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Bridgman growth, crystallographic characterization and electrical properties of relaxor-based ferroelectric single crystal PIMNT

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ABSTRACT

According to the molar ratio of $0.25Pb(In_{1/2}Nb_{1/2})O_3$–$0.44Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.31PbTiO_3$, PIMNT polycrystalline material was prepared by using the two-step columbite precursor route. Using the polycrystalline material prepared by solid-state reaction, 55 mm in diameter PIMNT single crystals with [1 1 0] orientation had been grown successfully by the seeded vertical Bridgman process with the optimum conditions. The crystal wafers on the [0 0 1]-cut were fabricated from the crystal boules oriented by the rotating orientation XRD method. As-grown crystal exhibits a peculiar phase evolution from rhombohedral to tetragonal phase along the growth direction due to the composition segregation in the crystal growth. As for [0 0 1]-oriented wafers fabricated from rhombohedral phase region, the crystal wafers exhibit a piezoelectric coefficient d_{33} of 1500–2100 pC/N, a dielectric permittivity ε of 4600–5800 and a dielectric loss tan δ of 0.5–1%. Compare to the binary crystal PMNT, the ternary crystal wafers possess a higher phase transition temperature T_{r-t} of 100–120 °C, a higher Curie temperature T_c of 160–195 °C and a larger coercive field E_c of 4.2–5.0 kV/cm, which are favorable for the higher power ultrasonic devices with a wider working temperature range.

1. Introduction

In the past decade, a series of relaxor-based ferroelectric single crystals, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMNT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZNT), have been attracting much interest in the field of piezoelectric technique [1–8]. Although PMNT crystals possess its ultrahigh piezoelectric coefficient d_{33} of 1500–2300 pC/N and electromechanical coupling factor k_{33} above 90, the material is still not desirable in the piezoelectric devices with broader operation temperature due to its relatively low Curie temperature T_c (130–170 °C). $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PIMNT) is a novel relaxor-based ferroelectric single crystal with high Curie temperature reported in recent years [9–11]. In contrast to the binary PMNT and PZNT crystals, the ternary single crystal exhibits some superior performances, such as a higher Curie temperature T_c and phase transition temperature T_{r-t}, in addition to maintaining the excellent piezoelectric and dielectric properties. The unique properties make the material to be valuable for piezoelectric device applications such as medical ultrasonic imaging probes, sonar transducers and actuators.

In the previous works, top-seeded solution method or melt Bridgman technique were used to grow PIMNT single crystals [9–12]. However, it is difficult to grow large-size crystals with high quality from the ternary solid-solution system. The main difficulties for the crystal growth are (1) melt leakage from the crucibles because of the serious corrosion, (2) low growth yield due to the polycrystal production and (3) the performance inhomogeneity owing to the composition segregation. In recent years, a modified vertical Bridgman process was applied to grow PIMNT single crystals for ultrasonic device application in our laboratory. Some effective techniques were applied to overcome the difficulties in the crystal growth. Large-size PIMNT single crystals were grown from the melt successfully and [0 0 1]-oriented crystal wafers were fabricated from the crystal boules. The piezoelectric, dielectric and ferroelectric properties of [0 0 1]-oriented crystal wafers were characterized. This paper reports the recent results about Bridgman growth, crystallographic characterization and electrical properties of PIMNT single crystals.

2. Experimental

2.1. Feed material synthesis

The feed material for PIMNT crystal growth were synthesized from the initial reagents of PbO, Nb_2O_5, In_2O_3, TiO_2 and $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$. According to the molar ratio of $0.25Pb(In_{1/2}Nb_{1/2})O_3$–$0.44Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.31PbTiO_3$, PIMNT

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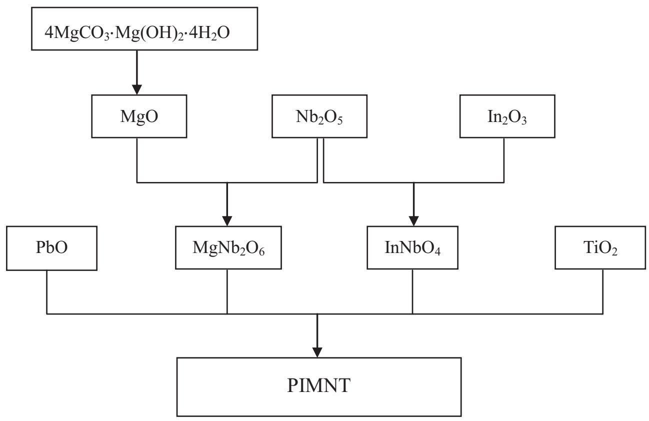

Fig. 1. Synthesis diagram of PIMNT polycrystalline material.

