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Detection of 90°-domain rotation in PZT ceramics by x-ray diffraction method

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The electric field-induced strain of tetragonal PZT ceramics is believed to be consist of two parts : one is the strain caused by piezoelectric effect of the crystal (S_p) and the other is that caused by 90°-domain rotation(S_d). In order to measure the degree of 90° -domain rotation, x-ray diffraction patterns of three kinds of PZT ceramics were measured under dc electric field. The domain rotation was detected as the change in the diffraction intensities of 100 and 001 peaks, and S_d was evaluated from the intensity ratio. The strain S_p was calculated from piezoelectric *d*-constant measured by the resonance technique. It was found that the sum of the two kinds of strain approximately agreed with the actual strain measured by an optical dilatometer.

1. INTRODUCTION

It is known that electric field-induced strain of PZT ceramics observed under high electric field is larger than that expected from piezoelectric *d*-constants, and that the difference between the observed and expected strain increases with electric field. This behavior is believed to be caused by rotations of anti 180°-domains.[1-5] The field-induced strain of PZT ceramics is consist of two parts: the strain caused by the piezoelectric effect (S_p) and that caused by the domain rotations (S_d). The actual strain (S_t) therefore should be the sum of the two strains (S_p+S_d), but quantitative analyses of this relation have not been done so far. The detection and analysis of domain rotation are important to design and improve the properties of PZT ceramics actuators.

In the present study, three kinds of PZT ceramics of tetragonal phase are fabricated and the degree of 90°-domain rotation is detected by x-ray diffraction (XRD) method. The S_t measured experimentally was compared with the sum of the strains due to the piezoelectric effect (S_p) and the domain rotations (S_d).

2. EXPERIMENTAL PROCEDURE

2.1 Sample Preparation

PZT ceramics were prepared by a solid sintering technique. The compositions in Table 1 were selected to form tetragonal phases which are suitable for XRD analysis. For all samples, 0.5mol%Nb_2O_5 was added to the composition in Table 1. High purity metal oxide powders were mixed in ethanol with zirconia balls using ball mill for a day. Mixed powders were calcined at 750℃ for 2h. Calcined powders were crushed in ethanol followed, and pressed by CIP at 100 MPa and sintered at 1180℃ for 2h. The obtained ceramics were cut by a diamond cutter to the shapes of 0.5mm in thickness and 15mm in diameter for XRD analyses, 5x5x2mm^3 for field-induced longitudinal strain measurements, and 2x2x10mm^3 for the d_{33} measurements by the resonance technique. These samples were polished with 3000 mesh SiC powder, and electrically poled under 3kV/mm at 120℃ in silicone oil after electroded with Au-sputtering.

Table 1 Chemical compositions

Name	Chemical compositions
PZT	$Pb(Zr_{0.5}Ti_{0.5})O_3$
PSZT	$(Pb_{0.85}Sr_{0.15})(Zr_{0.5}Ti_{0.5})O_3$
PLZT	$(Pb_{0.92}La_{0.08})(Zr_{0.5}Ti_{0.5})O_3$

2.2 Measurements

2.2.1 XRD under high electric field

The XRD intensity ratio of 100 and 001 peaks is theoretically 2:1 but 001 intensity was higher in some polished samples because of strain induced by polishing. An annealing at 700℃ for 3h was necessary to remove the strain. XRD intensity data were measured around 100 and 001 peak tops by a step scanning method. Under the electric field of 0-2kV/mm, the accumulation of the intensity data was carried out for 20sec. for each step at the interval of 0.02deg. The scheme of sample holder is shown in Fig.1. In spite that Au-electrodes were sputtered on the both surfaces, a thin electrode (~10nm) on the irradiated surface hardly affect on the diffraction intensity from PZT. To reach an equilibrium state of domain rotation, the step scanning was started after keeping electric field at a certain value for 5 min.

