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DOMAIN OBSERVATION IN $Pb(In_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ SOLID SOLUTIONS NEAR MORPHOTROPIC PHASE BOUNDARY BY POLARIZING MICROSCOPE

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Domain observation in $0.72Pb(In_{1/2}Nb_{1/2})O_3$-$0.28PbTiO_3$[0.72PIN-0.28PT] mixed crystal near a morphotropic phase boundary was investigated by a polarized light microscopy under various dc-electric fields and temperatures. Both the change in domain structures in the (001) plate of 0.72PIN-0.28PT with the phase transition from rhombohedral to tetragonal induced by applying the dc-field along the <010> direction at about 6kV/cm to 12kV/cm and the change in domain structures, reflecting the successive rhombohedral-tetragonal-cubic phase transition with heating were observed.
Key words; PIN-PT mixed crystal, morphotropic phase boundary, engineered domain, domain observation, polarizing microscope

1.INTRODUCTION

Much attention has been given to relaxor-based ferroelectric solid solution single crystals near a morphotropic phase boundary (MPB) for applications because of their superior piezoelectric properties compared to ceramics.[1-4] Recently it has been reported both experimentally[5,6] and theoretically[7] that a giant piezoelectric response may be due to the polarization rotation associated with the electric field-induced phase transition from rhombohedral (R) to tetragonal (T) near the MPB composition. The enhanced electromechanical properties under engineered domain configurations near the MPB region was proposed by Ishibashi and Iwata[8] to be induced by the instability perpendicular to the spontaneous polarization, named transverse instability. It is important to investigate the stability range of the R and T phase in the relaxor –PT solid solution system near the MPB under various conditions in order to improve piezoelectric properties. We reported previously on the dielectric and piezoelectric properties of the lead indium niobate-lead titanate, $(1\text{-}x)Pb(In_{1/2}Nb_{1/2})O_3$-$xPbTiO_3$[PIN-PT] single crystals with high Curie temperature T_c near a MPB[9,10]. In this work, the domain observation in PIN-PT mixed crystal near a MPB was investigated by a polarized light microscopy under various electric fields and temperatures. The effect of dc electric field on the domain configurations, and the change in domain structures, reflecting the successive rhombohedral-tetragonal-cubic phase transition with heating, on the (001) plate of 0.72PIN-0.28PT single crystal near a MPB were presented.

2.EXPERIMENTAL

Single crystals of the (1-x)PIN-xPT system near the MPB were obtained by a conventional flux method using PbO-PbF_2-B_2O_3 flux.[9,10]. The Ti concentration x of the solid solution (1-x)PIN-xPT obtained was determined using a fluorescent X-ray technique. For the domain-wall observation, the two samples with the thin thickness of the 0.72PIN-0.28PT were prepared because of the complexity of domain structure in relaxor-PT solid solution system near the MPB. One with the thickness of 30 μm (#1) is used for the study of the effect of dc-bias field on the domain structures. The other with the thickness of 32 μm (#2) is used for the effect of temperature on domain structures. The orientation of the crystal axis was determined by a X-ray diffractometer. The plate-like samples were cut out and polished with a polishing sheet (0.3 μm size). The domain structures were analyzed by means of polarizing light microscopy (Olympus BX60). To investigate the effect of an electric field on the domain configuration, the samples were evaporated on the both surfaces with semitransparent gold layers. A heating/cooling stage (Japan High Tech LK-600) mounted on the microscope was used for observing the change in the domain structures with both dc-electric fields and temperatures. Gold leads were attached to the sample with silver paste (Dupont No.4922).

3. RESULTS AND DISCUSSIONS

Figure 1 shows the X-ray powder diffraction (XRD) patterns on the ground samples of solid solution (1-x)PIN-xPT single crystals at room temperature, and indicate that the sample is a single perovskite phase. The inset (a) in Fig.1 shows the splitting in the (332) reflection of the XRD pattern in accordance with the rhombohedral (R) cell. The inset (b) in Fig.1 shows the change in the (200) reflection of XRD patterns with PT contents x. It is found from the inset (b) that the structure-sensitive maximum is a peak at $2\theta = 45^\circ$ at x <0.37, in accordance with the R, and is split at x>0.38, in accordance with the tetragonal (T) cell.

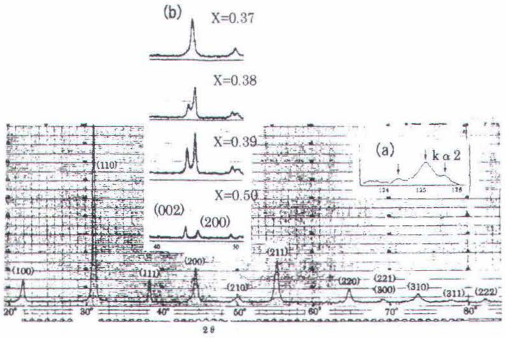

Fig.1 XRD pattern of (1-x)PIN-xPT for x=0.28 at room temperature. The inset (a) shows the splitting in (332) reflection in accordance with R cell. The inset (b) shows the change in (200) reflection with x=0.37,0.38,0.39 and 0.5.