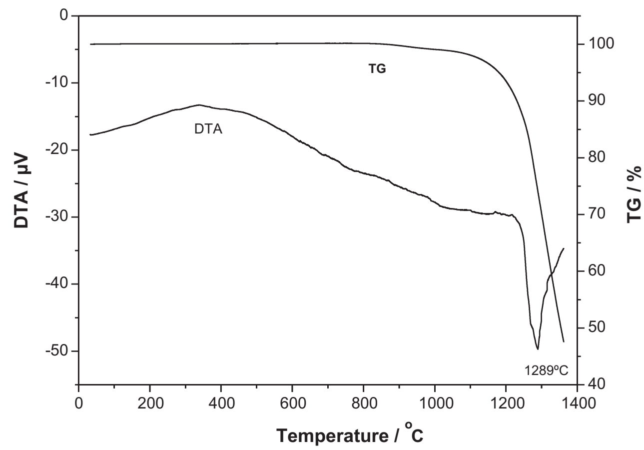

Fig. 2. DTA/TG curves of PIMNT polycrystalline material.

polycrystalline material was prepared by using the two-step columbite precursor route. The synthesis diagram of PIMNT polycrystalline material is presented in Fig. 1. Firstly, the columbite precursors $InNbO_4$ and $MgNb_2O_6$ were synthesized by sintering the mixtures of $4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$ and Nb_2O_5, In_2O_3 and Nb_2O_5 at 1100 °C for 6 h, respectively. Secondly, PIMNT polycrystalline material was synthesized by sintering the mixture of PbO, $MgNb_2O_6$, $InNbO_4$ and TiO_2 at 850 °C for 4 h. In order to compensate the volatilization of PbO in the crystal growth, an excess amount of 1–1.5 wt% PbO was added to the feed material. PIMNT polycrystalline material obtained by the described process appears to be a yellow-brown ingot without deliquescence. The polycrystalline material was verified to be the ternary solution compound PIMNT with perovskite structure by X-ray powder diffraction.

2.2. Crystal growth

PIMNT single crystal was grown by vertical Bridgman process in a resistively heated Bridgman furnace. The designed furnace chamber with three temperature zones exhibited a special temperature distribution along the axial direction. The Bridgman furnace was operated by controlling the high-temperature zone at 1350–1400 °C with an accuracy of ±0.5 °C during the crystal growth. The platinum crucibles used in the crystal growth were 55 mm in diameter and 180–220 mm in length with a seed well of 25 mm in diameter at the conical bottom to hold the seed crystal. Ø25 × 40–50 mm seed crystals with [1 1 0] axial direction were obtained from the initial crystal growth by spontaneous nucleation. After the seed crystal was put in the seed well, the feed material of 2000–2500 g was filled in the cylinder of crucibles. To decrease the volatilization of melt during the crystal growth, the assembled crucible was sealed approximately. The crucible together with the refractory tube was put into the furnace chamber.

In the seeded Bridgman growth, the seeding process in the furnace chamber under the controlled temperature was performed by adjusting the crucible to such a position that only the top region of the seed was melted. The feed material was melted with the top region of the seed for 6–7 h so that a stable solid–liquid interface can be established at an appropriate level. The temperature gradient across solid–liquid (s–l) interface was adjusted around 30–50 °C/cm. Growth process was carried out for 15–20 days continuously by lowering the crucible steadily at a rate of 0.3–0.6 mm/h. As-grown boule was annealed simultaneously in the lower zone so as to prevent the cracking resulting from thermal stress in the crystals. As the growth procedure had finished, the furnace was cooled down to room temperature and as-grown crystal boule was taken from the stripped crucible.

