DC Bias Effects on Piezoelectric Constants of Rhombohedral Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_3$–PbTiO$_3$ Single Crystals

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DC bias effects on piezoelectric constants of rhombohedral Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_3$–PbTiO$_3$ (PZN–PT) single crystals were characterized using optical measurements. Piezoelectric constants decreased with increasing DC bias due to a decrease in the dielectric constant. The 0.92Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ single crystal, which approximates morphotropic phase boundary (MPB) composition and may have a smaller phase transition energy barrier from rhombohedral to tetragonal, showed a bigger change in piezoelectric constant than the pure PZN and 0.955PZN–0.045PT single crystal, which are far from MPB composition. The different behavior in the piezoelectric constant under DC bias for the composition implies a different domain orientation energy from (111) to (001) or (011) directions.© 2010 The Japan Society of Applied Physics

1. Introduction

Relaxor ferroelectric single crystals such as Pb(Zn$_{1/3}$Nb$_{2/3}$)$_3$O$_3$–PbTiO$_3$ (PZN–PT) and Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$–PbTiO$_3$ (PMN–PT) approximating a morphotropic phase boundary (MPB) composition have been studied for their high electromechanical coupling factors, piezoelectric constant, electro-optical properties and acousto-optical properties.1–15 Especially, when rhombohedral single crystals are oriented along a direction different from the spontaneous polarization, giant strain with slight hysteresis were obtained in an electric field. This large strain was attributed to phase transition in the electric field.1–7

Though the piezoelectric constant is the differential of the slope of strain vs electric field, meaning that the piezoelectric constant can be measured with an applied electric field of small amplitude, the strain was measured with a large applied electric field and piezoelectric constants were calculated from the average slope of strain vs electric field.1–4 Technically, it is quite difficult to measure the differential of the slope of strain vs electric field under the large electric field using the usual $d_{33}$ meters. Meanwhile, that optical measurement method can not only detect small movements precisely, but it can also separate the electrics from the mechanical movement allowing DC bias to be applied to the samples.5–8

In this article, a small AC signal was applied under DC bias to rhombohedral PZN–PT single crystals and their piezoelectric constants were measured using the optical method. Using the experimental results, we will discuss the domain rotation behavior in the rhombohedral PZN–PT single crystals oriented along the different directions.

2. Experimental Procedure

The PZN–PT single crystals used in this investigation were grown using the flux method and oriented along the pseudo-cubic (001), (011), and (111) directions by with a Laue camera.1–4 Typical specimen dimensions were $2 \times 2 \times 2$ mm$^3$. Au was sputtered for the electrodes. Rhombohedral PZN, 0.955PZN–0.045PT, and 0.92PZN–0.08PT single crystals were poled at room temperature and tetragonal PMN–10PT single crystals were poled at a temperature approximately 50°C higher than the ferroelectric–paraelectric phase transition and then slowly cooled to room temperature under a field. The piezoelectric coefficients $d_{33}$, $d_{31}$, and $d_{32}$ of the single crystal specimens were measured using a Michelson interferometer in Fig. 1.6,17

Michelson interferometer is composed with one beam reflected by a mirror and the other beam reflected by the testing sample. We fixed the backside of the crystal on a solid substrate and the other side was attached with a tiny mirror to reflect the beam. In this experiment, we measured the $d_{33}$, $d_{31}$, and $d_{32}$ by attaching the mirror on the proper plane of single crystal separately. While applying the 1 kHz 4 V$_{p-p}$ AC signal with DC bias to the single crystals, the optical path length change from AC signal was detected with the Lock-in amplifier and the piezoelectric constants were calculated from the optical path length change. Here, it should be noted that 4 V$_{p-p}$ AC is small enough to induce a linear dimensional change. The DC bias was applied up to 10 kV/cm.

3. Results and Discussions

Figure 2 is a schematic of the domain configuration of a crystal. The phase of pure PZN, 0.955PZN–0.045PT, and 0.92PZN–0.08PT single crystals have the rhombohedral
and their spontaneous polarizations were along the (111) direction. When rhombohedral single crystals were oriented along the (111) direction, i.e., the direction of the spontaneous polarization, the piezoelectric constants $d_{33}$ were around 80–95 pC/N and were not changed by DC bias. However, when the rhombohedral single crystals were oriented along the (001) and (110) directions, single crystals have an engineered multi-domain structure and piezoelectric constants of $d_{33}$, $d_{31}$, and $d_{32}$ were decreased by DC bias. For the easiness, we presented the Table I to define the subscript of 1, 2, 3 in the single crystals oriented along the different directions. Figures 3–5 shows the piezoelectric constants of pure PZN, 0.955PZN–0.045PT, and 0.92PZN–0.08PT single crystals according to DC bias.

