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Growth and piezoelectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ crystals by the modified Bridgman technique

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Abstract

The Bridgman technique has been used to grow PMNT single crystals based on the understanding of the features of PMN–PT system and the thermal stability of PMNT crystals. The technique has some advantages for the control of spontaneous nucleation, parasitic growth, crystal size and perfection compared to conventional methods. In order to suppress the leaking of crucibles, improve the compositional uniformity and enhance the piezoelectric performance, some modifications were adopted in starting materials and crystal growth procedure. The PMNT crystals grown using this technique were large in size and excellent in piezoelectric properties. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Relaxor ferroelectric-based single crystals $x\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}-(1-x)\mathrm{PbTiO_3}$ [PMNT], $y\mathrm{Pb(Zn_{1/3}Nb_{2/3})O_3}-(1-y)\mathrm{PbTiO_3}$ [PZNT] have attracted a great attention in the ferroelectric field for their excellent piezoelectric properties [1]. However, some problems are still left unresolved in the growth of these novel piezoelectric single crystals. First, it was difficult for either high temperature solution methods [2–4] or vertical Bridgman ones adding PbO as flux [5] to control the spontaneous nucleation and to enlarge and maintain the crystal size for lack of crystal seeds. Second, it was difficult for those methods to control the growth process or a solid–liquid interface due to the variation in supersaturation of the solution. Therefore, the PZNT crystals grown by above methods were not ideal in the compositional uniformity and stability of properties yet [5,6]. Third, the lower growth rate in these methods could not meet the demands of industrial production. Our purpose is to seek a new method to grow PMNT single crystals and to discuss the problems in practical growth.

2. Experimental

The melting points of PMNT crystals or powders were measured by differential thermal analysis (DTA) and the method of measuring on the seed molting lines of boules. Their thermal stability was measured by thermal gravity analysis (TG) while crystal compositions were analyzed by X-ray fluorescence spectrometry.

In the Bridgman technique, the starting materials were PMNT powders in the ratios of PMN/PT of 76/24–67/33 near the morphotropic phase boundary (MPB) of PMNT system. Platinum (Pt) crucibles were used and crystal seeds placed at the bottom of them. The growth temperature was 1420°C and the descending rate of crucibles was set at 0.2–1.0 mm/h. Plates were processed from boules and poled under the electric field of 10 kV/cm after Cr and Au films were coated on them. The dielectric properties were tested using an impedance analyzer (YHP4192A) while the piezoelectric constant d_{33} was measured with a quasi-static d_{33} meter of Berlincourt type. The electromechanical coupling

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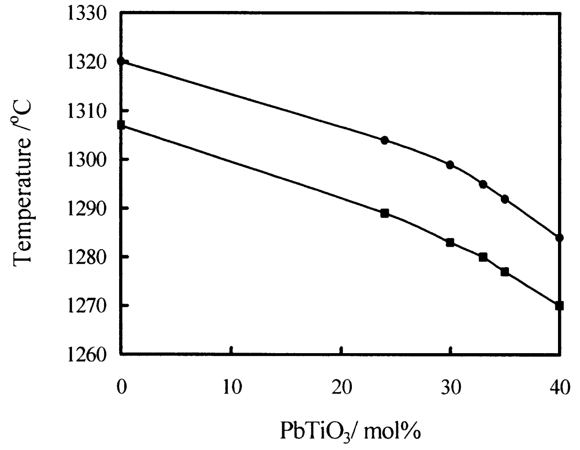

Fig. 1. Melting points of some PMNT compositions, ● data from DTA; ■ data from the melting line on boules.

factors of the thickness mode (k_t) and longitudinal bar mode (k_{33}) were obtained from the resonance and anti-resonance frequencies.

3. Results and discussions

3.1. The features of PMN–PT system

Fig. 1 indicates that the melting points available from the seed melting line on the boules are lower about 15°C and may be closer to equilibrium values than ones from DTA data. This is because in former condition, PMNT melts have far longer soaking time (more than 12 h) and the composition volatilization has been suppressed through sealed crucibles. It can be seen that the melting points fall down gradually with increasing $PbTiO_3$ (PT) content.