2.3. Characterization

PIMNT polycrystallite sample was analyzed by DTA/TG using a Perkin-Elmer Diamond thermal analyzer calibrated by Al_2O_3. 11.093 mg sample was tested in the air atmosphere with the range of 30–1365 °C at the heating and cooling rates of 10 °C/min. The crystallographic characterizations of as-grown crystals, including the crystal powder and the crystal wafer, were performed with X-ray diffractometer (Rigaku D/MAX-2400), using monochromatic Cu K_α radiation with a working voltage of 40 kV and current of 100 mA. A series of [0 0 1]-oriented crystal wafers were fabricated from as-grown crystal boule after it was oriented crystallographically by the rotating orientation XRD method.

The crystal wafers were coated both sides with silver film as electrodes and were treated at 600 °C for 2 h. The crystal wafers with electrodes were poled in silicon oil at 40–80 °C with an electric field of 10 kV/cm. The dielectric permittivity ε and dielectric loss tan δ of the crystal wafers were measured by a HP4294A impedance analyzer at frequencies of 0.1 kHz and 1 kHz controlled by a computer. The piezoelectric coefficients d_{33} of the crystal wafers were measured by a ZJ-3AN quasi-static piezo-d_{33} meter (Institute of Acoustics, CAS) at room temperature. The polarization versus electric field hysteresis loops were measured at 1 Hz by a Precision Premier II ferroelecric analyzer under the maximum electric field of 10 kV/cm and 12 kV/cm, respectively.

3. Results and discussion

3.1. Crystal growth

The first technical difficulty in PIMNT crystal growth was the melt leakage from the crucible due to the serious corrosion of the rich-lead melt at high temperature. The problem is typical for growing the lead-based ferroelectric crystals such as PMNT and PZNT as well as PIMNT. In order to avoid the melt leakage from the crucibles at high temperature, the double-shells crucibles fabricated with high purity platinum sheets were applied in the crystal growth. In addition, the feed material was presynthesized from the starting mixture prior to the crystal growth, which was confirmed to be helpful for alleviating the crucible corrosion. Another technical difficulty in PIMNT crystal growth was the polycrystal production owing to the multiple compositions in the ternary solid-solution system. It has been confirmed that the polycrystal production can be reduced significantly by the oriented growth induced with a seed crystal. In the seeded Bridgman growth, the seeding operation was performed at the seeding temperature of 1300–1310 °C, which was 10–20 °C higher than the melting point.

According to the DTA and TG curves presented in Fig. 2, the ternary solid-solution compound with the stoichiometric composition is melted congruently at the melting point of 1289 °C. By the fact that a distinct weight loss occurs above the melting point, the rich-lead melt is predicted to be volatile significantly in the crystal growth under an open atmosphere. The chemical analysis of the volatilized deposit proves that the composition PbO contained in the feed material is prone to volatile at high temperature. The assembled crucibles were sealed approximately so as to control the volatilization of melt during the crystal growth. Considering the complete enclosed system maybe bring out the melt leakage owing to the high pressure inside the crucibles, the crystal growth was performed under approximately sealed condition by remaining a tiny hole on the crucible top. It is confirmed that the limited volatilization still resulted in about 2–3 wt% mass loss corresponding to the charged feed material in the repeated experiments. To compensate the volatilization of PbO in the crystal growth, an excess amount of 1–1.5 wt% PbO was added to the feed material.

3.2. Crystal boules

By means of the process described above, large-size PIMNT single crystals with [1 1 0] orientation have been grown successfully.

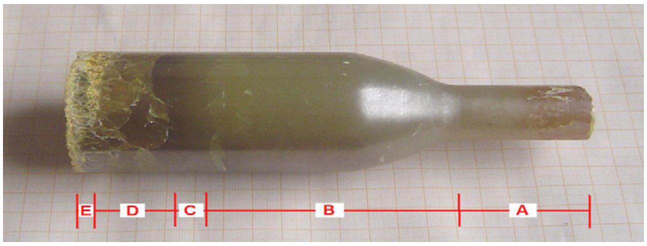

Fig. 3. PIMNT crystal boule grown by vertical Bridgman process: A, seed; B, rhombohedral region; C, mixed phase region; D, tetragonal region and E, segregation layer.