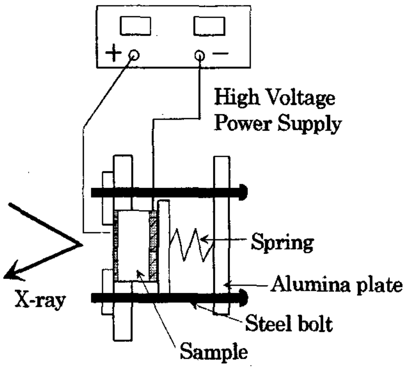

Fig.1 Scheme of a sample holder in XRD measurements

2.2.2 Field-induced strain and d_{33}

Field-induced strain (S_t) was measured using a non-contact optic dilatometer (Optometric, OM-15D). Electrodes were formed on the 5x5mm^2 surface of a 5x5x2mm^2 block. The voltage was changed step-by-step at 200V intervals to 4kV.

In the resonance technique, complex impedance of 2x2x10mm^3 bar was measured as a function of frequency using an impedance analyzer (hp4192A). The d_{33} constant was determined by a standard analyzing process from resonance and anti-resonance frequencies. The dielectric constant was evaluated from capacitance measured at 50kHz.

3 RESULTS AND DISCUSSION

Lattice parameters and *c/a* ratios of the PZT ceramics were listed in Table 2. The *a*-parameter is almost constant but the *c*-parameter changes with the chemical composition.

Table 2 Lattice parameters of specimens

	PZT	PSZT	PLZT
a (nm)	0.4030	0.4033	0.4033
c (nm)	0.4133	0.4095	0.4077
c/a	1.026	1.015	1.011

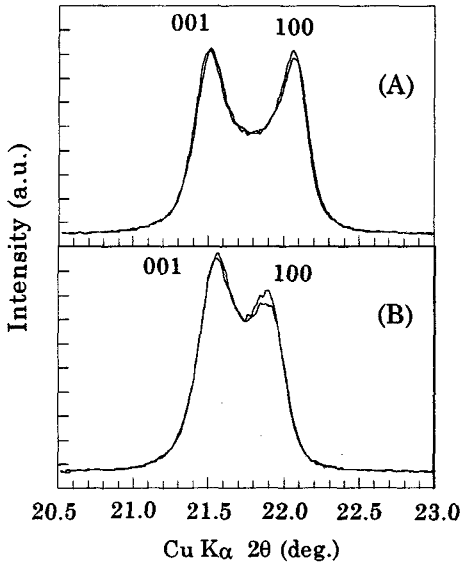

Fig.2 XRD patterns of (A)PZT and (B) PSZT. Patterns in dotted lines were obtained at 0V/mm and those in solid lines were obtained at 2.1kV/mm

Figure 2 shows XRD patterns of PZT and PSZT measured with and without electric field after poling treatment. The intensity ratio $I_{001}/(I_{100}+I_{001})$ was about 0.33 before the poling treatment but the ratio increased to 0.5 or more than that by the poling treatment. This is caused by the rotation of 90° -domains. As shown in XRD patterns (solid lines), the domain rotation also takes place in a poled samples by applying high electric field, i.e. the intensity of 001 peak increases while that of 100 peaks decreases slightly. The degree of this domain rotation is very small in comparison with that occurred in poling process.

Figure 3 shows changes in XRD intensity ratio and field-induced strain as a function of electric field.

The intensity ratio $I_{001}/(I_{100}+I_{001})$ at zero field is in the order of PZT<SPZT<PLZT

