Field-induced Strain Memory with Non-180° Domain-reorientation Control

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Using non-180° domain-reorientation control, we propose the strain memory effect in ferroelectric ceramics. Electric fields with asymmetric amplitudes were applied to soft-type lead zirconate titanate (PZT) ceramics, and the strain hysteresis and the polarization loop were measured. The butterfly curve became asymmetric under an electric field with a particular asymmetric amplitude. The asymmetric butterfly curve had two stable strain states at zero electric field. Thus, the strain memory effect was realized as the difference between the two stable strain states. An XRD analysis was carried out to verify the contribution of the non-180° domain reorientation to the strain memory effect. The non-180° domain reorientation was determined as the intensity ratio of the (002) to the (200) peak. The strain memory determined from macroscopic strain measurements had a linear relationship to the non-180° domain volume fraction. This result indicated the origin of the strain memory to be the non-180° domain reorientation.

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I. INTRODUCTION

Ferroelectric materials have spontaneous electric polarization, which can be reversed by means of an external electric field; thus utilizing its electric property, the non-volatile ferroelectric random access memory is intensively studied [1]. Moreover, they are also piezoelectric materials in which strain or stress can be induced by external electric fields, and these are widely utilized for sensors and actuators [2,3]. However, the strain properties of the piezoelectric materials do not have memory effects unlike their polarization properties do. Therefore, a conventional piezoelectric actuator requires a continuous operating voltages to keep its piezoelectric displacement. If ferroelectric materials had the strain memory effect, as their polarization properties do, a novel piezoelectric actuator, which could keep its piezoelectric displacement without an electric field, could be fabricated.

In this study, a non-180° domain reorientation is utilized in order to induce a strain memory effect of ferroelectric materials. Usually, most ferroelectric materials have 180° domains and non-180° domains. If the ferroelectric material is composed of only 180° domain, its electric-field-induced strain is derived only from the intrinsic piezoelectric strain; thus, it is linear in the external electric fields [4,5]. On the contrary, if the ferroelectric material has both 180° and non-180° domains, an extrinsic strain derived from the reorientation of the non-180° domains appears. The extrinsic strain is usually larger than the intrinsic strains; therefore, some research has tried to utilize non-180° domain reorientation in order to realize high-strain actuators [6–8]. However, there is no study using non-180° domain reorientation to the strain memory effect.

We propose a strain memory effect using non-180° domain reorientation control with asymmetric-amplitude external electric fields. Moreover, the contribution of the non-180° domain reorientation to the strain memory is verified using an X-ray diffraction (XRD) analysis. XRD is a typical and powerful way to reveal the non-180° domain states [9–13]. The experimental procedure is described in the following sections.

II. PRINCIPLE

Figure 1 shows the macroscopic principle of the proposed strain memory effect and a schematic of the domain states of the ferroelectric ceramics. Conventional hysteresis of the strain and the polarization of ferroelectric ceramics under bipolar electric fields are shown by dashed lines. As described above, the strain does not have a memory effect because the strain hysteresis has only one stable state at 0 electric field. However, when the amplitude of the applied electric field is controlled to induce in minor polarization loop shown by solid lines, the strain hysteresis also comes to have two stable states at 0 electric field. One state is a poled state, and the...
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III. EXPERIMENTAL PROCEDURE

A commercial soft-type lead zirconate titanate (PZT) ceramics (material D, Nihon Ceratech) was used for the experiments. The ceramics were disk shaped with diameter of 10 mm and thickness of 0.48 mm. The surfaces of the ceramics were polished and annealed at 600 °C for 3 hours to eliminate the surface texture change caused by mechanical treatment [14]. Platinum electrodes were sputtered by DC sputtering (SC-701, SANYU ELECTRON).

The strain hysteresis and the polarization hysteresis of the PZT ceramics were measured simultaneously. The strain of the ceramics in the thickness direction was measured with a linear variable differential transformer (LVDT). The contact pressure of the LVDT sensor was 4.5 MPa. This pressure is sufficiently weak so as not to affect the strain due to the ferroelastic switching [15]. The polarization hysteresis was measured with a ferroelectric tester (Precision LC, Radiant). The electrical fields were applied from the ferroelectric tester through the high-voltage amplifier. A schematic of the measurement system is shown in Fig. 2. A symmetric strain hysteresis and a symmetric polarization hysteresis were measured with triangular wave electric fields of 1.2 kV/mm. Various minor strains and polarization hystereses were measured with various asymmetric-amplitude triangular waves. The positive amplitude of the applied electric field was 1.2 kV/mm, and the negative amplitude was changed from 1.2 kV/mm to 0.4 kV/mm at a frequency of 0.25 Hz. All asymmetric measurements were carried out for four cycles after two cycles of symmetric applied electric fields. The asymmetric amplitude causes domain stabilization, and its hysteresis changes its shape in the first several cycles. Therefore, a symmetric electric field was applied to initialize the domain state before the asymmetric-amplitude measurement [16]. Positive and negative unipolar triangular electric fields were applied, respectively. The stable strain state was switched by using the external electric fields to verify the strain memory effect.

The XRD analysis was conducted by using powder X-ray diffraction (MiniFlexII, Rigaku) using Cu Kα radiation. The measurement was carried out after application of a positive unipolar electric field or a negative unipo-
lar electric field corresponding to the amplitudes of the asymmetric measurement. The XRD (002) and (200) reflection peaks were measured for each state. The integrated area of each peak was calculated. The relationship between the intensity ratio and the strain memory as a macroscopic one was investigated.

