

Growth and characterization of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{--BaTiO}_3$ lead-free piezoelectric crystal by the TSSG method

Wenwei Ge^{a,b,c,*}, Hong Liu^d, Xiangyong Zhao^{a,b}, Xiaoming Pan^{a,b},
Tianhou He^{a,b}, Di Lin^{a,b}, Haiqing Xu^{a,b}, Haosu Luo^{a,b}

^a State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Jiading, Shanghai 201800, China

^b R&D Center of Crystal, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Jiading, Shanghai 201800, China

^c Graduate School of Chinese Academy of Sciences, Beijing 10039, China

^d Jingdezhen Ceramic Institute, Jingdezhen 333001, China

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Abstract

In this paper, polycrystalline material of $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{--}0.06\text{BaTiO}_3$ (abbreviated as NBBT94/6) was synthesized by solid-state reaction techniques. DTA and TG analysis indicate the proper temperature for solid-state reaction is 1200°C . A single crystal with dimensions of $25\text{ mm} \times 10\text{ mm}$ was successfully grown by using the top-seeded solution growth (TSSG) method. X-ray fluorescence analysis revealed that the composition of the as-grown crystal is NBBT98/2. X-ray powder diffraction results show that the as-grown NBBT98/2 crystal possesses the perovskite structure and belongs to the rhombohedral system. The unit-cell constants of the as-grown NBBT98/2 crystal are $a=b=c=3.8862\text{ \AA}$ and $\alpha=\beta=\gamma=89.2^\circ$. At room temperature, the dielectric constant of $\langle 001 \rangle$ oriented NBBT98/2 crystal is 770 at 10 kHz and it decreases to 430 after poling under the E-field of 7 kV/mm. Maximum d_{33} values of 60, 65 and 30 pC/N were obtained for $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ oriented NBBT98/2 crystal, respectively.

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1. Introduction

In recent years, growing attention has been given the research and improving piezoelectric properties of lead-free piezoelectric materials, which are viewed as possible substitutes for lead-based piezoelectric materials from the viewpoint of environmental protection [1–3]. Sodium bismuth titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, abbreviated NBT) is a strong ferroelectric material with a high Curie temperature of $T_c=320^\circ\text{C}$, a remanent polarization of $P_r=38\text{ }\mu\text{C}/\text{cm}^2$, and a coercive field of $E_c=73\text{ kV}/\text{cm}$ at room temperature [4,5]. In view of these good

ferroelectric properties, NBT is considered to be a promising candidate for a lead-free piezoelectric material. However, the large coercive field and relatively large conductivity make pure NBT is hard to be poled and its piezoelectric properties are not desirable. Therefore NBT-based solid solutions were studied to improve piezoelectric properties [6–19]. Among these NBT-based solid solutions, $(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{--}x\text{BaTiO}_3$ (abbreviated as NBBT) system is the most attractive due to their excellent piezoelectric properties and was studied by several researchers [6–13]. There also exists rhombohedral–tetragonal morphotropic phase boundary (MPB) near $x=0.06\text{--}0.07$ in NBBT system and the piezoelectric properties can be enhanced near the MPB composition as it was previously reported in Pb-based perovskites, such as PMN-PT and PZN-PT [6,20]. It was reported that NBBT94/6 ceramics presented a relatively low dielectric constant of $\epsilon_{33}=580$, a high piezoelectric constant and electromechanical coupling coefficient of $d_{33}=125\text{ pC}/\text{N}$ and

* Corresponding author at: State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Jiading, Shanghai 201800, China.

E-mail address: wenweige@hotmail.com (W. Ge).

$k_{33} = 0.55$, and appear to be advantageous for high-frequency ultrasonic uses or piezoelectric actuator applications [6]. Improved electromechanical actuation can be achieved in single crystals oriented to optimize piezoelectric coefficients. Chiang has reported that NBBT94.5/5.5 single crystals on the (001) cut exhibit d_{33} value up to 450 pC/N, which close to some PZT ceramics [7]. But the investigations focused on NBBT solid solution single crystals are still scarce and not systematic, and the reported piezoelectric results are quite different [7,8,13]. There is still a lack of fundamental understanding of the structure–property relations and mechanism for high piezoelectric responses near the MPB compositions in lead-free materials, about which much research and development need to be done to optimize the piezoelectric properties in lead-free materials.