According to the principle of optical crystallography and crystal symmetry,[11] the domain structures of PIN-PT single crystals near a MPB were analyzed by means of polarizing microscopy. The polar R phase has the spontaneous polarization and the optical axis along the <111> directions, while the T phase has the spontaneous polarization and the optical axis along the <001> directions. The cross-section of the optical indicatrix exhibits extinction directions parallel to <110> directions for the R domains, while the T phase shows extinctions parallel to <100> directions on (001) planes. Figure 2 shows the domain structures of a (001) 0.72PIN-0.28PT plate sample(#1) in the R phase under various dc-electric fields applied along the <010> direction. Figure 2(a) shows the domain structure of a (001) 0.72PIN-0.28PT plate at a electric field E=0 kV/cm. According to the detailed analysis of the orientation states, straight and broad domain strips were observed along the $(\bar{1}10)$ planes and inside that planes, fine domains along the (010) planes were observed. These fine domain structure didn't change for various strength of electric fields below 4kV/cm as shown in Figs.2(a) and (b). The orientation states for these domain structures indicates the engineered domain. At about 6kV/cm, straight and broad domain strips along the $(\bar{1}10)$ planes start to change abruptly at the $(\bar{1}10)$ plane, and then a new phase appeared. New phase has the fine domains with the domain wall inclined at 45° to the fine domain along the (010) planes in the R phase. A new phase was distinguished to be tetragonal according to its extinction behavior on the (001) plate. Electric field induced phase transition from the R to the T phases begins to take place at about 6kV/cm as shown in Fig.2(c). The phase boundary between the R and T along the $(\bar{1}10)$ plane forwarded to the R region at the expense of the R region as shown in Figs.2 (d) at 8kV/cm and (e) at 12kV/cm. Both the R and T phases coexist in the wide applied electric field range from 6kV/cm to 12kV/cm. Such electric field induced phase transition from the R to the T one was found to be very diffuse. With further increasing dc-field, the domain wall density in the T phase decreases as shown in Fig.2(f). Such decrease in domain wall density with electric field in T phase shows a remarkable contrast to the behavior of domain structure with electric fields in the R phase mentioned above. These reveal the engineered domain behavior with field applied along the <010> direction in the R phase contrast to the domain behavior with field applied along the polar <010> direction in the T phase. The whole crystal is in the T phase as shown in Fig.2(f).

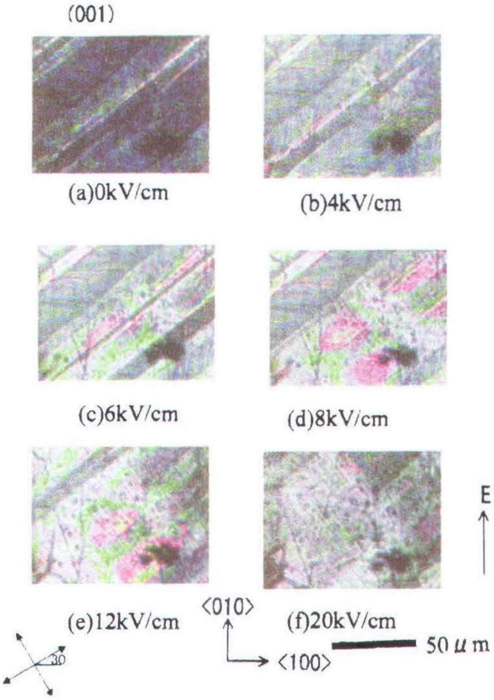

Fig.2 Domain structures in the (001) plate of 0.72PIN-0.28PT under various dc-electric fields applied along the <010> direction at room temperature.

Once the R phase transforms into the T phase with electric fields, the T phase remains solely after the applied field was withdrawn. After that, the electric field applied along the <010> direction to the (001) 0.72PIN-0.28PT plate (#1) was alternated to the <0$\bar{1}$0> direction. The polarization reversal in the T phase takes place as shown in Fig.3. Figure 3 (a) shows the straight and broad domain strips with domain walls along the {110} planes at 0kV/cm in the T phase. At about 4kV/cm, corresponding to the coercive field for P-E hysteresis loops, the polarization reversal begins to take place as shown in Fig.3(b),with moving the T stripe and broad domains with domain walls aligning along (1$\bar{1}$0) planes. With increasing field, these domain walls move along (1$\bar{1}$0) planes across the crystal, and its domain wall density decrease as shown in Figs.3(c),(d) and (e). With further increasing dc-fields, inside that planes, fine domain wall density along the (110) planes decreases and tend to vanish as shown in Fig.3(f).

