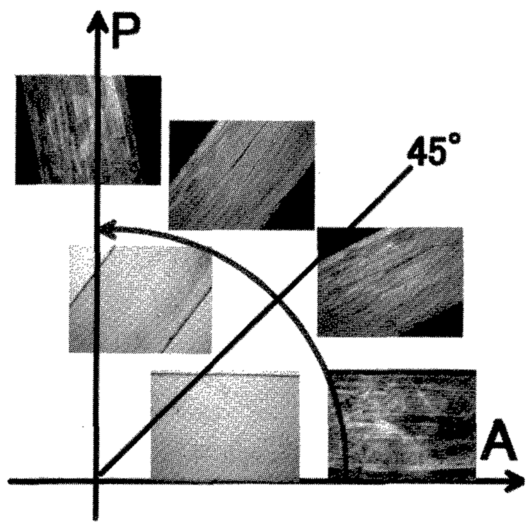

Fig.4 the random domain structure

The domain wall of (100) plane was not observed in this wafer, which means that the rhomb109 domain did not exist. The most of domain structures in this wafer were random domain, while some parts were the tetra90 and the rhomb71 domains.

Piezoelectric properties Figures 5 and 6 show the bipolar P-E and bipolar S-E curves of the PZN-9%PT single crystals with 3 kinds of domain structures. In Fig.5, the remnant polarization (Pr) of the random and the tetra90 domains were almost same values of 37±1μC/cm². On the other hand, that of the rhomb71 was 25.2μC/cm², and smaller than 37±1μC/cm². According to the crystallography, the Pr of the rhombohedral phase along [001] direction should be $1/\sqrt{3}$ of that of the tetragonal phase along [001] direction. Therefore, it can be expected that the Pr of the rhomb71 domain becomes to 20.5±0.5μC/cm², and in fact, the Pr (25.2μC/cm²) of the rhomb71 domain was very closed to 20.5±0.5μC/cm². This means that the random domain can be assigned to the tetragonal phase.

Moreover, it should be noted that the rhomb71 domain indicated a slight hysteresis over ±1.5kV/mm in Fig. 5. In Fig. 6, the rhomb71 domain indicated a giant hysteretic strain at ±1.5kV/mm. In general, the occurrence of the hysteresis behavior for P-E and S-E curves suggests the electric field induced phase transition. Thus, it was revealed that the rhomb71 domain exhibited the electric field induced phase transition at ±1.5kV/mm. The above results show that it is very important to measure both P-E and S-E curves at the same time. In Fig. 6, the random and tetra90 domains showed a large strain in opposite direction. This cause would be the domain reorientation behavior. To investigate the precise piezoelectric properties, the unipolar S-E curve were measured.

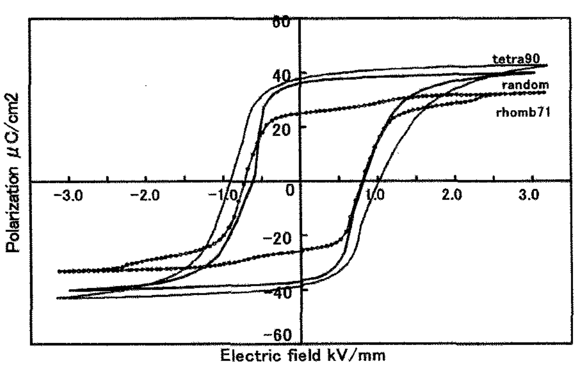

Fig.5 the bipolar P-E hysteresis curves of PZN-9%PT single crystals with various domains

