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Electric Field-Induced Phase Transition Behavior in Tetragonal $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ Single Crystals

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ABSTRACT

Electric field-induced phase transition from the tetragonal to rhombohedral phase was investigated for the <111> direction in tetragonal PZN-PT single crystals, which have spontaneous polarization along the <001> direction. From the strain and dielectric data, it was confirmed that the samples followed a tetragonal-orthorhombic-rhombohedral phase transition sequence with application of an electric field. This transition is different from the rhombohedral-tetragonal phase transition of <001> rhombohedral composition single crystals, in which a phase transition occurred without showing the intermediate orthorhombic phase.

Key words : Phase transition, Tetragonal, Ferroelectric, Single crystal

1. Introduction

The large electromechanical responses observed in relaxor ferroelectric perovskite materials near the Morphotropic Phase Boundary (MPB) between the ferroelectric rhombohedral and tetragonal phases have been the topic of numerous investigations over many decades.[1,2] The origin of the high electromechanical behavior has been attributed to an electrically induced rhombohedral to tetragonal phase transformation.[3-5] Recently, Noheda *et al.* reported ferroelectric monoclinic phase of $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) over a very narrow composition range near the MPB.[6,7] It was suggested that the "bridging" effect of the monoclinic phase between the tetragonal <001> and rhombohedral <111> polarization directions is responsible for the enhanced electromechanical properties in PZT near the MPB. In addition, in the compositions of $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) near the MPB, experimental evidence also shows the presence of a ferroelectric orthorhombic phase at compositions intermediate between rhombohedral and tetragonal phases.[8-10]

While most studies have focused on rhombohedral composition single crystals with engineering domain configurations,[3-5] which show high electromechanical properties, there have been few reports on material properties of tetragonal single crystals with engineering domain configurations such as <011> or <111> directions.[11] For optical applications, in order to obtain high transparency, most studies have focused on the <001> direction rather than engineering domain configurations.[12-15] Both from a fundamental science point of view and for electromechanical applications, it is worthwhile to shed light on the difference in the phase transition behavior between rhombohedral and tetragonal composition single crystals with engineering domain configurations. In this article, we discuss the phase transition behaviors in tetragonal (1-x)PZN-xPT (x=0.10, 0.12) single crystals with engineering domain configurations and compare them with the behaviors of rhombohedral composition single crystals.

2. Experimental Procedure

PZN-PT single crystals were grown by the flux method.[3,4,16,17] The crystals were orientated along the pseudo-cubic <001>, <110>, and <111> directions using a Laue camera. The typical sample size was 2×2 mm^2 in area and 0.5~1.0 mm in thickness. Pt-sputtered electrodes were used for electrical characterization. Tetragonal PZN-PT single crystals were poled with a 5 kV/cm electric field at a temperature of 50°C above the ferroelectric-paraelectric phase transition and then slowly cooled to room temperature under the electric field. The dielectric property as a function of temperature was measured at 1 kHz using an HP multi-frequency LCR meter (HP 4284A) equipped with a temperature chamber. A unipolar electric field was applied on the samples at 0.1 Hz, using a Trek 609C-6 high voltage dc amplifier. During testing the samples were submerged in Flourinert (FC-40, 3M), an insulating liquid, so as to prevent arcing.

3. Results and Discussion

It is known that ferroelectric single crystals exhibit ultrahigh strain when their spontaneous polarization directions

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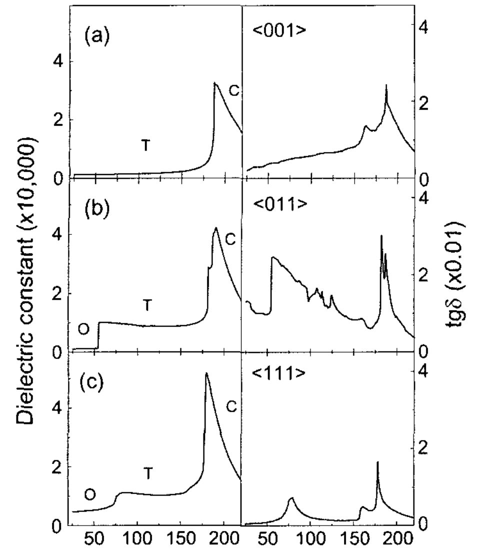

Fig. 1. Dielectric data of 0.90PZN-0.10PT measured along different crystal orientations: (a) <001> direction, (b) <011> direction, and (c) <111> direction. T, C, and O are for Tetragonal, Cubic, and Orthorhombic phase, respectively (after Ref. 10).