As-grown crystal boule as large as Ø55 × 100 mm is showed in Fig. 3. The grown crystal boule takes the same shape as the platinum crucible used in the crystal growth. The main part of as-grown crystal with 55 mm in diameter and 100 mm in length was grown from the seed crystal with 25 mm in diameter through the cone region in the middle zone. As illustrated in Fig. 3, the whole crystal boule consists of three sections, i.e. seed, main crystal and segregation layer. The main crystal section appears to be approximately opaque or translucent partially with olive green in color. There is a yellow aliquation layer with 3–4 mm in thickness on the boule top, which is derived from the composition segregation in the crystal growth. The region adjacent to the segregation layer is prone to cracking in the crystal growth because of the different thermal expansion coefficient between the crystal medium and the segregation layer. To eliminate the thermal stress inside the as-grown crystal, the crystal boule was annealed at 850 °C for 5–6 h. The crystal boule subjected to annealing treatment appears to be more homogeneous and lighter in color.

3.3. Crystallographic characterization

X-ray diffraction pattern of as-grown crystal illustrated in Fig. 4 proves the grown crystal to be perovskite phase without pyrochlore phase. As illustrated in Fig. 3, PIMNT single crystal boules exhibits a peculiar phase evolution from rhombohedral to tetragonal phase due to the composition segregation in the crystal growth. Based on the crystallographic characterization of the as-grown crystal boule, the main crystal section possesses the three regions, i.e. the rhombohedral region in lower zone, the tetragonal region in upper zone and the mixed phase region in the transitive zone. It is noted that X-ray diffraction patterns show a gradual splitting feature for (2 0 0) diffraction peak, which is also typical characteristic for the binary solid-solution crystals reported by other group' work as well [10,11]. Fig. 4(a) shows X-ray diffraction pattern for the sample obtained from the rhombohedral region, while Fig. 4(c) illustrates X-ray diffraction pattern for the tetragonal sample. X-ray diffraction pattern in Fig. 4(b) is attributed to the mixed phase region near morphotropic phase boundary (MPB) composition. The broader and splitting peak near $2\theta = 45^{\circ}$ indicates the phase transition inside the crystal medium evolved from the rhombohedral phase to tetragonal one.

The phase evolution from rhombohedral to tetragonal phase inside the crystal boule can also be observed by its appearance, i.e. the rhombohedral region is opaque with olive green and the tetragonal region is translucent with yellowish brown, while the mixed phase region appears to be transitive state in color and transparency. As for the crystal boules grown from the feed material mentioned above, more than two third of the main crystal section in length is attributed to the rhombohedral region and the remaining region belong to the mixed phase and the tetragonal phase. As the rhombohedral region possesses the desirable electrical properties for the piezoelectric application, we are trying to lengthen the rhombohedral region percentage in as-grown crystal boule by appropriate measurements such as adjusting the feed material compositions and improving the crystal growth conditions. Considering the composition segregation was related with the melt volatilization, the crystal growth was performed in approximately sealed crucibles so as to decrease the composition deviation throughout the growing process, which was also helpful for lengthening the rhombohedral region and decreasing the segregation layer as well.

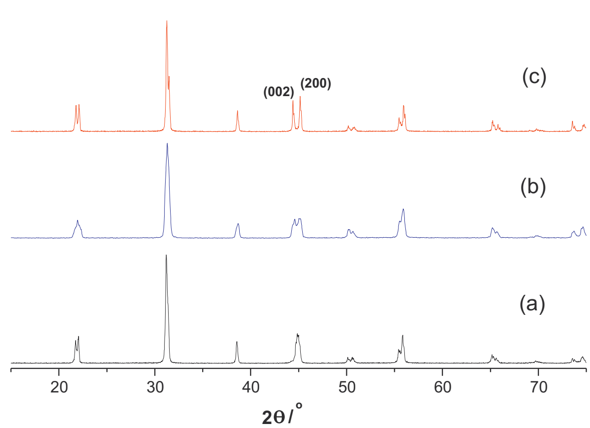

Fig. 4. X-ray powder diffraction pattern of PIMNT single crystal for the samples from (a) rhombohedral region; (b) mixed phase region; (c) tetragonal region.

