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Third ferroelectric phase in PMNT single crystals near the morphotropic phase boundary composition

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In the principle of optical crystallography and crystal symmetry, it is found that at room temperature, the 0.67 PMN-0.33 PT crystals near the morphotropic phase boundary composition present not only a rhombohedral $3m$ phase but also a monoclinic m phase with various angles of polarization rotation, the third ferroelectric phase in the PMN-PT solid solution system. The polarization rotation readily driven by composition suggests that it can be easily induced by electric field as well, thereby providing the structure base of the ultrahigh piezoelectric performance of 0.67 PMN-0.33 PT single crystals.

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It is well known that the morphotropic phase boundary (MPB) is very important in piezoelectric materials, ceramics or single crystals, with the pseudobinary or-ternary systems, such as $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$(PMNT), $(1-y)Pb(Zn_{1/3}Nb_{2/3})O_3$-$yPbTiO_3$(PZNT), $PbZrO_3$-$PbTiO_3$(PZT), $PbZrO_3$-$Pb(B_1B_2)O_3$-$PbTiO_3$, and $Pb(Sc_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$. In these materials, anomalously large dielectric and piezoelectric properties were observed for the compositions lying near their MPB. Recently, an ultrahigh piezoelectric response and a giant field-induced strain, about ten times higher than that available from conventional ceramics, have been achieved on the domain-engineered $(001)_{cub}$ cuts of PZNT and PMNT single crystals near their MPB compositions (see Refs. 1–8). Their electromechanical coupling factor k_{33} can reach up to 94% and their piezoelectric constant $d_{33} > 2500$ pC/N, which may revolutionize some applications in medical ultrasonic imaging, telecommunication, and ultrasonic devices. It is worthwhile to reveal the reason that they can exhibit such an excellent piezoelectric performance. Park *et al.*,[3] Liu *et al.*,[9] Paik *et al.*,[10] and Fu *et al.*[2] attributed the ultrahigh strain under electric field in these single crystals to the rhombohedral-to-tetragonal phase transition or the polarization rotation induced by electric field. However, crystal structures should be made clear before this question is answered finally.

For a long time, the MPB in the phase diagram of the PMN-PT solid solution system has been regarded as the boundary dividing the rhombohedral phase and the tetragonal one (see Ref. 11). It is located at $x=0.33$ (see Ref. 12), 0.35 (see Ref. 13), or within a range of $x=0.275-0.325$ (see Ref. 14). Nevertheless, the following facts demonstrate that a monoclinic m phase, the third ferroelectric phase in 0.67 PMN-0.33 PT single crystals near their MPB composition, can appear at room temperature, as well as the rhombohedral and tetragonal phases. This discovery is very similar to the case in the PZT system. Recently, Noheda *et al.*[15] discovered the existence of the monoclinic phase, a previously unreported ferroelectric phase, in the $PbZr_{0.52}Ti_{0.48}O_3$ sample below ~250 K by high-resolution synchrotron x-ray powder diffraction measurements.

0.67PMN-0.33PT single crystals were directly obtained from their melt by using the Bridgman method. Their size has reached up to $\phi 50\times 80$ mm (see Refs. 5–8). These crystals were processed into polished thin cuts with a thickness of less than 0.2 mm after their orientations were determined by using x-ray orientation devices combined with x-ray diffraction (XRD). Their phase structures were confirmed through the observation on ferroelectric domain configurations under polarization microscopes on the principle of optical crystallography and symmetry. The dielectric properties of crystal samples were measured by YHP4192A impedance analyzers while the values of piezoelectric constant d_{33} were measured with a quasistatic d_{33} meter of Berlincourt

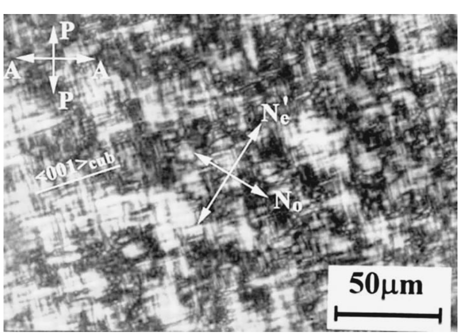

FIG. 1. The small spindlelike domains on $(001)_{cub}$ cuts in 0.67PMN-0.33PT single crystals under polarization microscopes. The orientation of optical indicatrixes illustrates that the crystals are of a rhombohedral phase.

