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Domain Contribution in the Electric-field-induced Strain of PZT Ceramics

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The contribution of the non-180° domains to the electric-field-induced strains (EFI-strains) of PZT ceramics was evaluated by an XRD method and by an interferometric method. The XRD intensity ratio of 200 and 002 diffraction peaks of tetragonal PZT was measured under strong electric fields. The amount of the 90° domain reorientation was evaluated and the strain due to the domain reorientation was calculated. It was confirmed that the EFI-strain of PZT ceramics was equal to the sum of the strain calculated from the d_{33} constant determined by the resonance-antiresonance method and the strain due to the 90° domain reorientation. The amount of the 90° domain reorientation has a linear relation with the c/a ratio in the "soft" PZT ceramics. A Mach-Zehnder interferometer was constructed to measure the EFI-strains vs. electric-field curves of PZT ceramics as a function of frequency. The EFI-strain vs. electric-field curve showed a hysteresis due to the effect of the non-180° domain reorientation when the applied voltage was high and its frequency was low. The apparent piezoelectric constant increased from the d_{33} value determined by the resonance-antiresonance method with decreasing frequency. This deviation was attributed to the non-180° domain contribution.

Key words : Terroelectric domain, PZT, Piezoelectricity, Interferometer

I. Introduction

Two kinds of domain structures, the 180° domains and the non-180° domains, exist in PZT ceramics. It is known that the application of strong electric fields induces the non-180° reorientation of the polarization in the non-180° domains (the non-180° domain reorientation) as well as the 180° switching of the polarization in the 180° domains. In the tetragonal PZT ceramics, the non-180° domains are equivalent to the 90° domains, and the reorientation of 90° doma- ins means that the a- and c-axis of tetragonal lattice are exchanged by the strong electric field. The difference in the a- and c-parameter gives rise to the strain; therefore, the non-180°(90°) domain reorientation contributes to the electric-field-induced strain (hereafter EFI-strain). The behavior of the non-180° domains is important because it affects various properties of PZT ceramics.[1-5]

It was reported that the EFI-strains of PZT ceramics observed under strong electric fields were larger than that expected from piezoelectric *d*-constant determined by the resonance-antiresonance method, and these large strains are regarded as the contribution of the non-180° domain reorientation.[3] Some researches[4,6] have be done to evaluated the contribution of the non-180° domain in the EFI-strains of PZT ceramics. Masuda[4] analyzed the EFI-strains of modified PZT as a superimposition of piezostriction and electrostriction, where it was assumed that the electrostriction was caused by the domain reorientation. Tani et al.[6] also separated the domain contribution from the total strains by assuming that the 90° domian reorientation was negligible at weak electric fields.

The 90° domain reorientation can be detected by the x-ray diffraction (XRD) method. Some researchers[7-10] have measured the 90° reorientation induced by the poling treatment under different electric fields. However, to establish the domain contribution in the EFI-strains, it is necessary to analyze the reorientation under the electric field. For this purpose, in situ XRD data should be monitored as a function of the electric field.

It is also considered that the velocity of non-180° domain wall motion is restricted because the domain wall motion is accompanied with the strains and relatively large ionic displacements in the crystal lattice. Therefore, it seemed to be possible to separate the non-180° domain contribution in the EFI-strains by measuring strains as a function of frequency. For this purpose, accurate equipment for strain measurements should be necessary. Laser interferometric methods have been frequently used to detect the EFI-strains of piezoelectric materials.[11-16]

In the present study, we have demonstrated the evalua-

Table. 1 Chemical Composition of Tetragonal PZT Ceramics

Sample name	Chemical composition
PZT	$Pb(Zr_{0.5}Ti_{0.5})O_3$+0.5 mol%Nb_2O_5
PS5ZT	$(Pb_{0.95}Sr_{0.05})(Zr_{0.5}Ti_{0.5})O_3$+0.5 mol%$Nb_2O_5$
PS10ZT	$(Pb_{0.90}Sr_{0.10})(Zr_{0.5}Ti_{0.5})O_3$+0.5 mol%$Nb_2O_5$
PL3ZT	$(Pb_{0.97}La_{0.03})(Zr_{0.5}Ti_{0.5})O_3$+0.5 mol%$Nb_2O_5$
PL8ZT	$(Pb_{0.92}La_{0.08})(Zr_{0.5}Ti_{0.5})O_3$+ 0.5 mol%$Nb_2O_5$

tion of domain contribution in the EFI-strains of PZT ceramics by means of XRD method and EFI-strain measurements as a function of frequency with a Mach-Zehnder type interferometer.