Table 1 shows the results of composition analyses for PMNT76/24 crystals. The samples 1–4 are plates 1.0 mm thick and away from the seed melting line at the distances of 1, 2, 3 and 4 cm, respectively. It can be seen that TiO_2 or PT content in crystals is slightly lower than that in the melt and increases upwards. In other words, slight macroscopical segregation exists during growth. The effective segregation coefficient (k_e) of PT was calculated as about 0.95. The case of $k_e < 1$ is in agreement with the slope of liquid phase line of PMN–PT system.

Table 1
Results of X-ray fluorescence spectrometry for 0.76PMN–0.24PT single crystals

Sample number	PbO (%)[a]	MgO (%)	Nb_2O_5 (%)	TiO_2 (%)
1	102.10	24.27	25.79	22.05
2	100.74	25.33	25.35	23.23
3	100.74	25.57	25.49	22.71
4	101.28	25.17	25.47	22.61
Theoretical	100.00	25.33	25.33	24.00

[a] Molar percent.

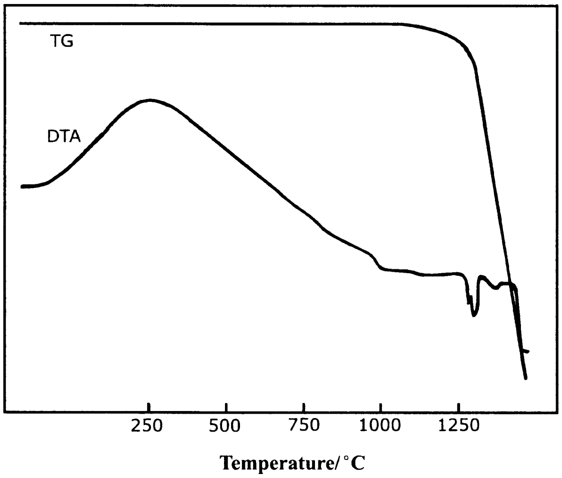

Fig. 2. DTA and TG curves of PMNT67/33 crystals.

The TG curve shows that the PMNT crystal decomposes obviously about 1200°C and it hardly changes below this temperature (Fig. 2). It has a higher thermal stability than PZN crystal [7]. It is possible to use a melt growth method or a Bridgman technique to grow PMNT crystal.

3.2. Growth of PMNT crystals

A Bridgman technique, which directly used PMNT melt, was adopted to grow PMNT crystals. The control of nucleation and growth becomes effective in this method since crystal seeds can be used and come into operation in the control of the spontaneous nucleation and parasitic growth. By this way, the single crystals can be enlarged fast and maintained stable and repeatable in size. Meanwhile, the shape and position of a solid–liquid interface are readily controlled during growth because the temperature at the solid–liquid interface maintains almost unchanged, being equal to their melting points.

From the above mentioned, the Bridgman technique is feasible for the growth of PMNT crystals. However, we found that it was not easy to grow PMNT crystals with both large size and high perfection using this technique so that some modifications were necessary.

First, Pt crucibles were apt to leak due to undergoing high temperature and the erosion of PbO. As a result, the gravity loss of starting materials took place more or less under conventional growth condition. The adopted protective measures included (1) use high-purity starting materials since the mixed dissociative metal may react with Pt as well and form Pt-metal alloys with lower melting point; (2) use Pt crucibles with thick walls to enhance its resistance to chemical erosion; (3) set a supported equipment to lessen

Fig. 3. The boules of PMNT crystals grown by the modified Bridgman technique.

the distortion degree of Pt crucibles under high temperature. The experiment demonstrated that these measures were effective. The leak of Pt crucibles could be suppressed to a great extent and the starting materials almost had no gravity loss.

Second, how to improve composition uniformity of PMNT crystals became a noticeable problem due to their complex compositions. For this purpose, PMNT powders, instead of oxide powders, were used as starting materials. Meanwhile, the growth temperature was lifted up to 1420°C and the soaking time of melts was prolonged properly to more than 12 h. These modifications in growth parameters could increase the diffusion degree of solutes in melts and the distribution uniformity of solutes in crystals.