IV. RESULTS AND DISCUSSION

1. Strain and Polarization Hysteresis under an Electric Field with an Asymmetric Amplitude

Figure 3 shows the strain hysteresis and the polarization hysteresis under various asymmetric-amplitude electric fields and the ordinal hysteresis. The ordinal symmetric butterfly curve and ordinal hysteresis appeared under the symmetric electric field. The 0 strain state was defined as a poled state. The remnant polarization and the coercive field were determined from the polarization hysteresis loop as 23.6 \( \mu \text{C/cm}^2 \) and 0.63 kV/mm, respectively. When the polarization is fully reversed, the strain states after electric field application are the same, regardless of the polarization direction. Therefore, the ferroelectric ceramics did not have a strain memory effect.

The butterfly curves under asymmetric-amplitudes were asymmetric with respect to the electrical-field axis. As the negative amplitude of the applied electric field was decreased, the left wing of the butterfly curve became smaller, and the symmetry of the butterfly curve decreased. A negative amplitude far below that of the coercive field did not induce a butterfly shaped hysteresis.

The strain states after application of a positive amplitude, in other words the poled state, were the same for every strain hysteresis. This indicates that the ceramics was fully poled after application of a 1.2-kV/mm electric field for each hysteresis loops. The asymmetric butterfly curve has a strain memory effect because it has two stable values at 0 electric field. We defined the value of the strain memory as the difference between these two strain states at 0 electric field as shown in Fig. 3. One stable state seems to be a fully-poled state, and the other stable state is partially-depoled state.

The polarization hysteresis loop showed minor hysteresis loops under asymmetric-amplitude electric fields. As the negative amplitude of the applied electric field was decreased, the switching polarization was gradually reduced. However, the switching polarization decreased drastically when the negative amplitude became smaller than that of the coercive field.

Figure 4 shows the strain memory and the polarization change as functions of the negative field amplitude. Both the strain memory and the polarization change were drastically changed when the negative amplitude was near that of the coercive field. This is reasonable because the coercive field is defined from the polarization hysteresis at 0 polarization, and the maximum strain memory value should be given when the macroscopic polarization is fully randomized. However, the maximum strain memory was actually given when the negative amplitude was slightly below that of the coercive field. This is because the strain memory is induced by the non-180° domain reorientations. The non-180° domain switching occurs slightly before 180° domain switching occurs [17].
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Fig. 5. Pulse operation of the ferroelectric ceramics.

The ferroelectric ceramics were operated by using a set of the unipolar positive or negative amplitude triangular waves, as shown in Fig. 5. The ferroelectric ceramics had two stable strains after the removal of the operating electric fields. Thus, a strain memory as the difference between the two strain states was realized. The obtained strain was stable, at least, for several tens of seconds. The retention property of a longer time is an ongoing study.

2. XRD Measurement

The volume fraction of the non-180° domain was measured as the intensity ratio of the (002) to the (200) peak. After a unipolar triangular electric field of positive or negative amplitude had been applied, the XRD measurement was carried out. The volume fraction of the non-180° domain was calculated as [11]

\[ \nu_{002} = \frac{I_{002}}{I_{002} + I_{200}}. \]

\( \nu_{002} \) indicates the volume fraction of the non-180° domain, \( I_{002} \) indicates the integrated intensity of the (002) peak and \( I_{200} \) indicates the integrated intensity of the (002) peak. The change of the volume fraction is given as the difference between the poled domain state and the partially-depoled domain state. The relationship between the macroscopic strain memory and the non-180° domain volume fraction is shown in Fig. 6. The obtained macroscopic strain memory was proportional to the volume fraction. This result indicates that the non-180° domain reorientation is the origin of the strain memory effect.

In the microscopic and theoretical view, the strain memory is given as the lattice distortion of the unit cell. With the tetragonal system, it is given as \( c/a - 1 \), where \( c \) and \( a \) are the lattice constant of the \( a \) and the \( c \) axes, respectively. Thus, the maximum strain memory can be given as \( c/a - 1 \). For one stable state, the polar axis is along the \( z \)-axis, and for the other stable state, the polar axis is perpendicular to the \( z \)-axis. In actual ceramics, the strain memory is restricted for some reasons. One reason is they are not single crystals, but ceramics. Ceramics are composed of many grains with grain boundaries. Grain boundaries restrict the domain wall motion and alignment of the polarization. Another reason is that not all the domains align parallel to the \( z \)-axis or perpendicular to the \( z \)-axis. The maximum fraction change of the non-180° domain was only 14%, as shown in Fig. 6.

Here, the maximum strain memory can be simply calculated from lattice constants as

\[ \left( \frac{c}{a} - 1 \right) \times 0.14 \% \],

where the first term indicates the maximum strain memory under identical conditions and the second term is the fraction of the reoriented non-180° domains. The calculated value was 0.14% and the measured macroscopic strain was 0.13%. Although these are of the same order, some differences exist. The difference comes from the simple calculation. In actual ceramics, the domains are constrained by neighbor domains, especially when non-180° domain switching occurs [12]. The constrained domains might be strained to make the strain smaller so as to reduce the internal stress. Another reason might be that XRD measurements provide only surface data. The surface domains are not stressed compared to the internal domains. This causes extra information on the domain reorientation, which leads to an extra expectation of a strain memory.

V. CONCLUSION

In this paper we proposed a strain memory effect in ferroelectric ceramics based on non-180° domain reorientation. The strain memory effect was demonstrated by
using electric fields with asymmetric amplitudes. The ferroelectric ceramics showed the strain memory effect under electrical field with a particular range of asymmetric amplitudes. XRD analysis showed the origin of the strain memory effect to be the unrecoverable non-180° domain reorientation.

This method can be applied to a wide range of ferroelectrics with non-180° domains and to lead-free materials. A novel piezoelectric actuator, which can keep its displacement without any operating voltages, was fabricated using this method. For practical application, a study on the retention, the fatigue, the stress effect and so on are ongoing.

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REFERENCES