Non-180° Domain Contribution in Electric-Field-Induced Strains of PZT Ceramics Measured by a Mach-Zehnder Interferometer

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マッハツェンダー型干渉計により測定した PZT セラミックスの 電界誘起歪における非180度ドメインの寄与

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In order to evaluate the contribution of the non-180° domain reorientation in the electric-field-induced strains of PZT ceramics, a Mach-Zehnder interferometer was constructed and the electric-field-strain of PZT ceramics was measured as a function of frequency. The performance of the interferometer was confirmed using a LiNbO₃ single crystal and PZT ceramics. The piezoelectric constant of PZT ceramics determined by the interferometer well agreed with that determined by the resonance method and the result of LiNbO₃ single crystal was also approximately consistent with the literature. The resolution of the interferometer was about 0.01 nm. The electric-field-induced strain curve showed a hysteresis under high electric fields and low frequencies. The apparent piezoelectric constant determined from the electric-field-induced strain increased with decreasing frequency under high electric fields. These behaviors were interpreted as the effect of non-180° domain reorientation.

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1. Introduction

Lead zirconate titanate (PZT) ceramics have two kinds of domain structures: the 180° domains and the non-180° domains, and it is known that strong electric fields (>1 kV/mm) induce switching of the 180° domains and reorientation of the non-180° domains. As the non-180° domain reorientation is ferroelastic, the reorientation is accompanied with a strain. The reorientation behavior of the non-180° domains is important because it affects various properties of PZT ceramics, such as dielectric constant,^{1)–5)} field-induced-strain,^{3)–6)} heat resisting property⁷⁾ and durability during high power applications.⁸⁾

In the field of piezoelectric actuators, the electric-field-induced strains (hereafter abbreviated as EFI-strains) of PZT ceramics observed under strong electric fields are usually larger than that expected from piezoelectric *d*-constant determined by the resonance technique.⁹⁾ The unexpected large strains observed under strong electric fields are regarded as the contribution of the non-180° domain reorientation.³⁾ Some researchers have evaluated the contribution of the non-180° domain reorientation in the EFI-strains of PZT ceramics. Masuda⁴⁾ analyzed the EFI-strains of modified PZT ceramics as a superimposition of piezoestriction and electrostriction, where the electrostriction was assumed to be caused by the non-180° domains. Tani et al.¹⁰⁾ also separated the domain contribution from the total strain by assuming that the non-180° domain reorientation was negligible at low electric fields. Recently, Tsurumi et al.¹¹⁾ directly observed the non-180° domain (90° domains in tetragonal PZT) reorientation by an X-ray diffraction (XRD) technique under the electric field and evaluated the domain contribution in EFI-strains. However, these methods involved some assumptions in the analyses and could not measure the behaviors of non-180° domain reorientation at high frequencies, which is important for practical applications.

We considered that the velocity of non-180° domain wall motion was restricted because the domain wall motion is accompanied with the strains and it needs 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.^{12)–18)} Both the Michelson type (single beam interferometer) and the Mach-Zehnder type (double beam interferometer) have been used for this purpose, but Kholkin et al.¹⁸⁾ have concluded that the Mach-Zehnder type was superior to the Michelson type especially in the high frequency measurements.

In the present study, we have made a Mach-Zehnder type interferometer and measured EFI-strains and strain vs. electric-field curves of PZT ceramics in order to separate the non-180° domain contribution in the EFI-strains.