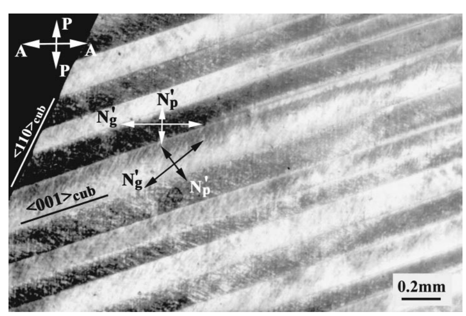

FIG. 2. The broad straight domains in 0.67PMN-0.33PT single crystals on $(001)_{cub}$ cuts under polarization microscopes. The N_g' of optical indicatrixes cross $\langle 001\rangle_{cub}$ at an angle of about 20°, illustrating that the crystals are neither of a rhombohedral phase nor of a tetragonal one.

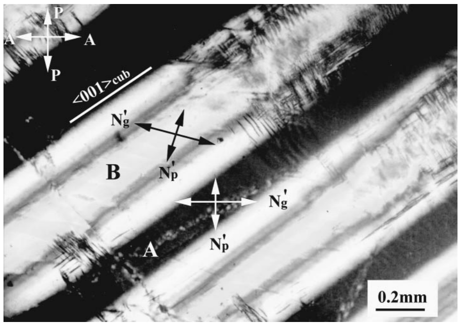

FIG. 3. The broad domains in 0.67PMN-0.33PT single crystals on $(001)_{\rm cub}$ cuts under polarization microscopes. One group of domains (A) shows the extinction position crossing $\langle 001\rangle_{\rm cub}$ at an angle of 30°, whereas the adjacent group of domains (B) exhibits the extinction along $\langle 110\rangle_{\rm cub}$.

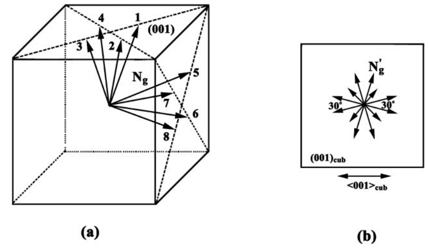

FIG. 4. The distribution of the long radii (N_g) of optical indicatrixes in the monoclinic 0.67PMN-0.33PT single crystal. The fractional space distribution is shown in (a), and the complete distribution of N_g' on $(001)_{\rm cub}$ cuts is shown in (b).

type. The thickness mode (k_t) and longitudinal bar mode (k_{33}) electromechanical coupling factors on $(001)_{\rm cub}$ cuts were calculated from resonance and antiresonance frequencies.

The orientations of optical indicatrixes on a cut, which reflect the projective directions of the polarization on this cut, can be readily determined by the extinction position of optical domains, consequently, the phase structures are checked expediently. As for the 0.67PMN-0.33PT single crystals naturally cooling down to room temperature in the Bridgman method, it was found that their domain configurations were somewhat complex due to the macrosegregation and structure fluctuation. Here the domain configurations are subdivided into two types.

The first type of domain cannot be visualized by the naked eye, but it presents small spindlelike morphology under polarization microscopes, the domain strips having wavy and blurred margin or walls along $\{110\}_{\rm cub}$ (Fig. 1), as do the domains in PZN single crystals (see Ref. 16). On $(001)_{\rm cub}$ cut, these optical domains exhibit the extinction along $\langle 110\rangle_{\rm cub}$ directions, i.e., the radius of index ellipse intersects $\langle 001\rangle_{\rm cub}$ at the angle of 45°. Obviously, they belong to the rhombohedral $3m$ phase with the spontaneous polarization along $\langle 111\rangle_{\rm cub}$. These domains are 71° or 109° macrodomains.