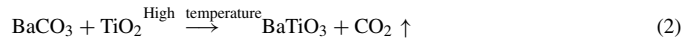
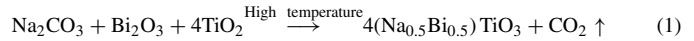
Single crystals provide the opportunity to conveniently investigate the physical properties as a function of crystallographic orientations and find the optimum crystallographic cuts for practical applications. Up to now, many growth methods have been tried to obtain NBT-based crystals, including Czochralski method [5,21–24], flux method [7,8,22,23], and Bridgman method [8,13]. However, it is not easy to fabricate high-quality NBT-based single crystals by Czochralski method because the high volatility of the bismuth and potassium components at melting temperature results in crystal growth deviating from stoichiometry and combined with many defects [22]. NBT-based single crystals have been also grown by the flux slow-cooling method [7,8,22,23], but these obtained crystals were too small (most of them were mm-level) to systematically characterize their piezoelectric properties as a function of crystallographic orientations. In this paper, NBT-BT single crystal with dimensions of 25 mm × 10 mm has been successfully grown by the top-seeded-solution growth (TSSG) method. The dielectric and piezoelectric properties for as-grown crystal were measured along $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ crystallographic directions.

2. Experimental

2.1. TG–DTA measurements for polycrystalline material synthesis

Chemical materials of Na_2CO_3 , Bi_2O_3 , TiO_2 and BaCO_3 with 99.99% were used to synthesize the polycrystalline material of $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – 0.06BaTiO_3 (abbreviated as NBBT94/6) by conventional solid-state reaction

techniques. Before solid-state reaction, these compounds were weighted according to the following chemical reaction equation and characterized by TG–DTA experiments using a simultaneous thermal analyzer (NETZSCH STA 449C) at a heating rate of $10^\circ\text{C}/\text{min}$ in an air atmosphere. After these thermal measurements, the proper temperature to synthesize the polycrystalline material of NBBT94/6 crystal was determined:



2.2. Crystal growth and characterization

High purity Na_2CO_3 , Bi_2O_3 , TiO_2 and BaCO_3 were weighted according to stoichiometrical ratio of $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – 0.06BaTiO_3 . After these compounds were ground and mixed, they were put into a platinum (Pt) crucible and heated to 1200°C for 10 h to decompose the carbonate and form NBBT94/6 polycrystalline material. Then the NBBT94/6 polycrystalline materials were ground and mixed with 20 wt.% of excess Na_2CO_3 and Bi_2O_3 as a self-flux for compensating the composition change. These mixtures were heated to 900°C for an hour.

NBBT94/6 single crystal was grown from a Pt crucible, which was heated by using a resistance furnace under air atmosphere. A platinum wire was used as the seed for crystal growth. In order to avoid the formation of polycrystal in the crystal growth process, a temperature 30 – 50°C higher than the melting temperature of polycrystalline material was required initially, to melt the micro-crystal particles in the Pt crucible and keep that temperature for an hour. The temperature was then lowered to the melting temperature. Initially, a randomly oriented crystal was obtained by spontaneous nucleation on the end of a platinum wire by restricting the diameter of the crystalline material so that only one crystal should be grown. The pulling rate was 2 – 2.5 mm per day after the crystal diameter reached a certain value; the rotating rate was 10 – 30 rpm. After growth, the crystal was cooled to room temperature at a rate of 30 – $50^\circ\text{C}/\text{h}$.

The X-ray fluorescence analysis method was used to measure the concentrations of Ba, Bi, Ti and Na elements in the as-grown crystal. Based on the measured results, the effective segregation coefficients of Ba, Bi, Ti and Na in the as-grown crystal were calculated. The polycrystalline material was used as compared standard samples.

Prior to dielectric and piezoelectric measurements, the crystal symmetry of the as-grown crystal was checked by using X-ray powder diffraction (XRPD). Then it was cut into crystal wafers along $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions determined by an X-ray diffractometer and fired silver electrodes were formed on both sides of these samples at 600°C . These samples were poled under an electric field of 0.5 – 7 kV/mm for 15 min at 150°C in silicon oil and cooled to room temperature with the half of the applied electric field. The HP4192A impedance analyzer was used to measure the dielectric constants as a function of temperature within the temperature range of 30 – 400°C at the frequency of 100 Hz to 1 MHz. The piezoelectric constants were measured in quasistaticmeter for Berlingcourt type at about 55 Hz.

