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Study on the inhomogeneity of $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ single crystal along the growth direction

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The bulk single crystals $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$(PIN–PMN–PT) were grown spontaneously using the Bridgman method. The properties of as-grown PIN–PMN–PT single crystals along the growth direction were measured: along the crystal length, its structure was transformed from the mixed phase to tetragonal phase; the piezoelectric constants d_{33} of (001) and (110) samples decreased from 1900 to 1100 pC/N, and from 1200 to 500 pC/N respectively; the Curie temperature T_c increased from 206.0 to 223.4 °C; and the melting as well as crystallizing points all decreased by about 25–30 °C. These phenomena indicated the inhomogeneous properties of the PIN–PMN–PT single crystals. The experiment of elemental analysis verified that gradually increasing the concentration of the cation Ti along the growth direction would result in unstable properties of the crystal. Apparently, such a disadvantage decreased the effective ratio of the PIN–PMN–PT single crystal, and would further limit its applications.

1. Introduction

The single crystals, such as $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZN–PT), $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) and $Pb(In_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PIN–PT), were considered as an important progress in the piezoelectric field for the past fifty years [1–8]. These crystals have been applied to transducers, actuators and medical imaging. Recently, the cation In^{3+} was introduced into the PMN–PT single crystal to grow the new piezoelectric crystal $Pb(In_{1/2}Nb_{1/2})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$(PIN–PMN–PT). PIN–PMN–PT possesses excellent dielectric, piezoelectric and ferroelectric properties. Meanwhile, $T_{R/T}$ (temperature from the rhombohedral phase to the tetragonal) as well as T_c (Curie temperature) of PIN–PMN–PT have increased by 20°–30 °C over those of PMN–PT and the coercive field has also increased two times than that of PMN–PT. These properties extend the available temperature range of the crystals' applications [9–13]. The PIN–PMN–PT crystals could also be utilized in high driven fields.

Most recently, the researchers have focused on the growth and excellent electrical properties of PIN–PMN–PT single crystals, while its inhomogeneity was to some extent ignored. The investigations only focused on the excellent electrical properties of the crystals PIN–PMN–PT [11,12]. Until now, as far as we know, no report investigates the inhomogeneity of PIN–PMN–PT single crystals. In fact, considering the PIN–PMN–PT single crystals' applications, more attention should be paid to the study of its inhomogeneity. The longitudinal properties of the crystals are vital to their applications, which are concerned with the effective ratio of the crystals. Near the morphotropic phase boundary (MPB) the ternary PIN–PMN–PT single crystals have a wide range of compositions. Furthermore, the investigations of inhomogeneity will also assist to grow more stable PIN–PMN–PT single crystals. Therefore, the inhomogeneity along the crystal growth direction is an important research issue, which is helpful for us to understand the quality of the crystals and the performances of devices. In this paper, the PIN–PMN–PT crystals were grown spontaneously using the Bridgman method. As-grown crystals showed inhomogeneity in various properties along the growth direction, such as structure, piezoelectric constant d_{33}, Curie temperature T_c, densities and melting/crystallizing temperatures. Then the performed elemental analysis illustrated a variation of the cation Ti along the crystal growth direction from the segregation effect, which resulted in the inhomogeneous properties of PIN–PMN–PT.

2. Experimental details

The PIN–PMN–PT (starting composition 25/44/31) single crystals were grown spontaneously by the Bridgman method, as shown in Fig. 1(a). The main part of the crystal PIN–PMN–PT was black, which became green and transparent after annealing. Fig. 1(b) shows that the crystal was grown along the ⟨110⟩ direction. It is very effective to use the ⟨110⟩-oriented cross sections to study the inhomogeneity along the crystal growth direction.

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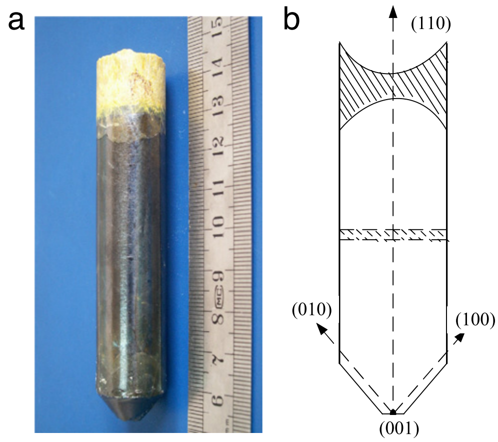

Fig. 1. (a) PIN–PMN–PT single crystal; (b) Sketch of PIN–PMN–PT single crystal.

The phase analysis of PIN–PMN–PT single crystals was performed by X-ray powder diffraction (XRD) (Rigaku D/MAX-2400 model, Japan). The piezoelectric constant d_{33} was measured using a quasistatic piezo-d33 meter (ZJ-2 Model, Institute of Acoustics, Chinese Academy of Sciences). The densities of the PIN–PMN–PT single crystals were measured by the Archimedes method. The Curie temperature was measured by an Olympus Bx51 microscope accompanied with a heater (THMS600 Model, Linkam Scientific Instrument). The differential thermal analysis (DTA) of the crystal powder was measured by the DTA (STA 449C Jupiter, Netzsch). The samples in a nitrogen gas atmosphere were heated from the room temperature to 1380 °C with a rate of 10 °C/min, and cooled similarly. Elemental analysis of the PIN–PMN–PT single crystal was measured by using a VISTA-PRO CCD Simultaneous ICP-OES.