are different from the crystal orientation directions.[3,4] This ultrahigh strain can be explained by the E-field induced phase transition, which is possible with the engineering domain configuration. For example, when rhombohedral crystals (pure PZN, 0.954PZN-0.45PT, 0.92PZN-0.8PT), which have spontaneous polarization along the <111> direction, are oriented along the <001> direction, ultrahigh strain is induced from the rhombohedral-tetragonal phase transition. On the contrary, it has yet to be identified how a phase transition is induced with an electric field when tetragonal (1-x)PZN-xPT (x=0.10, 0.12) single crystals, which have spontaneous polarization along the <001> direction, are oriented along the <111> direction, the spontaneous polarization direction of rhomboheral phase.

Fig. 1 is the dielectric data acquired from single crystals of 0.90PZN-0.10PT oriented and poled along three crystallography directions: <001>, <011>, and <111>, respectively. From previous dielectric and optic data, 0.90PZN-0.10PT single crystals poled along <001> direction have a single domain, exist in the tetragonal phase at room temperature, and transition to the cubic paraelectric phase at 185°C. For 0.90PZN-0.10PT single crystals poled along <011> direction, a poling electric field induces a phase transition from the tetragonal to the orthorhombic phase and an orthorhombic single domain was confirmed via optical microscopy at room temperature.[10] As the temperature increases, orthorhombic-tetragonal and tetragonal-cubic phase transitions occur at 55°C and 188°C, respectively. For <111> oriented 0.90PZN-0.10PT crystals, optic observation reveals no sign of a single domain state and the dielectric data display two transitions at 78°C and 188°C. The phase transition at 188°C is from tetragonal to cubic while observations at 78°C imply that the room temperature phase is neither tetragonal nor rhombohedral phase but trapped orthorhombic phase.[10]

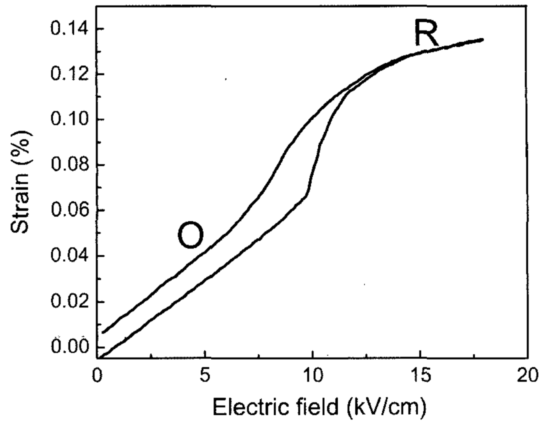

Fig. 2. Unipolar strain curve of 0.90PZN-0.10PT single crystals poled along the <111> direction.

In order to investigate the electric field-induced phase transition behavior, we first measured the unipolar strains of 0.90PZN-0.10PT crystals as a function of an electric field. While strain increases linearly without slope change (piezoelectric constant) with an electric field for the single phase, there should be a distinctive slope change for the phase transition. As is known, samples poled <001> and <011> directions already have a single domain state and hence strain increases with an electric field linearly without a phase transition. However, in Fig. 2, the single crystals poled in the <111> direction show a slope change, which reflects the phase transitions at a higher field. Given that the single crystals poled along the <111> direction have a trapped orthorhombic phase after the poling process (see Fig. 1(c)), this slope change indicates that there is a phase transition from orthorhombic to rhombohedral with the electric field along the <111> direction. From both the dielectric data in Fig. 1(c) and unipolar data in Fig. 2, it was confirmed that a tetragonal 0.90PZN-0.10PT single crystal poled along the <111> direction follows a "tetragonal-orthorhombic-rhombohedral" phase transition sequence.

However, as the poling electric field already induced the orthorhombic phase in 0.90PZN-0.10PT single crystals poled along the <011> and <111> directions, it is difficult to study the phase transition behavior from tetragonal to orthorhombic or rhombohedral phase. Here, 0.88PZN-0.12PT single crystals were employed for the phase transition measurement with an electric field. Contrary to 0.90PZN-0.10PT single crystals, as 0.88PZN-0.12PT composition is far from the MPB, all <001>, <011>, and <111> 0.88PZN-0.12PT single crystals hold stable tetragonal phases without a phase transition even after the poling process.