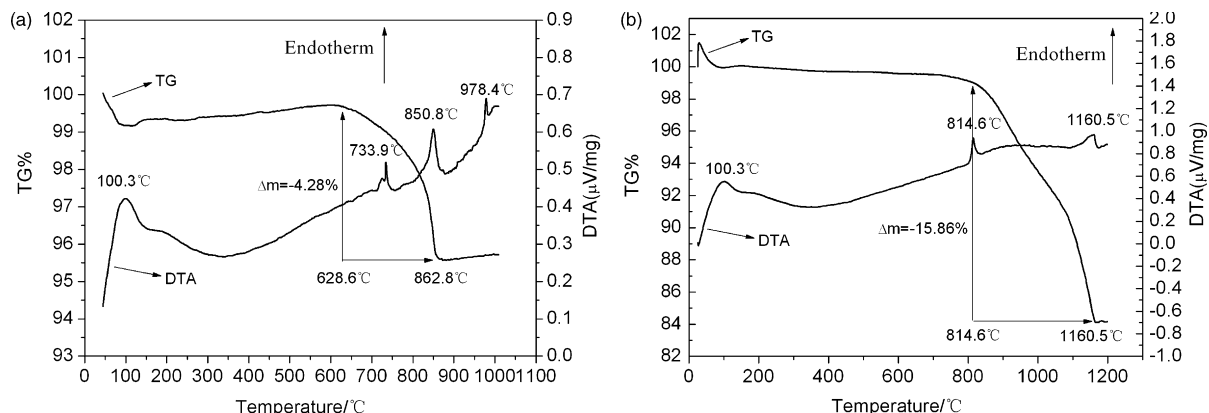


Fig. 1. TG–DTA curves for mixture powder of (a) $\text{Na}_2\text{CO}_3 + \text{Bi}_2\text{O}_3 + 4\text{TiO}_2$ and (b) $\text{BaCO}_3 + \text{TiO}_2$.

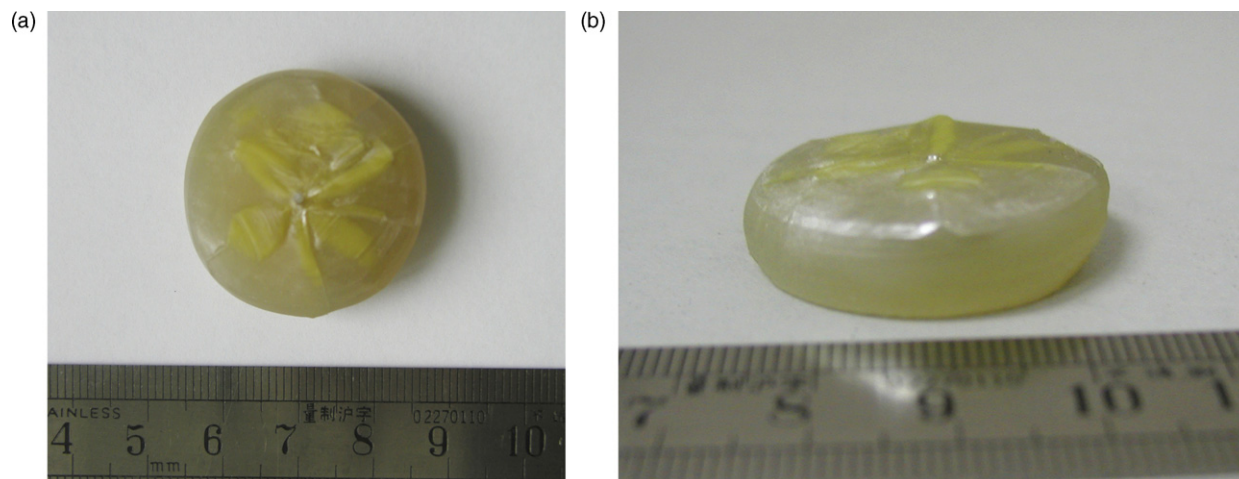


Fig. 2. The photograph of as-grown NBBT crystal: (a) top view; (b) side view.