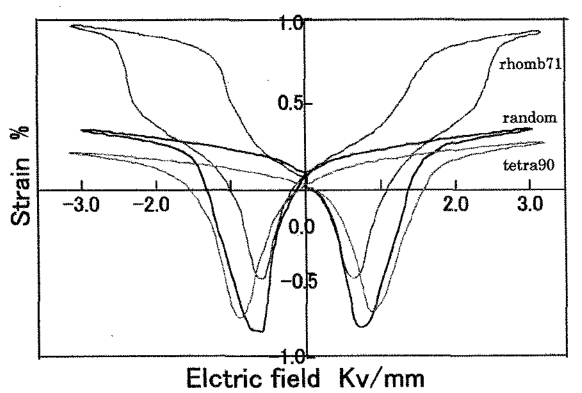

Fig.6 the bipolar S-E curves of PZN-9%PT single crystals with various domains

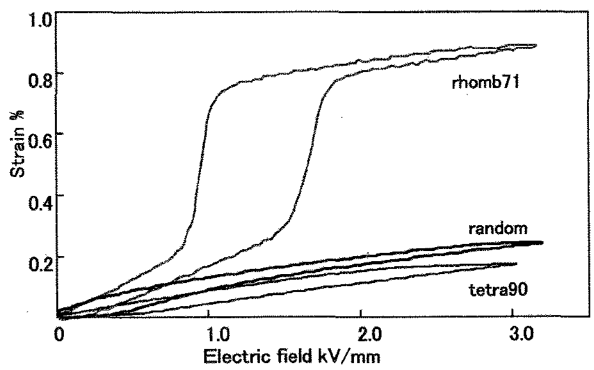

Fig.7 the unipolar S-E curves of PZN-9%PT single crystals with various domain

Figure 7 shows the unipolar S-E curves of the PZN-9%PT single crystals with 3 kinds of domain structures. The rhomb71 domain indicated a giant hysteretic strain of 0.9% over 1.5kV/mm, while below 1.0kV/mm, the rhomb71 domain showed large hysteresis-free strain. On the other hand, the tetra90 domain and the random domain showed a small hysteresis-free strain over the whole electric field. It should be noted that the slope of the S-E curve means the piezoelectric constant (d_{33}). Thus, for the rhomb71 domain, the d_{33} over 2.0kV/mm was 600pm/V, while the d_{33} below 1.0kV/cm was 2,500pm/V. On the other hand, for the tetra90 and the random domains, the d_{33} was 610pm/V. Thus, over 2.0kV/mm, all samples exhibited almost same piezoelectric constants of 600pm/V, which means that all samples were tetragonal phase. Therefore, it was confirmed that the random domain was composed of the laminated domain layers of tetragonal phase. Moreover, in Fig. 7, the rhomb71 domain indicated a giant strain at 1.5kV/mm. The large hysteretic strain of 0.9% was originated from the electric field induced phase transition from rhombhedral to tetragonal phase.

Following these results, the PZN-9%PT single crystal with the rhomb71 domain showed 2,500pm/V, while those with the random and the tetra90 domains indicated 610pm/v at the weak electric field. This means that for the PZN-9%PT single crystals, the piezoelectric properties were significantly dependent on the domain structures. Therefore, it becomes to the serious problem for the transducer application of the PZN-9%PT single crystal.

3.1 PZN-7%PT

3.2.1 Domain structures In order to improve the different piezoelectric properties of the PZN-9%PT, the chemical composition of the PZN-PT should be changed. Figure 8 shows the phase diagram of the PZN-PT system

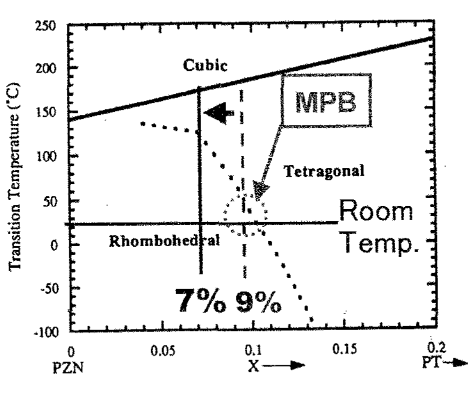

Fig.8 the schematic phase diagram of PZN-PT

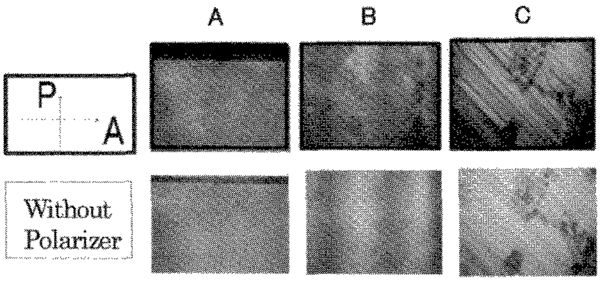

Fig.9 3 kinds of domain structures observed in PZN-7%PT single crystals

[6,7]. The MPB of the PZN-PT system is 9%PT at room temperature. Thus, if we chose the 9%PT composition, it is possible that two phases of tetragonal and rhombohedral can coexist in one crystal. This study revealed that the different piezoelectric properties were originated from the coexistence of rhombhedral and tetragonal phases. In order to solve this problem, the chemical composition of PZN-PT should be shifted from MPB to rhombhedral phase. Therefore, the PZN-7%PT single crystals were grown by the Brigdeman method.

Figure 9 shows the domain structures observed under crossed nicols for the [001] oriented PZN-7%PT single crystal wafer. In the PZN-7%PT single crystal wafer, the clear domain wall was not observed. But, there were also 3 kinds of domain structures. Here, we named 3 domains "A", "B" and "C", respectively. The "A" and "B" domains had almost same structures. But, the "C" domain resembled the random domain in the PZN-9%PT. The birefringence was observed at any angles in the sample "C". The 3 pieces of 3×1×0.4 mm rectangular bar were formed from (001) wafer.