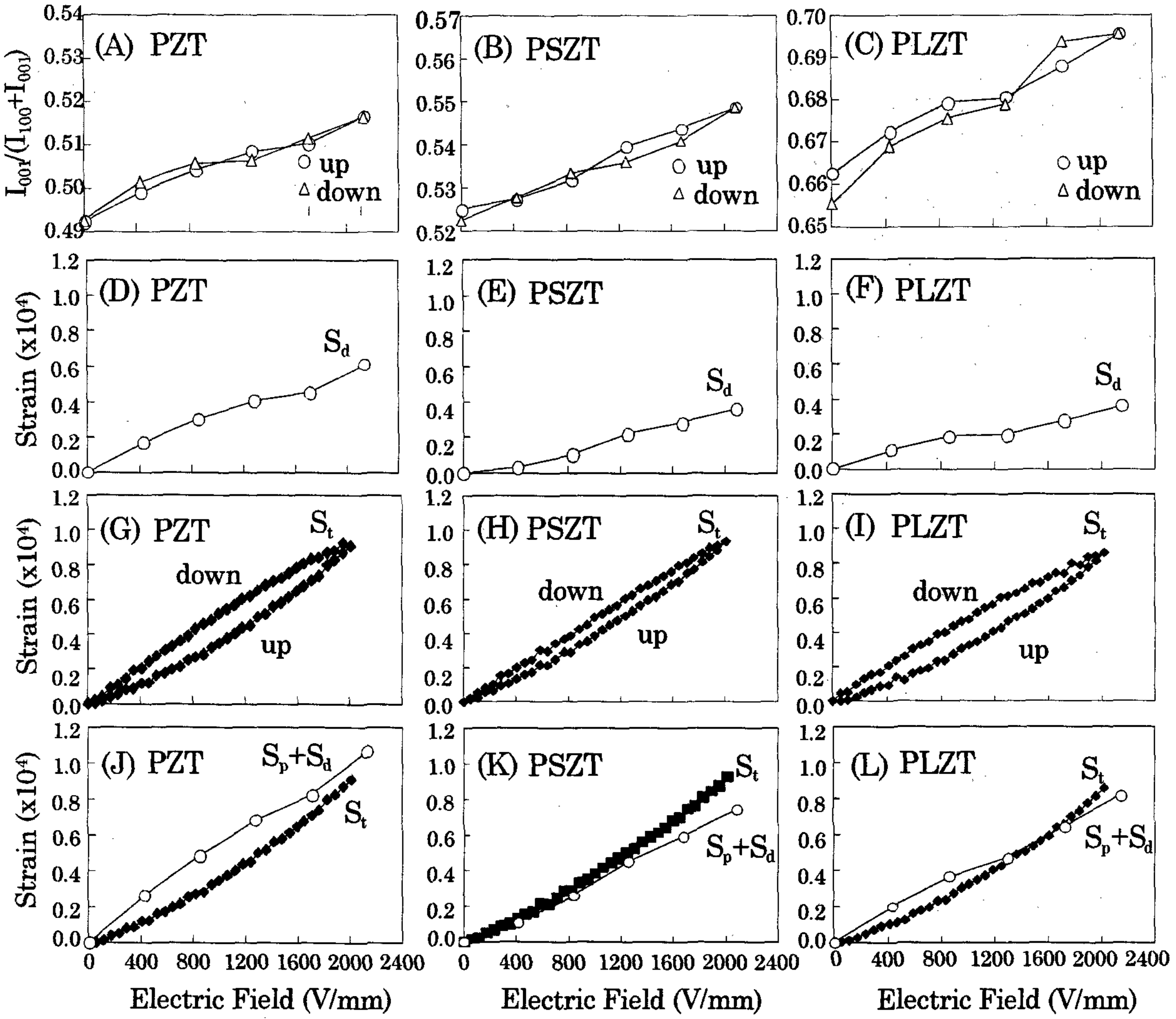

Fig.3 (A)-(C) XRD intensity ratios $I_{001}/(I_{100}+I_{001})$,
(D)-(F) Strain (S_d) due to 90°-domain rotations evaluated from the XRD intensity ratio
(G)-(I) Field-induced strain measured (S_t)
(J)-(L) Field-induced actual strain and the sum of strains due to piezoelectric effect (S_p) and 90°-domain rotation (S_d)

because the domain rotations is easy when the *c/a* ratio is small (Table 2). It was found that this 90°-domain rotation is reversible with the change of electric field and the degree of domain rotation is in the order of *c/a* ratio.