3.4. Wafer fabrication

It was found that the twin-crystals or even polycrystals were prone to occur in PIMNT crystal growth, which was attributed to the multiple composition for PIN-PMN-PT ternary solid-solution system. To ensure the single crystal growth without polycrystals production, the seeded Bridgman process was applied to grow PIMNT single crystals by using [1 1 0]-oriented crystal seeds in this work. Three slices of [1 1 0]-oriented crystal wafers with 0.5 mm in thickness were obtained by the direct cutting along the cross section from bottom, middle and upper region of as-grown crystal. In order to demonstrate the mono-crystallinity of as-grown crystal, the normal X-ray scan pattern of the [1 1 0]-oriented wafers were measured on X-ray diffractometer. Based on the fact that the single diffraction peak corresponding (1 1 0) plane appears in X-ray scan pattern illustrated in Fig. 5, as-grown crystal boule can be verified to be mono-crystallized along [1 1 0] orientation.

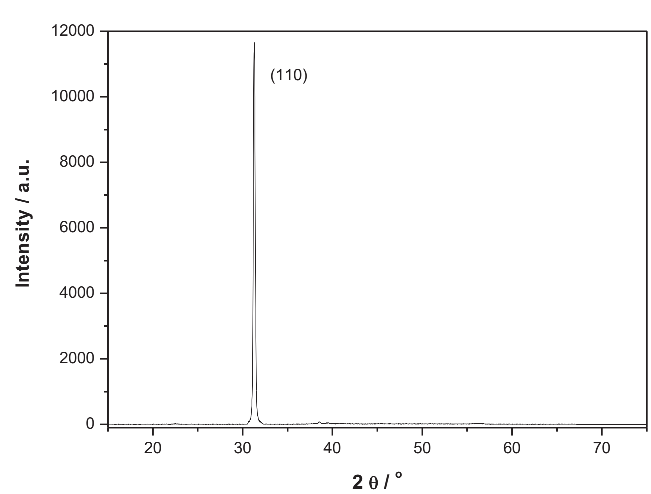

Fig. 5. X-ray scan pattern of [1 1 0]-oriented PIMNT crystal wafer.

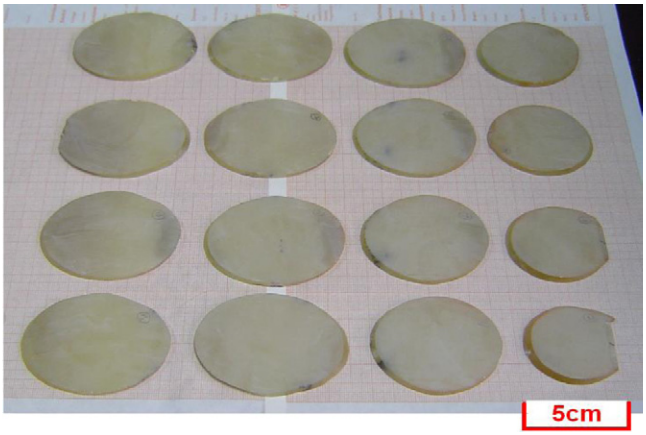

Fig. 6. [0 0 1]-oriented crystal plates cut from PIMNT crystal boule.

It has been confirmed that [0 0 1]-oriented PIMNT crystal wafer possesses the highest electrical parameters such as piezoelectric and dielectric constants among the various oriented wafers [12]. The [0 0 1]-oriented PIMNT crystal wafers were supplied for the manufacture of the ultrasonic devices such as sonar transducers and ultrasonic motors in our laboratory. After the orientation [0 0 1] of as-grown crystal boule was determined crystallographically by the rotating orientation XRD method [13], a series of [0 0 1]-oriented crystal plates, as presented in Fig. 6, were cut from different locations of the crystal boule. To meet the demand for the ultrasonic device manufacture, the ring-shaped crystal wafers with 0.5–2 mm in thickness were fabricated from the crystal plates by the carving technique. Fig. 7 displays a series of [0 0 1]-oriented ring-shaped crystal wafers with 16 mm in outer diameter and 6 mm in core diameter.