II. Experimental Procedure

1. XRD measurements

Samples used for XRD measurements were tetragonal PZT ceramics prepared by a conventional solid sintering technique. The chemical compositions of these ceramics are listed in Table 1.

As the 90° domain reorientation is a phenomenon where the a- and c-axis of the tetragonal lattice are exchanged, the amount of the reorientation is possibly detected by XRD method. A schematic representation of the 90° domain structure in a representative cubic grain of tetragonal PZT ceramics is shown in Fig. 1. The small arrows indicate the direction of polarization in each domain. By applying an electric field, the reorientation of polarization occurs and the domain wall o-p in the figure moves to o'-p'. In the XRD measurement, the change in the ratio of area A and area B due to the electric field could be measured as the change in the intensity ratio of the h00 and 001 diffraction peaks.

In this study, the XRD intensities of the 002 and 200 peaks of tetragonal PZT ceramics were measured as a function of the electric field using an x-ray diffractometer(Rigaku, RAD II). The structure of a hand-made sample holder for XRD measurements is shown in Fig. 2. Au-spattering electrodes were formed on the both sides of ceramic plate (15 mmϕ). On the x-ray irradiating surface, the electrode was made as thin as possible (~10 nm) for electric contact to avoid x-ray absorption by Au. A positive voltage was applied to the x-ray irradiating surface during the poling treatment. A bipolar power supply/amplifier (KEPCO, BOP 1000 M) was used to apply voltages on the x-ray irradiating surface. A step scanning method was used in the data accumulation where the XRD intensity was measured for 20 s for each step at an interval of 0.02 degrees around the 002 and 200 peak tops. To achieve an equilibrium state of the domain reorientation, the step scanning was started after maintaining the electric field for 5 min.

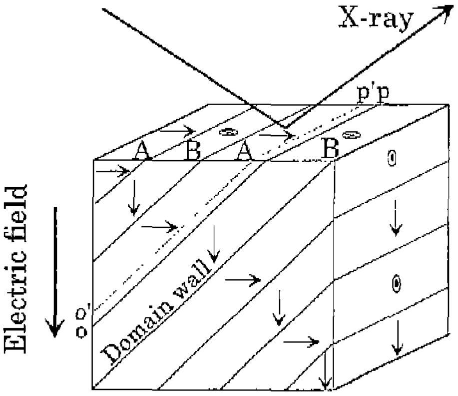

Fig. 1. The 90° domain structure of a representative cubic grain in tetragonal PZT ceramics.

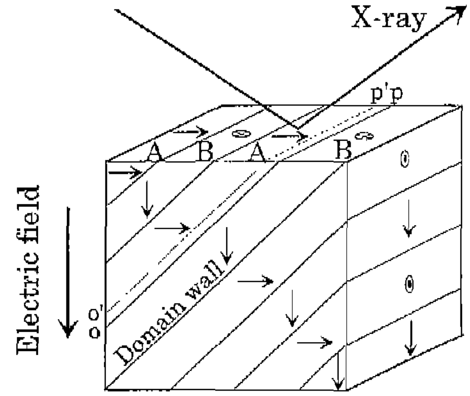

Fig. 2. Structure of sample holder for XRD measurements under the electric field.

The piezoelectric d33 constant of the PZT ceramics was determined by the resonance-antiresonance method according to the procedure of EMAS-6100 set by the Electronic Manufacturing Association of Japan. The total EFI-strain was also measured using a non-contact laser displacement meter (Optometric, OM-15D).