The strain caused by the 90°-domain rotation was calculated by assuming that the *c*-axes of all crystals were parallel or perpendicular to the direction of electric field. The strain S_d is given by

$$S_d = \frac{(y-x)(c-a)}{(1-x)a+xc}$$

where x is the ratio $I_{001}/(I_{100}+I_{001})$ under 0V/mm, y is $I_{001}/(I_{100}+I_{001})$ under a certain electric field, a represents the *a*-parameter, and c represents the *c*-parameter. The results of calculation are shown in Fig.3 (D)-(F). In spite that the change of $I_{001}/(I_{100}+I_{001})$ is in the order of PZT < PSZT < PLZT, the order of S_d is PZT > PSZT=PLZT because of the effect of *c/a* ratio. This indicates that a small *c/a* ratio makes domain rotation easy but hardly contributes to the increase in strain. Figure 3 (G)-(I) show field-induced strain S_t measured by an optical dilatometer. A small hysteresis was observed in S_t-E curve of each sample. The shapes of the curves and the strains were approximately the same on the three samples.

Physical constants determined by the resonance technique are listed in Table 3. The dielectric constant increases while the coupling constant decreases with the addition of Sr^{2+} or La^{3+}.

Table 3 Physical constants determined by the resonance technique

	PZT	PSZT	PLZT
density (g/cm^3)	7.804	7.603	7.697
k_{33}	0.612	0.558	0.551
ε_{33r}	1137	1229	1453
s_{33}^E (pm^2/N)	12.37	10.20	10.35
d_{33} (pC/N)	216.2	185.8	213.6

The piezoelectric strain is calculated by

$$S_p = d_{33} \times E$$

where E is electric field. On Fig.3 (J)-(L) the sum of the strains (S_p+S_d) was compared with the strain S_t actually measured for each sample. We found that fairly good agreements were observed between S_t and S_p+S_d. A small difference between them observed in PZT ceramics is attributable to the experimental errors in XRD measurements and to the approximation used in the calculation of S_d. However, the results obtained here first demonstrated the validity of the relation S_t=S_p+S_d.

The relation above indicates that the electric field-induced strain of piezoceramics is consist of the strain caused by the piezoelectric effect and that caused by the domain rotation. From the strains measured at 2.1kV/mm, the ratios of the strain due to domain rotation to the total strain were roughly estimated to be 57%, 48% and 44% for PZT, PSZT and PLZT, respectively. Approximately, half of the field-induced strain is caused by the domain rotation. These ratios are mainly determined by the *c/a* ratio, i.e. domains in a sample with a small *c/a* ratio easily rotate by the electric field but the resultant strain is small. This kind of information obtainable by XRD measurements seems to be important in order to design piezoceramics used for the piezoelectric actuators.

4. CONCLUSION

1. The degree of 90°-domain rotation in tetragonal PZT ceramics could be evaluated from XRD intensities of 100 and 001 peaks measured under high electric field.
2. The strain due to 90°-domain rotation (S_d) is dominated by the *c/a* ratio rather than the degree of the rotation, i.e. a sample with a small *c/a* ratio shows a large domain rotation but resultant strain is small.
3. The sum of strains (S_p+S_d) approximately coincides with S_t, which verifies the fact that the field-induced strain is consist of two parts: strain due to the piezoelectric effect and that due to the domain rotation.

REFERENCES

1) N.Uchida and T.Ikeda, Jpn. J. Appl.Phys., 6, 1079 (1967)

2) K.Furuta and K.Uchino, Advanced Ceramic Materials, 1, 61 (1986)

3) Y.Masuda and A.Baba, Jpn. J. Appl.Phys., 26, Suppl. 26-2, 132 (1987)

4) T.Tani, N.Watanabe, K.Takatori and S Hori, Jpn. J. Appl.Phys., 33, 5352 (1994).

5) Y.Saito, Jpn.J.Appl.Phys., 34, 5313 (1995).