Third, the orientation growth technique was adopted to effectively enlarge the size of PMNT crystals. The anisotropy in growth rates appeared evidently in the growth of PMNT crystals, which was favorable for the washing out of polycrystals. It was observed that the {111} orientation predominated in the cuts normal to the growth direction or the longitudinal one of cylinder boules while no crystal seed or a polycrystalline crystal seed was used. This crystal habit was used to the orientation growth of PMNT crystals. Recently, the PMNT crystal boule grown along [111] has reached the size of ∅50 mm × 80 mm (Fig. 3) and its XRD spectrum illustrated that it was of pure perovskite structure (Fig. 4). The orientation, crystal boundary and domain configuration of the plates, which came from different parts of the boule in Fig. 3, were checked and observed using an X-ray orientation device and an optical microscope. The results showed that various parts of the boule had the same orientation and no crystal boundary appeared, or the whole PMNT boule was one single crystal.

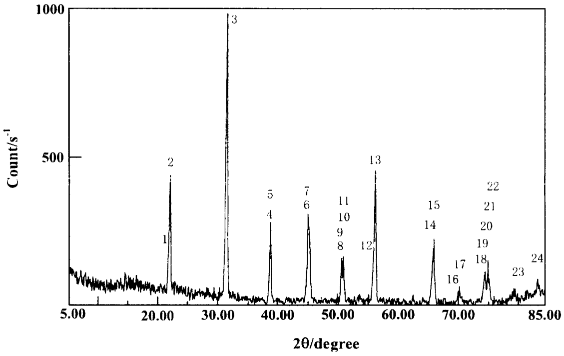

Fig. 4. XRD spectrum of PMNT67/33 crystal powders.

3.3. Piezoelectric properties

The piezoelectric properties of PMNT crystals vary with compositions and cut types (Table 2). Considering the temperature stability of dielectric and piezoelectric properties, the preferred compositions are suggested as to be PMNT68/32–PMNT69/31, which exhibit a high temperature of phase transition from one ferroelectric to another ferroelectric phase (T_{F-F}) as well as excellent piezoelectric properties. Like PZNT crystals [2], the optimal cut is (001) for rhombohedral PMNT crystals.

The piezoelectric properties of PMNT crystals fluctuated somewhat for either the different plates or different points on the same plate, which might arise from the macroscopical segregation in compositions, the fluctuation in structures and the existence of structural defects and space charge field. The macroscopical segregation was considered as the main reason for this property inhomogeneity since the successive variations in the values of dielectric constant ε, piezoelectric constant d_{33} and Curie point (T_C) were observed amongst different plates cut along growth

Table 2
The piezoelectric properties of PMNT single crystals

Sample number	Composition	Orientation	ε	tan δ (%)	k_t	k_{33}	d_{33} (pCN^{-1})	T_{F-F} (°C)	T_C (°C)
1	76/24	(001)	3600	0.7	0.55		850–940		110
2	76/24	(001)	3250	0.8	0.57		890–1000		109
3-a	67/33	(110)	3700	0.8	0.51		590		
3-b	67/33	(111)	910	1.1	0.42		130		
3-c	67/33	(001)	5500	0.5	0.62	0.94	2400–2600	55	152
4	68/32	(001)	5000	0.7	0.62	0.94	2000–2200	68	150
5-a	69/31	(001)	4800	0.6	0.62	0.92	1800–2100	73	147
5-b	69/31	(001)	4300	0.6	0.61	0.91	1700–1900	85	143
5-c	69/31	(001)	3800	0.5	0.61	0.90	1600–1700	98	139

direction, as in the case of PMNT69/31 from the sample 5-a to 5-c (Table 2). Obviously, the inhomogeneity in property within a (001) cut was related to the growth direction along [111] due to the macroscopical segregation. In order to lighten macroscopical segregation and enhance the property uniformity, we intend to change the growth direction from [111] to [001] and further modify the growth art in the next work.

4. Conclusions

The PMN–PT system can be regarded as a system with slight segregation and high thermal stability, thus the Bridgman technique is feasible for the growth of PMNT crystals. But modifications in starting materials and growth method are necessary in order to obtain PMNT crystals with large size, high perfection and uniformity in composition and properties. Several kinds of PMNT crystals with different compositions have been grown using this technique, and they not only reach the size of ∅50 mm × 80 mm but also exhibit excellent piezoelectric properties. The next task is to reduce the segregation degree of this solid solution system.

Acknowledgements

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