3.2.2 Electric measurement Figure 10 shows the S-E curves of the PZN-7%PT and the PZN-9%PT single crystals (unipolar). In Fig. 10, the strain of all PZN-7%PT is bigger than the random domain, but slight smaller than the rhomb71 domain. In fact, the piezoelectric constants (d_{33}) of "A", "B" and "C" were 1800, 2300, 2350pm/V, respectively. On the other hand, for the rhomb71 domain, the d_{33} over 2.0kV/mm was 600pm/V, while the d_{33} below 1.0kV/mm was 2,500pm/V and those with the random and the tetra90 domains indicated 610pm/V at the weak electric field. Following these results, to change the chemical composition of the PZN-PT, we can obtain homogeneous piezoelectric properties despite of the domain structures. For PZN-7%PT, the dependence of strain behavior on domain structure was much smaller than that of PZN-9%PT. PZN-7%PT also showed slight different of strain behaviors between domain structures. Therefore, ultrasonic transducer technology using PZN-7%PT single crystals could make rapid progress.

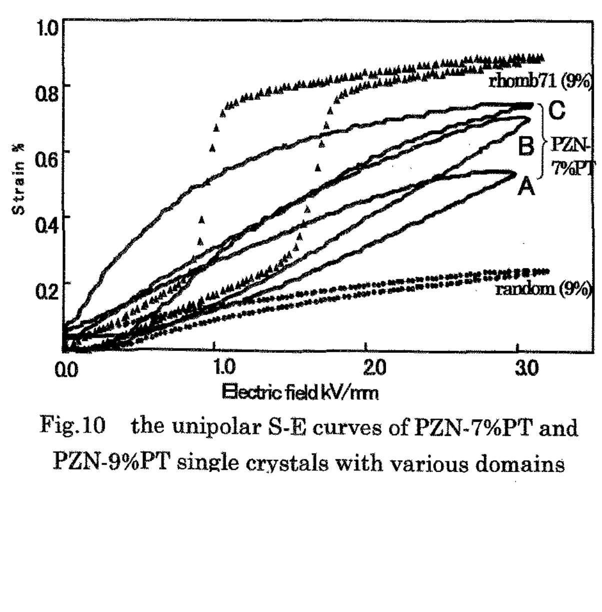

Fig.10 the unipolar S-E curves of PZN-7%PT and PZN-9%PT single crystals with various domains

4 CONCLUSION

Electric field induced strains of PZN-9%PT single crystals were measured as a function of the domain structure in order to investigate its contribution to the piezoelectric properties. In a PZN-9%PT single crystal wafer, the rhombohedral 71° domains, the tetragonal 90° domains and the random domains were observed using a polarizing microscope. The samples with the uniform domain structure were cut from the crystal wafer, and their polarization and strain behaviors were measured using a modified Sawyer -Tower circuit and LVDT. The sample with the rhombohedral 71° domains indicated a large hysteretic strain behavior, and it was assigned to the electric field induced phase transition. On the other hand, the samples with the tetragonal 90° domains and the random domains showed a small hysteresis-free strain behavior. Therefore, it was revealed that the electric field induced strain behaviors were significantly dependent on the domain structures using the PZN-9%PT single crystals. This phenomena was originated from the two-phase coexistence of tetragonal and rhombohedral. In order to solve this problem, the chemical composition of the PZN-PT was shifted from the MPB to the rhombohedral phase, and thus the PZN-7%PT single crystals was chosen. In a PZN-7%PT single crystal wafer, 3 kinds of the unknown domains were observed, but there was slight difference of their electric field induced strain behaviors despite of the domain structures. Therefore, it was confirmed that the homogeneous piezoelectric properties were obtained using the PZN-7%PT single crystals. More study is required in order to understand the details.

5 ACKOWLEDGWMENT

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6 REFERENCES

(1) J.Kuwata,K.Uchino,and S.Nomura, Jpn.Appl.Phys. 21(1982), pp1298
(2) T.Kobayashi,Y.Hosono,M,Izumi,K.Itsumi,K.Harada,and Y.Yamashita 10th US-Japan Seminar on Dielectric and Piezoelectric Ceramics.,(2001)pp229
(3) T.Tsurumi,K.Okamoto,N.Ohashi,and Y.Yamashita 9th US-Japan Seminar on Dielectric and Piezoelectric Ceramics.,(1999)pp91
(4) E.I.Eknadiosiants,V.Z.Borodin,V.G.Smotrakov,V.V.Ere mkin and A.N.Pinskaya Ferroelectrics,(1990) vol.111pp283-289
(5) K.Harada ,Y.Ymashita,Jpn.J.Appl.Phys.,39(2000)pp3117 -3120
(6) M.L.Mulvihill,L.E.Cross,K.Uchino ,J.Am.Ceram.Soc,78, [12],(1995)3345-51
(7) M.Ozgul,K.Takemura,S.T,McKinstry,and C.A.Randall 10th US-Japan Seminar on Dielectric and Piezoelectric Ceramics.,(2001)pp253

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