2. Setup of the Mach-Zehnder type interferometer

The XRD method mention above is applicable only to the tetragonal PZT ceramics, but the most of industrially used PZT ceramics has the composition near the Morphotropic

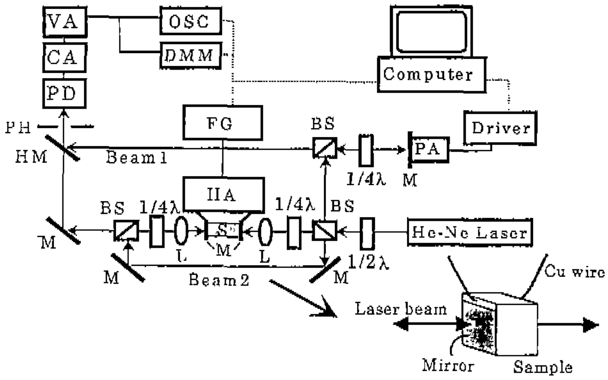

Fig. 3. Schematic diagram of Mach-Zehnder interferometer BS: Beam splitter, 1/4λ: 1/4λ plate, L: Lens, S: Sample, 1/2λ: 1/2λ plate, PH: Pin hole, HM: Half mirror, M: Mirror, PA: Piezoelectric actuator, PD: Photo-detector, VA: Voltage amp., CA: Current amp., OSC: Digital oscilloscope, DMM: Digital multi meter, HA: High voltage amp.

Phase Boundary (MPB) where the tetragonal and rhombohedral phases coexist in the ceramics. As the velocity of the non-180o domain wall motion seems to be restricted, it may be possible to separate the domain contribution by measuring EFI-strains as a function of frequency. A Mach-Zehnder interferometer was constructed for the measurements of EFI-strains. The specimen used for the measurements was a PZT ceramics with the composition of $PbZr_{0.53}Ti_{0.47}O_3$+ 0.5 mol% Nb_2O_5. The d_{33} constant determined by the resonance-antiresonance method is 370 pm/V.

A schematic diagram of the interferometer is shown in Fig. 3. The basic structure is the same as that reported by Khohlkin et al.[16] A He-Ne laser beam is split into two directions (beam1 and beam2) by a polarized beam splitter. The beam1 is a reference beam which goes to a photo-detector after reflected by a small mirror attached on a piezoelectric actuator. The beam2 is reflected by the two mirrors attached on the both surfaces of PZT ceramics. The beam1 and beam2 are joined at a half mirror to make interference fringes. The piezoelectric displacement of the specimen moves the fringes, which can be detected as a change of light intensity. The signal of the photo-detector was first amplified by the current amplifier and successively by a low noise amplifier (Ithaco, 1201) and stored in a digital oscilloscope (Kikusui, com7061A). High voltages of 400V-1kV were applied on the sample to increase the displacement using a high voltage amplifier (Trek, 609D-6). The frequency of applied electric field was restricted by the slew rate and the current limit of the high voltage amplifier below 10 kHz.

III. Results and Discussion

1. Domain Contribution Observed by XRD method

The change in the XRD pattern by the electric field is shown in Fig. 4. The application of the electric field increases the 002 intensity whereas decreases the 200 intensity, indicating that the reorientation of 90° domains occurs in the PZT ceramics. This change is caused entirely by the 90° reorientation because the switching of the 180° domain cannot be detected by XRD method. The strain caused by the 90° reorientation (Sd) was approximately estimated by the following equation;

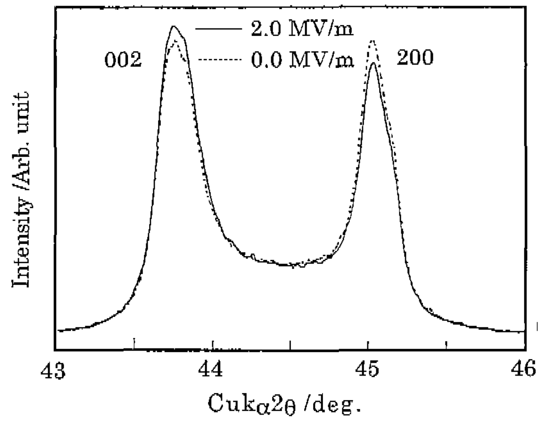

Fig. 4. Change in XRD pattern of PZT by the electric field.