3. Results and discussion

3.1. TG–DTA analysis

Fig. 1(a) shows the TG–DTA curves for the mixture of Na_2CO_3 , Bi_2O_3 , and TiO_2 with the molar ratio of 1:1:4. From Fig. 1(a), four endothermic peaks centered at 100.3, 733.9, 850.8 and 978.4 °C are observed. The first endothermic peak is attributed to the evaporation of water molecules with mass loss of 0.75% on the TG curve. The second endothermic peak can be ascribed to the phase transformation of Bi_2O_3 from α -phase to β -phase [25]. The third endothermic peak results from the fusion of Bi_2O_3 [25]. The fourth endothermic peak is assigned to the formation of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ by combination reactions of Na_2O , Bi_2O_3 and TiO_2 . In addition, there is an obvious mass loss of 4.28% during the temperature rising from 628.6 to 862.8 °C on the TG curve, which indicates the decarbonation of Na_2CO_3 . But the mass percentage of Na_2CO_3 in the mixture was only 11.88% and as a result, there is no obvious endothermic peak corresponding to the decarbonation of Na_2CO_3 on the DTA curve.

Fig. 1(b) shows the TG–DTA curves for the mixture of BaCO_3 and TiO_2 with the molar ratio of 1:1. It can be seen that there is also an endothermic peak at 100.3 °C on the DTA curve, which is attributed to the evaporation of water molecules. There is an obvious mass loss of 15.86% during the temperature rising from 814.6 to 1160.5 °C on the TG curve, which indicates the decarbonation of BaCO_3 . The endothermic peaks appearing at 814.6 and 1160.5 °C can be ascribed to the decarbonation of BaCO_3 and the formation of BaTiO_3 by combination reactions of BaO and TiO_2 . According to the TG–DTA measurements, the proper temperature to synthesize the polycrystalline material of NBBT94/6 crystal was chosen to be 1200 °C.

3.2. Crystal, structure and effective segregation coefficients

Fig. 2 shows the NBBT crystal boule grown by the TSSG method. The dimensions of the as-grown crystal are 25 mm in

diameter and 10 mm in length. Fig. 3(a) shows the X-ray powder diffraction (XRPD) patterns of the as-grown NBBT crystal. In addition, the XRPD patterns of BaTiO_3 crystal which was grown by the TSSG method were also given in Fig. 3(b). It can be seen that these two crystals almost have the same XRPD patterns. Since the barium titanate is a typical perovskite-type structure compounds, it can be deduced that the as-grown NBBT crystal also possess the perovskite-type structure. The unit-cell parameters were calculated through the TEROR program according to the 2θ in the XRPD patterns. The unit-cell parameters of the as-grown NBBT crystal are $a = b = c = 3.8862 \text{ \AA}$ and $\alpha = \beta = \gamma = 89.2^\circ$, which are similar to the data of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ previously reported in Ref. [4]. The diffraction indices corresponding to each diffraction peak are marked on the patterns. There is no splitting of peaks in the XRPD pattern of NBBT crystal, while the splitting of (002) and (200) peaks can be observed in the XRPD pattern of BaTiO_3 crystal. These results indicate that the as-grown NBBT crystal belongs to the rhombohedral crystal system and its rhombohedral unit cell are very close to the cubic ones and can be regarded as pseudo-cubic structure.

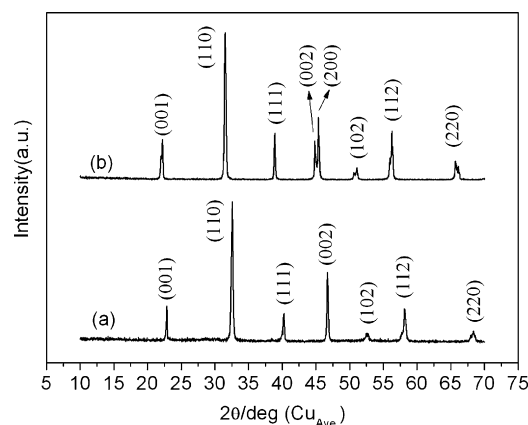


Fig. 3. X-ray powder diffraction patterns of (a) as-grown NBBT crystal and (b) BaTiO_3 crystal.