Fig. 3 shows the unipolar strain for single crystals poled along the <111> direction. Strain increases linearly up to

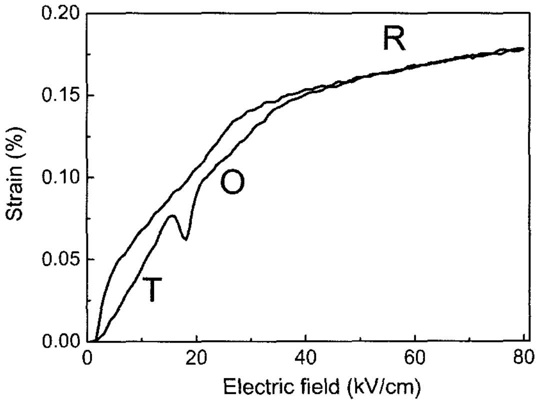

Fig. 3. Unipolar strain curves of 0.88PZN-0.12PT single crystals poled along the <111> direction.

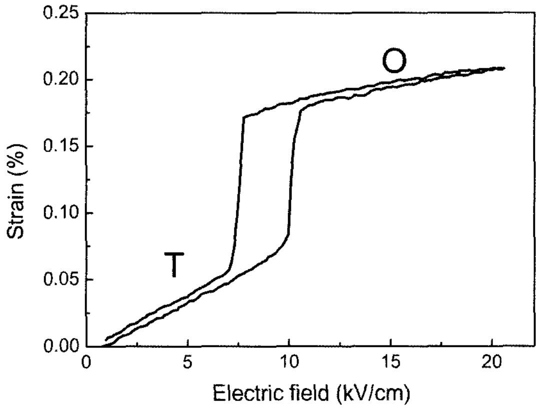

Fig. 4. Unipolar strain curves of 0.88PZN-0.12PT single crystals poled along the <011> direction.

roughly 18 kV/cm and, interestingly, suddenly drops and shows a bump. With further increase of the electric field, the strain shows a slope change near 38 kV/cm and increases linearly up to 80 kV/cm. If we consider the tetragonal-orthorhombic-rhombohedral phase transition sequence in the <111> poled sample, it can be hypothesized that the bump is related with the orthorhombic phase. To understand the phase transition behavior from the tetragonal to the orthorhombic phases, the unipolar strain was measured for a <011> poled sample, as shown in Fig. 4. The <011> poled sample reveals a slope change, which is typical phase transition behavior, and does not show any bump during the phase transition from the tetragonal to the orthorhombic phase. This different phase transition behavior between the <011> and <111> poled samples indicates that even though the induced phases are same, the samples may follow different phase transition pathways depending on the poling directions.

In the <001> poled rhombohedral single crystals, which have spontaneous polarization along the <111> directions, theoretical and experimental data have shown that polarization rotation can follow the "d" pathway under an electric field (see Fig. 5).[3-7,19] However, in the <111> poled tetragonal single crystals, which have spontaneous polarization along the <001> directions, experimental results show that polarization rotation does not follow the "d" pathway but induces a stable orthorhombic phase between the tetragonal and the rhombohedral phase. In addition, it should be noted that the <111> poled tetragonal single crystals did not follow the "a" pathway, which the <011> poled tetragonal single crystals followed to induce the orthorhombic phase. From these observations, we anticipate that the <001> polarization rotates toward the <111> direction and at a certain electric field changes to the <011> direction to induce the orthorhombic phase ("b" pathway), and finally follows the "c" pathway.

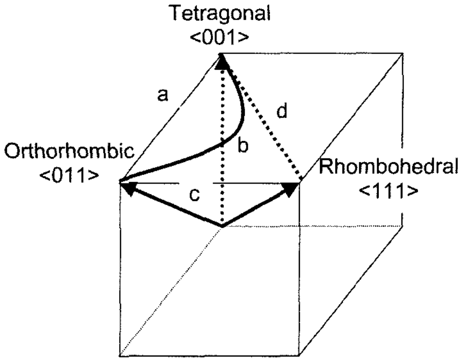

Fig. 5. Schematic domain configuration of single crystal.

4. Conclusions

In summary, tetragonal PZN-PT single crystals poled along the <111> direction show an intermediate orthorhombic phase during transformation from tetragonal to rhombohedral phase under an electric field. Strain measurement with an electric field revealed that there exists orthorhombic phase during the phase transition from tetragonal to rhombohedral phase. This phase transition sequence is different from the phase transition from rhombohedral to tetragonal phase, which showed no intermediate orthorhombic phase during the transition.

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