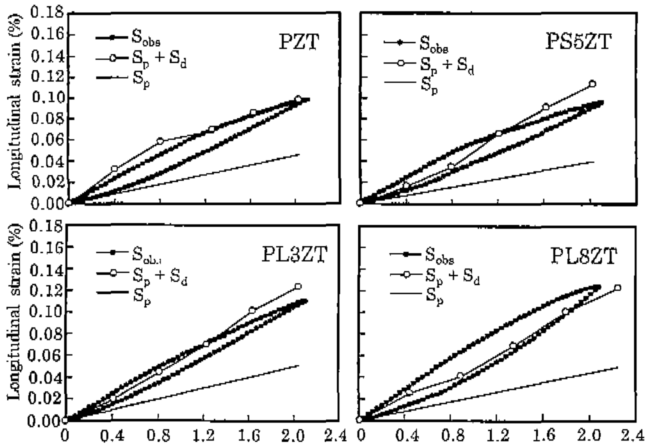

Fig. 5. Changes in S_{obs}, S_p+S_d and S_p as a function of the electric field.

$$Sd = \frac{(R(E)-R(0))(c-a)}{(1-R(0))a+R(0)c},\ R(E) = \frac{I(002)}{I(002)+I(002)} \quad (1)$$

where I(002) and I(200) are the XRD intensities of the 002 and 200 diffraction peaks, a and c are lattice parameters, and $R(E)$ is an XRD intensity ratio as a function of the electric field E in MV/m. The denominator of S_d in eq. (1) denotes the averaged lattice constant along the electric field in a hypothetical grain shown in Fig.1, and the numerator denotes the change of the average lattice constant by the electric field: [(1-$R(E)$)a+$R(E)c$]-[(1-$R(0)$)a+$R(0)c$].

The total EFI-strain (S_{obs}) consists of the strain due to the "intrinsic" piezoelectric effect (S_p) and that due to the reorientation of the 90° domains (S_d), where we used the term of "intrinsic" as that determined by the resonance-antiresonance method but the domain contribution should exist in it. As the S_{obs} has the two components as mentioned above, the equation S_{obs}=S_p+S_d should be valid, but it has not been confirmed yet. Figure 5 shows the S_{obs} and S_d+S_p as a function of the electric field. The equation S_{obs}=S_p+S_d is experimentally confirmed for all specimens in the limit of experimental errors. The strain due to the domain reorientation is not negligible and is comparable to that of the "intrinsic" piezoelectric effect.

From eq.(1), the strain caused by the 90° domain reorientation is the product of the amount of the reorientation by the difference between the a- and c-parameter. The factor determining the amount of the reorientation is considered in the following. The intensity ratio of 002 and 200 diffraction peaks after the poling ($R(0)$) was plotted as a function of tetragonality c/a in Fig. 6(a). The theoretical value of $R(0)$ before poling is 1/3. The poling induced the domain reorientation and the $R(0)$ increased to 0.5-0.6 as shown in the figure. A linear relation is observable in Fig. 6(a), which indicates that the internal stress by the domain reorienta-

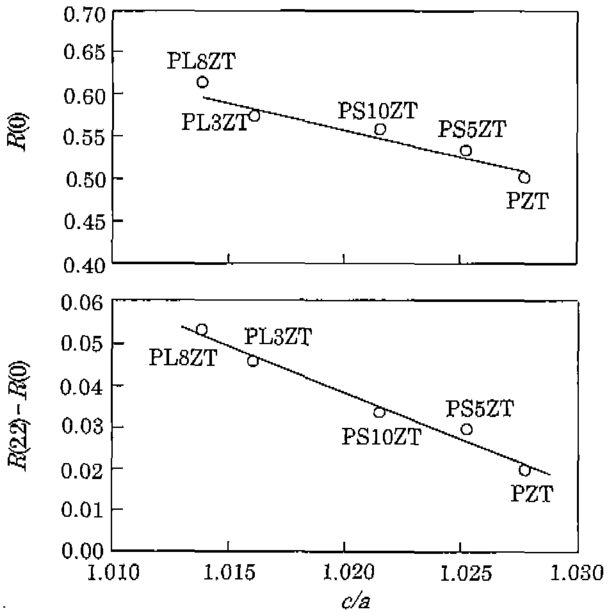

Fig. 6. The relation between the XRD intensity ratio (R(E) in eq.(1) in the text) and *c/a* ratio. (A) *R(0)* after poling treatment, and (B) *R(2.2)-R(0)*, where *R(2.2)* is the XRD intensity ratio measured at 2.2 MV/m.