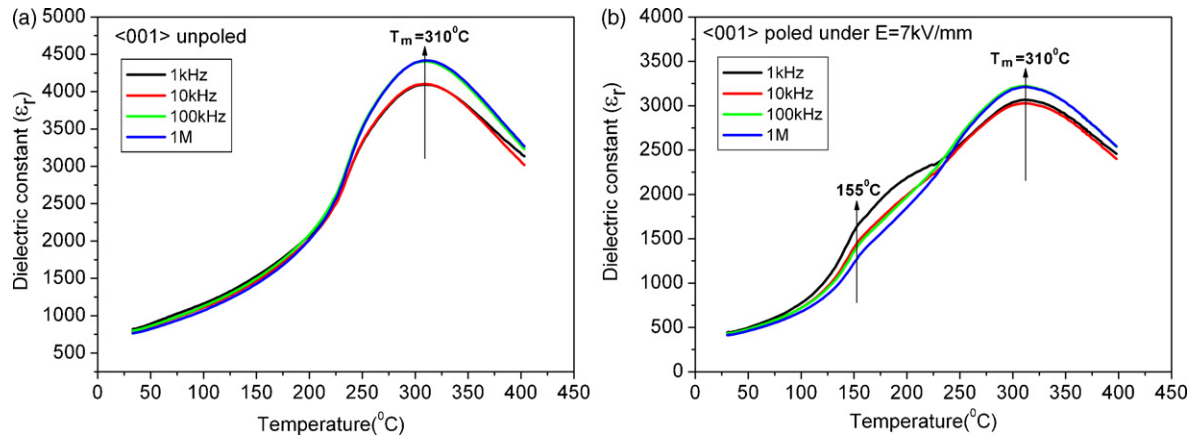


Fig. 4. Dielectric constants as a function of temperature and frequency for (a) unpoled and (b) poled $\langle 001 \rangle$ -oriented NBBT98/2 crystal.

Table 1
Concentration and effective segregation coefficient of elements in as-grown NBBT crystal

	Na	Bi	Ba	Ti
[Standard] (wt.%)	5.07	46.08	3.87	22.47
[NBBT] (wt.%)	4.34	48.20	1.25	23.39
k_{eff}	0.86	1.05	0.32	1.04

Table 1 shows the concentration and effective segregation coefficients of Na, Bi, Ba and Ti elements in the as-grown NBBT crystal. According to the measured concentrations of the Na, Bi, Ba and Ti elements, the as-grown NBBT crystal is confirmed to be NBBT98/2. From Table 1, it can be seen that the segregation coefficients of Bi and Ti elements are very near 1. But the segregation coefficients of Na and Ba elements are smaller than 1. Especially, the segregation coefficients of Ba element is only 0.32. These results indicate that more BaCO_3 should be added to the starting materials if we want to obtain the MPB crystal of NBBT94/6. The appropriate ratio of starting materials will be further studied.

3.3. Dielectric and piezoelectric properties of as-grown NBBT98/2 single crystal

Fig. 4 shows the dielectric constants ϵ_r as a function of temperature at different frequencies for the poled and unpoled $\langle 001 \rangle$ -oriented NBBT98/2 crystal. It can be seen that the dielectric constants show obvious frequency dispersion and exhibit broad dielectric peaks with a maximum at a T_m of 310°C , which is connected with the transition towards the cubic paraelectric state, as previously reported for NBBT system ceramics [6]. These results indicate that the as-grown NBBT92/8 crystal is a relaxor ferroelectric and the T_m is 10°C lower than that of pure $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ [4]. At room temperature, the dielectric constant (ϵ_r) of $\langle 001 \rangle$ -oriented NBBT98/2 crystal is 770 at 10 kHz and it decreases to 430 after poling. Compared with the unpoled sample, the temperature dependence of dielectric constants for the poled $\langle 001 \rangle$ -oriented NBBT98/2 crystal shows an obvious hump around 155°C . The humps in the temperature range of $170\text{--}230^\circ\text{C}$ in the $\epsilon(T)$ curve were also reported

in pure NBT [17], NBBT system ceramics [11] and NBBT94/6 crystal [13] and these researchers all proposed that this hump results from the phase transition from rhombohedral ferroelectric to tetragonal antiferroelectric. However, other experimental results such as X-ray diffraction [22], Roman and neutron scattering [26,27] did not indicate the existence of antiferroelectric phase. Since the hump is only observed in the poled sample according to our experimental results, the possible origination of this phenomenon can be attributed to the macro-micro domains switching as it has been discussed in the $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ and PLZT relaxor ferroelectric ceramics [28].