3. Results and discussions

3.1. XRD analysis

Fig. 2 shows XRD patterns for the cross sections of PIN–PMN–PT single crystal, from the bottom to the top. The result reveals that the pure perovskite phase exists in the crystal. From Fig. 2(a) to (c) the reflections near the 2θ angle of 45° become broader and split, indicating that the phase transition occurs and the intensity of the $(002)_T$ peak increases. In Fig. 2(a) the coexistence of both the $(002)_R$ and $(002)_T$ suggests that the rhombohedral phase is mixed with the tetragonal one. And the $(002)_R$ intensity is dominant. Furthermore, the phase is also shown in Fig. 2(b). The Fig. 2(c) shows that the $(002)_T$ increases along the crystal axis while the $(002)_R$ further decreases. Finally, the (002) reflection splits clearly two peaks, which indicate that the phase structure transits from the mixed phase to the tetragonal one [14–16].

3.2. Piezoelectric constants d_{33}

Fig. 3 illustrates the piezoelectric constants d_{33} of both the (110) samples and the (001) ones. The (110) samples are the cross sections along the crystal growth. Their piezoelectric constants d_{33} descend from nearly 1200 pC/N to a few hundreds. Because the crystal devices require the (001) wafers, both the bottom (001) wafer and the top one have been measured, about 1900 pC/N and 1100 pC/N respectively. In a word, the piezoelectric constants d_{33} of PIN–PMN–PT single crystal are descending along the crystal axis gradually.

Furthermore, the constant d_{33} in the (110) horizontal areas perpendicular to the crystal growth direction fluctuates within a range of 10–35 pC/N. It may be caused by two reasons,

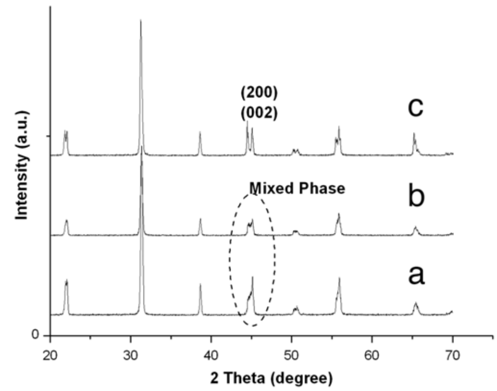

Fig. 2. XRD patterns of PIN–PMN–PT single crystal powders: (a) for the bottom sample; (b) for the middle one; (c) for the upper one.

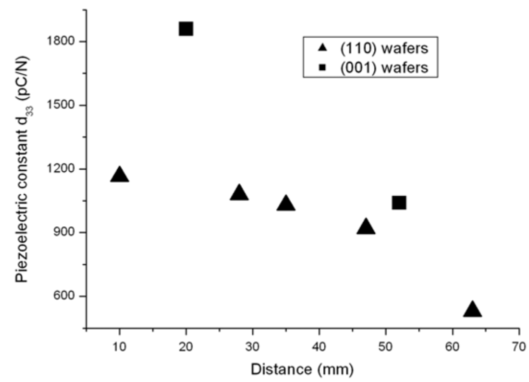

Fig. 3. Piezoelectric constants d_{33} of PIN–PMN–PT single crystal along the growth direction: the triangles for (110) samples; the rectangles for (001) samples.

such as ⟨110⟩-orientation of crystal growth and upper convex interface of solid–liquid during growth, which will cause slightly different composition due to segregation of the components or impurities. The results suggested that PIN–PMN–PT single crystals grown by the ⟨001⟩-oriented seed Bridgman would improve the homogeneity of ⟨001⟩-oriented wafers.

3.3. Density analysis

Fig. 4 shows a fluctuation of the density along the crystal growth direction. From the bottom wafers to the top ones, the crystal density is decreasing. The triangles are the experimental data, and the line is the theoretical linear fitting by the least-squares method. The theoretical result shows the density has a descending tendency. The reason is that the segregation effect causes inhomogeneity in the composition of the PIN–PMN–PT single crystal.

3.4. Curie temperature T_c

The four figures from Fig. 5(a) to (d) are the corresponding thermal-induced domain transitions of four samples along the crystal growth direction. Fig. 5(b) shows the domain transition of (001) wafer, and the others are the domain transitions of (100) samples. In Fig. 5(a) the domain begins to transit from the upper zone. The dark area is the cubic phase, which the arrow aims at. In other figures the domains transitions begin from the right side. At the Curie temperature, the domain strips disappear slowly and vanish finally. When all the domains vanish, the single crystal PIN–PMN–PT transits from the tetragonal phase to the cubic one. The domain transitions show the thermal-induced phase transformations of PIN–PMN–PT single crystal. Furthermore, compared with these domain transitions, it is found