tion is determined by the c/a ratio, therefore, a small c/a ratio gives a large amount of the domain reorientation. The domain reorientation which contributes the EFI–strains is given by *R(E)-R(0)*. The relation between *R(E)-R(0)* and the c/a ratio is shown in Fig. 6(b). A linear relation is also observed. The 90° domain reorientation easy occurs when the c/a ratio is close to unity, but in this case, the resultant strain is small because of the small difference in a- and c-parameter. It should be noted that the linear relation in Fig. 6 is valid for "soft" PZT ceramics where the domain wall motion is relatively free.

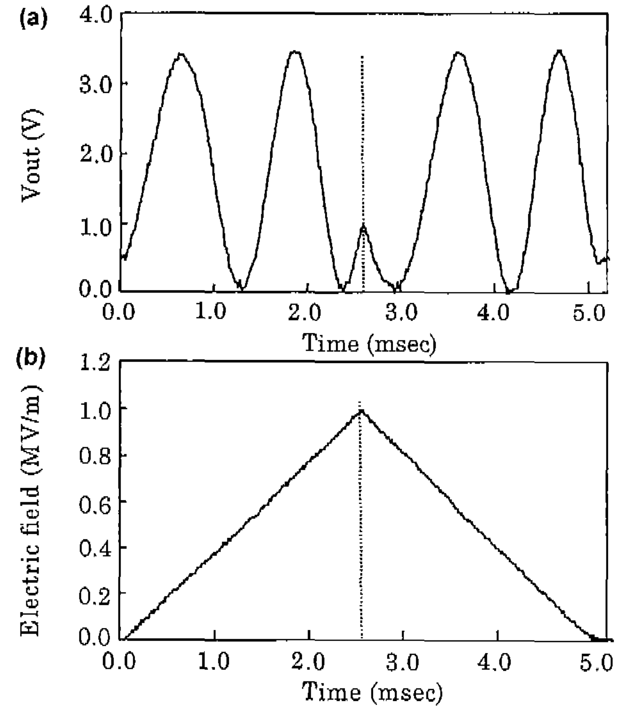

Fig. 7. Typical signals stored in the digital oscilloscope. (A) Signal (Vout) of photo-detector after amplified by two amplifiers. (B) Signal of electric field applied to the sample.

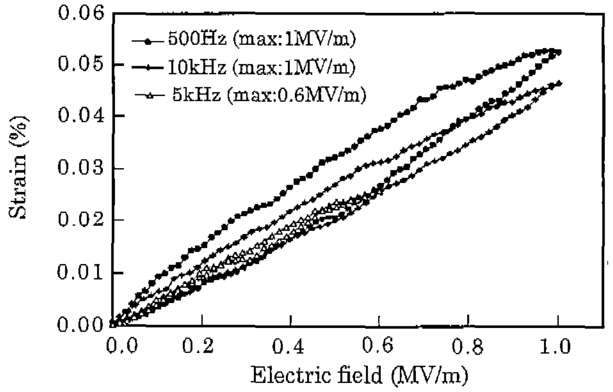

Fig. 8. Electric-field-induced strain of PZT ceramics as a function of applied electric field.

2. *Domain Contribution Observed by Interferometer*

The EFI-strain vs. electric-field curves were measured by the Mach-Zehnder interferometer. A typical waveform stored in the oscilloscope (V_{out}) is shown in Fig. 7 with the signal of