Fig. 5 shows the piezoelectric constants d_{33} as a function of poling electric field for the $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ -oriented NBBT98/2 crystal samples. For $\langle 001 \rangle$ and $\langle 110 \rangle$ -oriented NBBT98/2 crystal samples, d_{33} increases firstly as the poling electric field increases and then decrease when the poling electric field exceeds 3 kV/mm . Maximum d_{33} values of 60 and 65 pC/N at the poling electric field of 3 kV/mm were obtained for $\langle 001 \rangle$ and $\langle 110 \rangle$ -oriented NBBT98/2 crystal. For $\langle 111 \rangle$ -oriented NBBT98/2 crystal samples, the d_{33} values increase moderately as the poling electric field increases. Maximum d_{33} value is 30 pC/N for $\langle 111 \rangle$ -oriented NBBT98/2 crystal. Although $\langle 111 \rangle$ is the polar direction for rhombohedral NBBT98/2 crystal, however, such cuts exhibit low piezoelectric

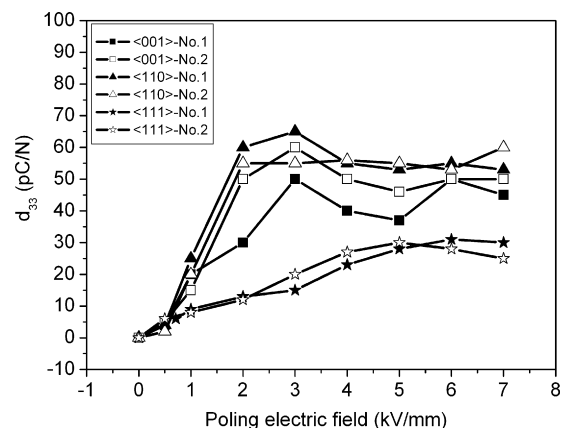


Fig. 5. Piezoelectric constants d_{33} as a function of poling electric field for $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ -oriented NBBT98/2 crystal.

constants d_{33} as a function of poling electric field as shown in Fig. 5. Since it has been reported that the piezoelectric in rhombohedral single crystal of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ can be obviously enhanced when it was poled along its nonpolar pseudocubic $\langle 001 \rangle$ direction and come into engineered domain state [20]. Perhaps there is the same mechanism enhances the piezoelectric properties of lead-free rhombohedral NBBT98/2 crystal as shown in Fig. 5, which will be further studied combined with *situ* domain observation under DC-bias using a polarizing microscope.

4. Conclusion

Polycrystalline material of NBBT94/6 was prepared by the high temperature solid-state reaction. DTA and TG analysis indicate the proper temperature for solid-state reaction is 1200 °C. The single crystal of NBBT solid solution with dimensions of 25 mm × 10 mm was successfully grown by the TSSG method. X-ray fluorescence analysis indicates that the composition of the as-grown crystal is close to NBBT98/2. X-ray powder diffraction results show that the as-grown NBBT98/2 crystal possess the perovskite-type structure and belongs to the rhombohedral system. Dielectric measurements demonstrated that the as-grown NBBT98/2 crystal is relaxor ferroelectric. At room temperature, the dielectric constant of $\langle 001 \rangle$ oriented NBBT98/2 crystal is 770 at 10 kHz and it decreases to 430 after poling under the E-field of 7 kV/mm. Maximum d_{33} values of 60 and 65 pC/N were obtained for $\langle 001 \rangle$ and $\langle 110 \rangle$ oriented NBBT98/2 crystal. However, the maximum d_{33} value is only 30 pC/N for $\langle 111 \rangle$ oriented NBBT98/2 crystal. These results indicate that the concept of crystallographic engineering also can be used to enhance the piezoelectric performance of NBBT system lead-free single crystals.

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