In fact, the piezoelectric constant ($d$) is the differential slope of strain vs electric field or electrical displacement vs stress. This means that $d$ should be obtained from the linear relation. However, for real applications, strain is usually measured with a large electric field and $d$ is calculated from the average slope of strain vs electric field. From previous results, when the electric field is applied continuously, (001) oriented rhombohedral single crystals showed a linear relationship between strain and electric field without the slope change. However, in our experiment, DC bias was applied in addition to a small electric field to measure $d$ under the DC bias. Figures 3–5 shows that as the DC bias increased, $d$ of (001) oriented rhombohedral single crystals were decreased gradually. This change in $d$ with DC bias means that the differential of the slopes of strain vs electric field decreased with DC bias. When we calculate the percent change in the $d$ from 0 to 10 kV/cm, the composition approximating MPB showed a large change. Pure PZT, 0.955PZN–0.045PT, and 0.92PZN–0.08PT single crystals showed 13, 18, and 28% changes, respectively. It is believed that the change in $d$ with DC bias may be related to the domain rotation and phase transition. When an electric field was applied along the (001) direction for the rhombohedral single crystals, domains along the spontaneous (111) directions rotated and arranged along the (001) direction resulting in a phase transition from a rhombohedral to a tetragonal phase. The larger change in piezoelectric constant of 0.92PZN–0.08PT may be related to the ease of phase transition. As the 0.92PZN–0.08PT approximates MPB, where various phases coexist, a rhombohedral phase could easily be transformed into a tetragonal phase.

The piezoelectric effect of ferroelectrics with centrosymmetric paraelectric phase may be considered as the electrostrictive effect biased by the spontaneous polarization and $d$ can be written as

$$d = 2\varepsilon_0 K^T Q$$

where $\varepsilon_0$ is the permittivity of vacuum ($= 8.854 \times 10^{-12}$ F/m), $K^T$ is the dielectric constant, $P$ is the spontaneous polarization, and $Q$ is the electrostrictive coefficient in the cubic phase. When the electric field is applied along the (001) direction, the domain along the (111) direction would arrange along the (001) direction and polarization along the (001) direction would increase. Nevertheless, as $Q$ is the fundamental property and does not change with the electric field, decrease of $d$ with DC bias may result from the decrease of dielectric constant with DC bias.
Similarly, for the $h_011$ oriented rhombohedral single crystals, the 0.92PZN–0.08PT single crystal showed a larger change in $d$ than pure PZN and 0.955PZN–0.045PT single crystals with DC bias. However, different from the $h_001$ direction, $d$ of 0.955PZN–0.045PT single crystals oriented along the $h_011$ direction did not change much up to around 5 kV/cm and changed gradually with higher DC bias. This result reveals that domain rotation behavior between $h_111$ and $h_011$ might be quite different from that between $h_001$ and $h_011$. No much change in piezoelectric constant under DC bias up to 5 kV/cm indicated that there might be an energy barrier for the domain to be rotated from (111) to (011) direction. Meanwhile, (011) oriented 0.92PZN–0.08PT single crystal showed gradual decrease of $d$ with DC bias. Similar to the (001) oriented single crystal, as a 0.92PZN–0.08PT single crystal approximates MPB, the energy barrier for the domain rotation between (111) and (011) direction might be quite small.

4. Conclusions

The piezoelectric constant $d_{33}$, $d_{31}$, and $d_{32}$ of rhombohedral PZN–PT single crystals were measured under DC bias. Increasing DC bias was associated with a decrease in piezoelectric constant ($d$). The 0.92PZN–0.08PT single crystal, which approximates MPB, showed a larger decrease in $d$ with DC bias than pure PZN and 0.955PZN–0.045PT single crystals. The larger change in 0.92PZN–0.08PT single crystals with DC bias can be explained by lower energy barrier for domain rotation from the $h_111$ to (001) or (011) direction. In addition, a continuous decrease in $d$ with DC bias may be related to the gradual domain rotation and phase transition from rhombohedral to tetragonal. The difference in the change of piezoelectric constant with DC bias between (001) and (011) oriented rhombohedral single crystals might be related to the different phase transition to tetragonal and orthorhombic phase. Changes in $d$ with DC bias might be mainly related with the decrease in dielectric constant with DC bias.

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