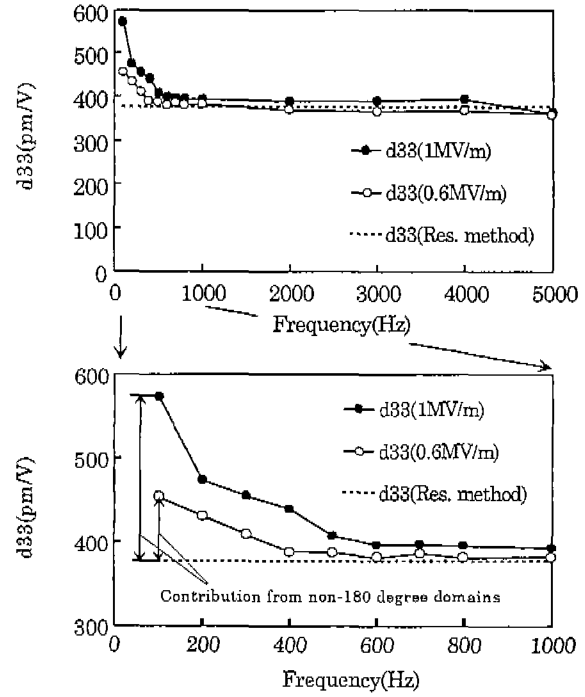

Fig. 9. Apparent piezoelectric constant of PZT ceramics as a function of frequency. Apparent piezoelectric constant was determined from the electric-filed-induced strain at maximum electric field (600 V/mm or 1kV/mm). The contribution of non-180° domain reorientation in the piezoelectric constant was shown in the figure.

applied voltage. A sinusoidal change of the signal was observed with the triangular applied voltage. The waveform of signal was almost symmetrical with respect to the peak of applied voltage in this figure. The asymmetry of the waveform implied a hysteresis in the strain curve.

The EFI-strain vs. electric-field curves of PZT ceramics are shown in Fig. 8. Smooth and reasonable curves indicate that the strain curve is measurable by the Mach-Zehnder interferometer. The curves were almost linear when the applied electric field was relatively low (<600 V/mm) and the frequency was relatively high (>5 kHz). The piezoelectric constant determined from the slope of line was about 370 pm/V, which was consistent with the piezoelectric constant determined by the resonance-antiresonance method. On the other hand, the strain curve showed a hysteresis when the applied voltage was high and the frequency was low. Both the hysteresis and slope of curves increased with increasing maximum electric field. These are the effect of non-180° domain reorientation. It was found that the non-180° domain reorientation gave the hysteresis to the strain vs. electric field curves and increased apparent EFI-strains.

The apparent piezoelectric constant calculated from EFI-strain at maximum electric field is shown in Fig. 9 as a function of frequency. At high frequencies, the apparent piezoelectric constant was consistent with d_{33} determined by the resonance-antiresonance method (370 pm/V), but it increased with decreasing frequency. This behavior became notable when the applied field is high. The deviation of apparent piezoelectric constant from 370 pm/V was due to the contribution of non-180° domains to the EFI-strain. However, there is a possibility of the non-180° domain contribution in the piezoelectric constant of 370 pm/V determined by the resonance-antiresonance method. In this case, the non-180° domain contribution shown in Fig. 9 does not necessarily indicate the entire contribution of non-180° domains. However, it was indicated that the non-180° domain contribution was possibly separated, even if it was partial, from EFI-strain by measuring strains as a function of frequency using the Mach-Zehnder interferometer. The separation was possible because the velocity of non-180° domain wall motion was restricted by the strain or ionic motion in the crystal. The non-180° domain reorientation could not follow the electric field at high frequencies and gave a piezoelectric relaxation at a certain frequency. This relaxation frequency should change with materials, electric field strength, temperature and so on. The Mach-Zehnder interferometer is a very useful technique for these measurements to elucidate the relaxation of non-180° domain reorientation, in other word, the domain dynamics, which seems to be essential to understand the properties of piezoelectric ceramics.

IV. Summary

The non-180° domain contribution in the EFI-strain of PZT ceramics was evaluated by XRD method and the interferometer. The results obtained are summarized as follows::

1. The amount of the 90° domain reorientation was evaluated by XRD method under the electric field for tetragonal PZT ceramics. The domain contribution in the EFI-strain was estimated from the amount of the 90° domain reorientation and the lattice parameters.
2. It was experimentally confirmed that the EFI-strain of PZT ceramics was equal to the sum of the strain calculated from the d_{33} constant determined by the resonance-antiresonance method and the strain due to the 90° domain reorientation.
3. The amount of the 90° domain reorientation has a linear relation with the c/a ratio in the "soft" PZT ceramics.
4. The velocity of the non-180° domain wall motion was relatively slow. Therefore, the domain contribution in the EFI-strain could be evaluated by measuring EFI-strain as a function of frequency using the Mach-Zehnder type interferometer.
5. The non-180° domain reorientation gave rise to the hysteresis in the EFI-strain vs. electric-field curve. The effect of the domain contribution increases with increase of electric field and decrease of frequency.