The second type of domain can be visualized by the naked eye, and shows as broad laminar domains with the clear and straight walls along $\{110\}_{\rm cub}$, as in the case of $PbTiO_3$ crystals. It is surprising that the radius senses of optical indicatrixes in the domain strips are inconsistent with either the rhombohedral phase or the tetragonal one. There are two cases of extinction for these optical domains on $(001)_{\rm cub}$ cuts. The first case is that in which their extinction position intersects $\langle 001\rangle_{\rm cub}$ at the variable angles of 5–35° (Fig. 2). The second case is that in which one group of domains (A domains in Fig. 3) shows the same extinction angle as the first case, whereas the adjacent group of domains (B domains in Fig. 3), which is arranged alternatively with the former group, exhibits the extinction along the $\langle 110\rangle_{\rm cub}$ directions. The radius senses of the optical indicatrixes reflected by the above extinction angles deviate largely from those in the rhombohedral or tetragonal phase. In our review, this cannot be explained by the local strain or domain superposition inside crystals. The above distribution of optical indicatrixes is found to be agreeable with that in the monoclinic m phase (Fig. 4). Therefore the 0.67PMN-0.33PT crystals with the above domains are actually of a monoclinic m phase. This new phase is the third ferroelectric phase in the PMN-PT solid solution system besides the rhombohedral and tetragonal phases. Obviously, the lattice constants of the monoclinic phase vary with compositions in a range since the extinction angles are variable.

In situ observation on domains under electric field was also carried out to verify the existence of the monoclinic phase. It was found that a single domain could form under 1.75 kV/cm for the $(111)_{\rm cub}$ cuts of rhombohedral 0.76PMN-0.24PT single crystals (see Ref. 17). However, the single domain state could not be achieved under the field of 15 kV/cm, higher than four times the coercive field for both the $(111)_{\rm cub}$ and $(001)_{\rm cub}$ cuts of the above monoclinic 0.67PMN-0.33PT crystals. The single domain should appear on $(111)_{\rm cub}$ cuts if these 0.67PMN-0.33PT crystals are rhombohedral, or it should appear on $(001)_{\rm cub}$ cuts if the crystals are tetragonal. Therefore, these crystals should belong to another phase, i.e., the monoclinic one.

Dielectric and piezoelectric measures indicated that the monoclinic 0.67PMN-0.33PT single crystals exhibited excellent properties on $(001)_{\rm cub}$ cuts: dielectric constant $\epsilon \sim 5400$, dielectric loss $\tan\delta \sim 0.6\%$, Curie point $T_c \sim 425$ K, piezoelectric constant $d_{33} \sim 2400$ pC/N, electromechanical coupling factors $k_t \sim 62\%$ and $k_{33} \sim 93\%$.

It has been observed in 0.67PMN-0.33PT crystal boules that there is a general trend from wavy narrow domains to straight broad domains, or from a rhombohedral $3m$ phase to a monoclinic m phase along the growth direction due to macroscopic segregation. The above two phases are intimately mixed up in most of the boules, implying that their free energies are very close. The appearance of the monoclinic m phase with various extinction angles suggests that there are transitional states with different angles of polarization rotation during the polarization rotation from a rhombohedral phase to a tetragonal one. The fact that the polarization rotation can be driven by the slight variation in composition can be regarded as the structure base of the polarization rotation from the rhombohedral-monoclinic-tetragonal phase induced by the electric field along $\langle 001\rangle_{\rm cub}$. It is owing to the structure feature in 0.67PMN-0.33PT crystals that they-can exhibit an ultrahigh piezoelectric response.

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