2. Experimental

2.1 Sample preparation

PZT ceramics with the composition of Pb(Zr_{0.53}Ti_{0.47})O₃ + 0.5 mol% Nb₂O₅ were prepared by an ordinal ceramic sintering process. The starting materials were extra-pure reagents of PbO, ZrO₂, TiO₂ and Nb₂O₅. They were mixed with a wet ball-milling for 24h and calcined at 800°C for 2h. The calcined powder was ground and pressed into disks of 15 mm in diameter. The disks were sintered at 1180°C for 3h to make ceramic samples. The sample was cut with a diamond cutter into the shape of 2×2×10 mm³, and electroded with a silver paste on the 2×2 mm² surfaces. The ceramic bar thus obtained was electrically poled under the electric field of 3 kV/mm at 120°C in silicon oil for 0.5h. Piezoelectric *d*-constant (*d*₃₃) was measured by a resonance technique according to the procedure of EMAS-6100 set by the Electronic Manufacturing Association of Japan for the measurement of piezoelectric ceramic elements. The *d*₃₃ of the sample was determined to be 370 pm/V.

For the interferometric measurements, a PZT ceramic sample with 2×2×2 mm³ in size was prepared. Two small mirrors, which were made by Pt-sputtering cover glasses

used for optical microscope, were attached on the ceramic surfaces with an epoxy resin after the electric poling procedure. A LiNbO₃ single crystal with 2×2×4 mm³ in size was also used as a sample to confirm the reliability of the interferometer.

2.2 Setup of Mach-Zehnder interferometer

A schematic diagram of the Mach-Zehnder interferometer constructed in the present study is shown in Fig. 1. The basic structure is the same as that reported by Kholkin et al.¹⁸⁾ A He-Ne laser beam is split into two directions (beam 1 and beam 2) by a polarized beam splitter. The beam 1 is a reference beam which goes to a photo-detector (Electro-optics Tech., ET-2000) after reflected by a small mirror attached on a piezoelectric actuator. The beam 2 is reflected by the two mirrors attached on the both surfaces of PZT ceramics and goes to the detector. The beam 1 and beam 2 are joined at a half mirror to make interference fringes. The piezoelectric displacement of the sample moves the fringes, which can be detected as a change of light intensity through a pin-hole. A 1/2λ plate was used to balance the light intensities of beam 1 and beam 2. In the measurement of small displacements, it should be necessary to adjust and keep the optical path length of interferometer at the most sensitive position, the so-called λ/4 condition. To solve this problem, we detected light intensity as a function of optical path length changed by the piezoelectric actuator.

The samples were suspended by thin Cu-wires as shown in Fig. 1. The advantage of this interferometer is that the sample is measured without clamping to a sample stage. The clamping of samples brings about mechanical resonance at low frequencies and loss of elastic energies to the sample stage.

Two kinds of electric setups (setup 1 and 2) were used: the setup 1 was for measuring very small displacements, where the signal of the photo-detector was amplified by a current amplifier (Stanford Research Sys., SR570) and its dc- and ac-component were measured by a digital voltmeter (hp34401A) and lock-in amplifier (NF5610B), respectively. The voltage applied to the sample was 1–6 V. The setup 2 was for measuring EFI-strain vs. electric-field curves. In this case, the lock-in amplifier was not useful because it could not measure the waveform of signal of the photo-detector. Therefore, the signal of the photo-detector was

Fig. 1. 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., LA: Lock-in amp., OSC: Digital oscilloscope, DMM: Digital multi meter, FG: Function generator, HA: High voltage amp.

first amplified by the current amplifier and successively by a low noise amplifier (Ithaco, 1201) and stored in a digital oscilloscope (Kikusui, com7061A). However, a small displacement of sample was not measured because the sensibility of the oscilloscope was much less than that of the lock-in amplifier. Therefore, high voltages of 400 V–1 kV 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.