Acknowledgments

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References

1. S. Li, W.Cao, R. E. Newnham and L. E. Cross, "Electromechanical Nonlinearity of Ferroelectric Ceramics and Related Non-180° Domain Wall Motions," *Ferroelectrics*, **139**, 25-49 (1993).
2. E.I.Bondarenko, V.Yu.Topolov and A.V.Turik, "The Effect of 90° Domain Wall Displacements on Piezoelectric and Dielectric Constants of Perovskite Ferroelectric Ceramics," *Ferroelectrics*, **110**, 53-56 (1990).
3. N.Uchida and T.Ikeda, "Temperature and Bias Characteristics of Pb(Zr-Ti) Families Ceramics," *Jpn. J. Appl. Phys.*, **4**, 867-80 (1965).
4. Y. Masuda, "Variation of Dielectric Constant Affected by Domain Structure and Electric-Field-Induced Strain in Ferroelectric Ceramics," *Jpn. J. Appl. Phys.*, **33**, 5549-54 (1994).
5. M.Hirose, M.Takada, H.Oka and K.Miyabe, "Relationship between Poling Condition and Heat resisting Properties in Lead Zirconate Titanate," *Jpn. J. Appl. Phys.*, **33**, 5345-47 (1994).
6. T.Tani, N.Watanabe, K.Takatoshi and S.Hori, "Piezoelectric Properties for Doped Lead Zirconate Titanate Ceramics under Strong Electric Field," *Jpn. J. Appl. Phys.*, **33**, 5352-55 (1994).
7. A. Yamada, Y.-K. Chung, M. Takahashi and T. Ogawa,

"Poling Field dependence of Ferroelectric Domains in Tetragonal Lead Zirconate Titanate Ceramics," *Jpn. J. Appl. Phys.*, **35**, 5232-35 (1996).

8. S. Li, C.-Y. Hung, A. S. Bhalla and L. E. Cross, "90°-Domain Reversal in Pb(Zr_xTi_1-x)O_3 Ceramics," *Ferroelectr. Lett.*, **16**, 7-19 (1993).
9. Y. W. Zeng, W. R. Xue and G. F. Fu, "Investigation of Switching Behavior og 90° Ferroelectric Domains in ($Pb_{0.85}Sm_{0.10}$) ($Ti_{0.95}Mn_{0.02}$)O_3 Piezoelectric Ceramics of Ultra-High Electromechanical Anisotropy by the X-ray-Diffraction Tech- nique," *J. Mater. Sci.* **26**, 4293-97 (1991).
10. J. Mendiola and L. Pardo, "A XRD Study of 90° Domains in Tetragonal PLZT under Ploing," *Ferroelectrics* **54**, 539-42 (1984) .
11. Q.Zhang, W.Pan and L.E.Cross, "Laser Interferometry for the Study of Piezoelectric and Electrostrictive Strains," *J. Appl. Phys.*, **63**, 2492-96 (1988).
12. Q.Zhang, W.Pan and L.E.Cross, "High frequency Strain response in Ferroelectric and Its Measurement Using a Modified Mach-Zehnder Interferometer," *J. Appl. Phys.*, **65**, 2807-13 (1989).
13. S.T.Vohra and F.Bucholtz, "Characterization of the Dynamic Strain responce of Lead Magnesium Niobate based Ferroelectric Relaxor Using a Fiber Optic Interferometer," *Ferroelectrics*, **160**, 243-53 (1994).
14. J.F.Li, P.Moses and D.Viehland, "Piezoelectric Spectroscopy," *Ferroelectrics*, **153**, 365-69 (1994).
15. T.Yamaguchi and K.Hamano, "Interferometric Method of Measuring Complex Piezoelectric Constant of Crystals in a Frequency Range up to about 50kHz," *Jpn. J. Appl. Phys.*, **18**, 927-32 (1979).
16. A.L.Kholkin, Ch.Wutchrich, D.V.Taylor and N.Setter, "Interferometric Measurements of Electric Field-Induced Displacements in Piezoelectric Thin Films," *Rev. Sci. Instrum.*, **67**, 1935-41 (1996).