3.5. Electrical properties

The piezoelectric, dielectric and ferroelectric properties of [0 0 1]-oriented PIMNT crystal wafers were characterized in this work. It was found that the electrical parameters vary along the axial direction of as-grown crystal due to the composition segregation in the crystal growth. As for [0 0 1]-oriented wafers fabricated from the rhombohedral region of the as-grown crystal boule, the piezoelectric coefficient d_{33} of [0 0 1]-oriented wafers is measured to be in the range of 1500–2100 pC/N. Based on the investigation on the composition variation of as-grown crystal boules, PT component exhibits a continuous increase along the growth direction

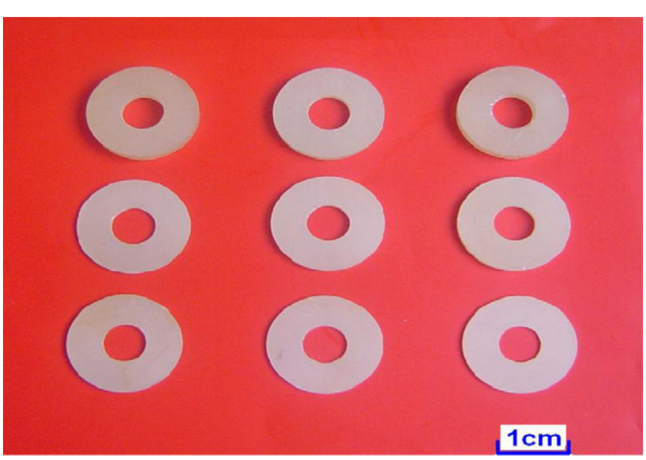

Fig. 7. [0 0 1]-oriented ring-shaped crystal wafers applied in ultrasonic device.

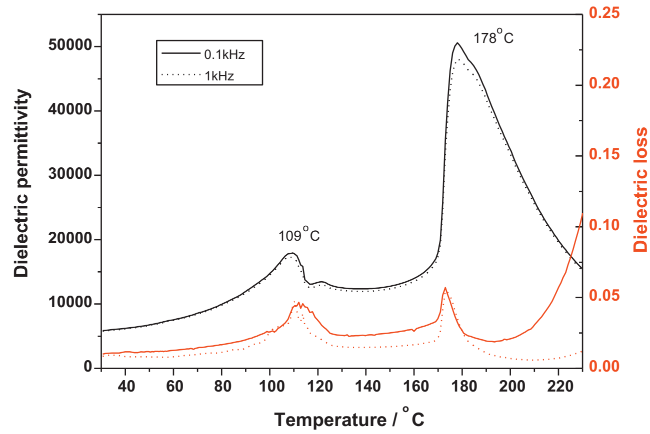

Fig. 8. Temperature dependence of dielectric permittivity (black line) and dielectric loss (red line) of [0 0 1]-oriented PIMNT crystal wafer. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

from the top region of crystal seed. With PT component increases in the rhombohedral region, the piezoelectric coefficient of [0 0 1]-oriented wafers increases from 1500 to 2100 pC/N. Of particular interest is that the mixed phase region near MPB composition exhibits an even higher piezoelectric coefficient with a maximum value of 2280 pC/N. However, as for the crystal wafers from tetragonal region with higher PT composition, the piezoelectric coefficient decreases steeply to a low level below 1000 pC/N.