2.3 Analysis of experimental data

The analyzing procedure of signals in the setup 1 was as follows. The intensity (I) of light after interference is given by

$$I = \left[A_1 \exp i \left(\omega t + B_1 + \frac{4\pi \Delta L}{\lambda} \right) + A_2 \exp i \left(\omega t + B_2 + \frac{4\pi \Delta l}{\lambda} \right) \right] \times [c.c.] \quad (1)$$

where A_1 and A_2 are amplitudes of beam 1 and beam 2, B_1 and B_2 are initial phase angles of beam 1 and beam 2, t is time, ω is an angular frequency of light, λ is wave length of light (633 nm), ΔL is a change of optical pass length by the piezoelectric actuator, Δl is that by the piezoelectric effect of the sample and $[c.c.]$ is a complex conjugate. If the electric field applied to the specimen is an ac-signal with the angular frequency ω_0 and the amplitude of E_0 , Δl is given by

$$\Delta l = d E_0 \cos(\omega_0 t - \delta) \quad (2)$$

where d is a piezoelectric constant (d_{33}), l is a length of the sample and δ is a phase delay due to the imaginary part of piezoelectric constant which was ignored in this analysis. The light intensity is composed of dc- and ac-part, $I = I_{dc} + I_{ac}$, where I_{dc} is changed by ΔL and I_{ac} oscillates due to the change of Δl (Eq. (2)) with the angular frequency of ω_0 . The I_{dc} shows maximum and minimum values with the change of $\Delta L = \lambda/2$. The Eq. (1) is simplified using the maximum and minimum values of I_{dc} , $I_{dc}(\max)$ and $I_{dc}(\min)$, as follows.

$$I = \frac{I_{dc}(\max) + I_{dc}(\min)}{2} + \frac{I_{dc}(\max) - I_{dc}(\min)}{2} \times \cos \left(B + \frac{4\pi(\Delta L - \Delta l)}{\lambda} \right) \quad (3)$$

where B is an initial phase angle and constant. If the Δl is much smaller than λ , the amplitude of I_{ac} ($I_{0,ac}$) can be approximately calculated as

$$I_{0,ac} = \frac{2\pi [I_{dc}(\max) - I_{dc}(\min)] d E_0}{\lambda} \sin \left(B + \frac{4\pi \Delta L}{\lambda} \right) \quad (4)$$

and the piezoelectric constant d is obtained from

$$d = \frac{\lambda I_{0,ac}(\max)}{2\pi [I_{dc}(\max) - I_{dc}(\min)] E_0 l} \quad (5)$$

where $I_{0,ac}(\max)$ is a maximum value of the amplitude of ac-part ($I_{0,ac}$).

In the real measurements, the light intensity was replaced by the signal voltage of photo-detector (V_{dc} , $V_{0,ac}$) because the linear relation between them was confirmed beforehand. Most of d -constants of samples were determined from the Eq. (5), but for some data, non-linear least squares fitting of V_{dc} and $V_{0,ac}$ was also carried out, where the signal intensities were calculated from Eq. (1) without any approximations as a function of driving voltage of the piezoelectric actuator.

In the setup 2, the driving voltage of the piezoelectric actuator is not changed during the measurements. The light intensity in this case is simplified as

$$I = A + A' \cos \left(B + \frac{4\pi \Delta l}{\lambda} \right) \quad (6)$$

where A , A' and B are constants. If the intensity shows maximum and minimum with the change of Δl , Δl between them should correspond to $\lambda/2$. From the relation thus obtained, the displacement of sample can be calculated from the light intensity.

3. Results and discussion

3.1 Reliability and resolution of the interferometer

The change of V_{dc} and $V_{0,ac}$ of PZT ceramics measured in the setup 1 is shown in Figs. 2(A) and (B) as a function of the driving voltage of the piezoelectric actuator. The amplitude and frequency of ac-signal on the sample was 2 V and 6 kHz, respectively. The V_{dc} shows a sinusoidal curve with the change of ΔL . The solid lines in the figures were calculated using Eq. (1). Some parameters in the equation were determined to explain the observed results by non-linear least squares calculation. The piezoelectric constant determined by the fitting was 377 pm/V. The calculated results well explained the changes of V_{dc} and $V_{0,dc}$, indicating that the performance of the interferometer constructed in this study was consistent with the theoretical expression.