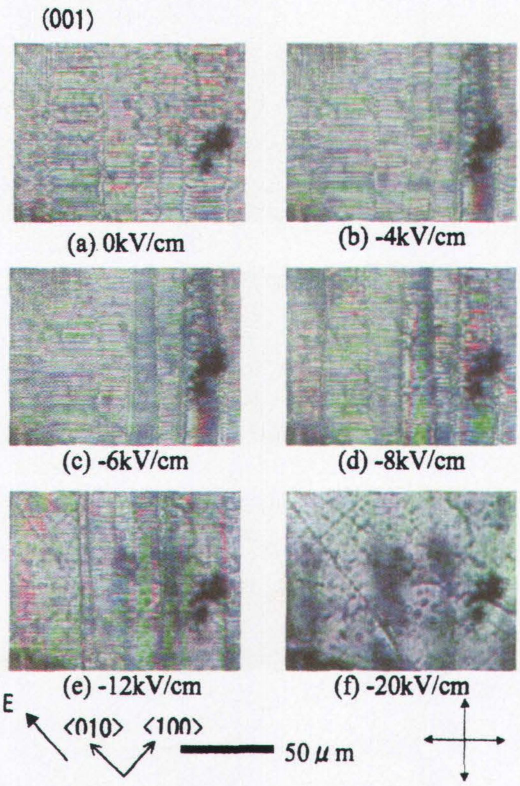

Fig.3 Domain structures with polarization reversal in the (001) plate of 0.72PIN-0.28PT under various dc-electric fields applied along the <010> direction at room temperature.

Figure 4 shows the domain structures and phase transformations of a (001) plate sample (#2) of the 0.72PIN-0.28PT single crystal under various temperatures. Domain structures are very complex. The ellipses in Fig.4(b) show the ellipsoid of the refraction index for two kinds of domains. One domain pattern (see the domain with the ellipse denoted as ① in Fig.4(b)), that is, the R domain having diagonal position parallel to the <100> direction, shows brightness and interference color when observed with crossed polarizers parallel to <100>. The other domain pattern (see the domain with ellipse denoted as ② in Fig.4(b), that is, the T domain characterized with the extinction position parallel to <100> direction, and shows darkness. The two phases are actually intimately mixed with each other. With heating, first, the T phase grows at the expense of the R one as shown in Figs. 4(a), (b) and (c), and the R phase transforms into the T one. The whole crystal is in the T phase with striped domains with domain walls aligning along the ($\bar{1}$10) planes at temperatures larger than 125℃. With further heating, the T phase changes to the cubic one with the growth of the isotropic regions denoted as the wedge type dark areas as shown in Fig.4(e). At 300℃, the whole crystal is in the cubic phase as shown in Fig.4(f). Consequently the T phase exists partly even at room temperature.

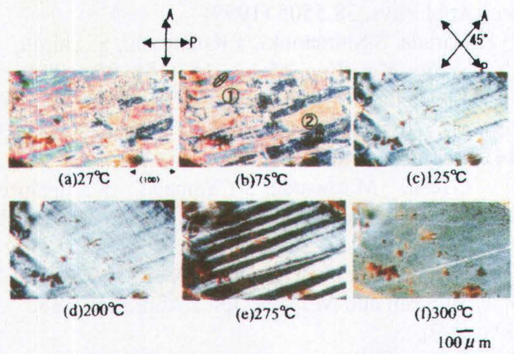

Fig.4 Domain structures in the (001) plate of 0.72PIN-0.28PT under various temperatures.

The morphotropic phase boundary of PIN-PT system is characterized with such coexistence of both the R and T phase in the wide temperature range.

4.SUMMARY

The change in domain structures in the (001) plate of 0.72PIN-0.28PT with the phase transition from R phase to T one induced by applying the dc- field along the <010> direction at about 6kV/cm to 12kV/cm was observed. Furthermore, the change in domain structures, reflecting the successive rhombohedral-tetragonal-cubic phase transition with heating was observed. The 0.72PIN-0.28PT single crystal near a MPB exhibits complex domain structures, which consist of both the R and the T phase intimately mixed together. Such phenomena was reported previously for relaxor –PT solid solution system, such as PMN-PT[11,12] and PZN-PT[13,14] system. The phase transition from the R phase to T one with dc-fields and temperatures in the PIN-PT system near a MPB composition was found to be induced easily and very diffuse. This may be related to the high electromechanical coupling coefficient and its excellent temperature characteristics in the PIN-PT single crystals near a MPB composition. More detailed study for the observation of the change in the domain structures with electric field applied along different crystallographic directions in order to improve piezoelectric properties in PIN-PT system near a MPB composition is now in progresss.

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