Fig. 8 shows the temperature dependence of dielectric permittivity ε and dielectric loss tan δ at frequencies from 0.1 to 1 kHz for a poled crystal wafer from the rhombohedral region. Two dielectric permittivity peaks appear at the temperature of 109 °C and 178 °C with the increasing temperature, respectively, which indicate the sequent rhombohedral–tetragonal–cubic phase transition in the single crystal. It is revealed that rhombohedral to tetragonal phase transition occurs at the temperature $T_{r/t}$ of 109 °C and the tetragonal to cubic phase transition at the Curie temperature T_c of 178 °C. As for the series of [0 0 1]-oriented crystal wafers from the rhombohedral region, the rhombohedral to tetragonal phase transition temperature T_{r-t} was measured to be 100–120 °C and the Curie temperature T_c to be 160–195 °C. Compared to the reported data of $T_{r/t}$ (60–95 °C) and T_c (130–170 °C) for PMNT crystals [1–8], the temperatures of $T_{r/t}$ and T_c for PIMNT crystals have acquired a significant elevation. The dielectric permittivity ε and dielectric loss tan δ for the crystal wafers from the rhombohedral region are measured to be in the range of 4600–5800 and 0.5–1% at room temperature, respectively.

Fig. 9 displays the polarization hysteresis loops measured with [0 0 1]-oriented crystal wafers from the rhombohedral region under maximum electric field of 10 kV/cm and 12 kV/cm at room temperature. If the electric field is controlled as zero, the remnant polarization P_r remains a non-zero value. As the coercive field E_c is applied on the sample, the polarization of the crystal wafer changes to zero value. According to the two ferroelectric hysteresis loops shown in Fig. 9, the coercive field and remnant polarization under different maximum electric field are summarized as $E_c \sim 4.2$ kV/cm, $P_r \sim 27.0$ μC/cm^2 under 10 kV/cm and $E_c \sim 5.0$ kV/cm, $P_r \sim 28.5$ μC/cm^2 under 12 kV/cm, respectively. As a comparison, a coercive field of 2.3 kV/cm for a PMN-0.33PT crystal sample was obtained under the same measuring conditions in this work. Zhang et al. reported a coercive field of 2 kV/cm for a PMN-0.29T crystal, while PIMNT crystal exhibits a coercive field as large as 5.5 kV/cm under maximum electric field 20 kV/cm [14].

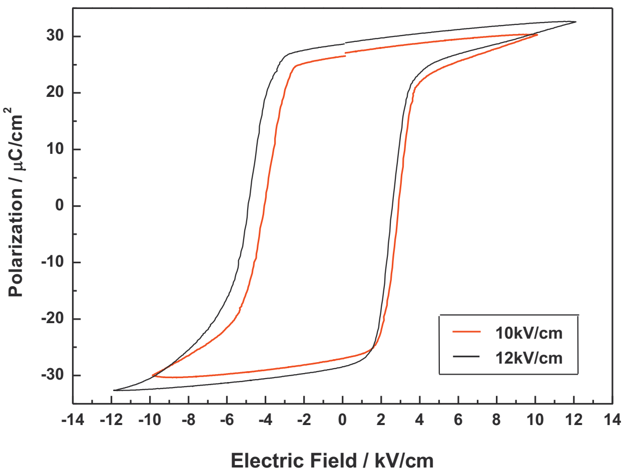

Fig. 9. Polarization hysteresis loops of [0 0 1]-oriented PIMNT crystal wafer.

4. Conclusion

Using the polycrystalline material synthesized by the columbite precursor route [1 1 0]-oriented PIMNT single crystal with size of Ø55 × 100 mm was grown successfully by seeded vertical Bridgman process. The mono-crystallinity of [1 1 0]-oriented crystal wafers can be verified by the fact that only (1 1 0) diffraction peak appears in the normal scan pattern. As-grown crystal shows a peculiar phase evolution from rhombohedral to tetragonal phase along the growing direction. As for [0 0 1]-oriented wafers fabricated from rhombohedral phase region, the crystal wafers possess desirable piezoelectric, dielectric and ferroelectric properties. In addition to the large piezoelectric coefficient d_{33} and dielectric permittivity ε, PIMNT crystal exhibits a higher phase transition temperature T_{r-t}, a higher Curie temperature T_c and a larger coercive field E_c in contrast to the binary crystal PMNT. The excellent electrical properties enable the ferroelectric material to be a favorable candidate for the higher power ultrasonic devices with a wider working temperature range. PIMNT crystal wafers produced in our laboratory have been used to manufacture sonar transducers and ultrasonic motors now.

Acknowledgements

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