The piezoelectric constant (d_{33}) determined from Eq. (5) is shown in Fig. 3 as a function of frequency. The d_{33} -values were about 370 pm/V which was well consistent with that determined by the resonance technique. The d_{33} -value tends to increase with frequency above 70 kHz. This seemed to be experimental errors due to the band width of the current amplifier or mechanical resonance. The maximum frequency of the interferometer was about 50 kHz at present. Figure 4 shows the piezoelectric constant (d_{33}) of a LiNbO₃ single crystal as a function of frequency. Measurements at higher frequencies could not be done because the displacement of the sample was too small. The

Fig. 2. The changes of V_{dc} (A) and $V_{0,ac}$ (B) as a function of the driving voltage of the piezoelectric actuator. The calculated results were obtained from Eq. (1), where some parameters were determined by non-linear least squares calculation. The piezoelectric constant determined by the fitting was 377 pm/V.

Fig. 3. Piezoelectric constant (d_{33}) of PZT ceramics determined by the interferometer as a function of frequency. The electric field applied to the sample was 1 V/mm.

Fig. 4. Piezoelectric constant (d_{33}) of a LiNbO₃ single crystal determined by the interferometer as a function of frequency. The electric field applied to the sample was 1 V/mm.

d_{33} -values were between two values previously reported as shown in Fig. 4. We thought that the reliability of the interferometer was confirmed.

Figure 5 shows the displacements of PZT ceramics and LiNbO₃ single crystal as a function of amplitude of ac-signal. In the both results, the slope of $\log(\Delta l)$ vs. $\log(V)$ curve is about unity, which indicates that the displacement is caused by the piezoelectric effect. The resolution of the interferometer was about 0.01 nm.

3.2 EFI-strain curves and contribution of non-180° domain reorientation

A typical waveform stored in the oscilloscope (V_{out}) in the setup 2 is shown in Fig. 6 with the signal of 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 strain vs. electric field curve was obtained by analyzing the similar results as shown in Fig. 6.

EFI-strain curves of PZT ceramics are shown in Fig. 7. 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

Fig. 5. Relation between the displacements of PZT ceramics (A) and a LiNbO₃ single crystal (B) and the amplitude of ac-signal applied to the specimen.

Fig. 6. Typical signals stored in the digital oscilloscope. (A) Signal (V_{out}) of photo-detector after amplified by two amplifiers. (B) Signal of electric field applied to the sample.

by the resonance 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.

Fig. 7. Electric-field-induced strain of PZT ceramics as a function of applied electric field.

Fig. 8. Apparent piezoelectric constant of PZT ceramics as a function of frequency. Apparent piezoelectric constant was determined from the electric-field-induced strain at maximum electric field (600 V/mm or 1 kV/mm). The contribution of non-180° domain reorientation in the piezoelectric constant was shown in the figure.

The apparent piezoelectric constant calculated from EFI-strain at maximum electric field is shown in Fig. 8 as a function of frequency. At high frequencies, the apparent piezoelectric constant was consistent with d_{33} determined by the resonance 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 technique. In this case, the non-180° domain contribution shown in Fig. 8 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 words, the domain dynamics, which seems to be essential to understand the properties of piezoelectric ceramics.

4. Conclusion

In this study, a Mach-Zehnder interferometer was constructed and EFI-strains of PZT ceramics were measured in order to evaluate the contribution of non-180° domain reorientation in EFI-strains of PZT ceramics. Major conclusions are summarized as follows.

(1) The piezoelectric constant (d_{33}) of PZT ceramics measured by the interferometer was consistent with that determined by the resonance method. The piezoelectric constant of a LiNbO₃ single crystal was also between the two reported values.

(2) The resolution of the interferometer was about 0.01 nm.

(3) 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.

(4) The apparent piezoelectric constant increased from the d_{33} -value determined by the resonance method with

decreasing frequency. This deviation was attributed to the non-180° domain contribution.

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