

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

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Received 3 January 2007; accepted 20 February 2007

Available online 28 February 2007

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 mm × 10 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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PACS: 81.10.Dn; 77.84.Dy; 81.70.Pg; 61.10.Nz; 77.22.Ch; 77.80.Bh; 77.65.Bn

Keywords: Ferroelectrics; Crystal growth; X-ray diffraction; Dielectric response; Piezoelectricity

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 $P_r = 38 \mu\text{C}/\text{cm}^2$, 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

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$k_{33} = 0.55$, 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.

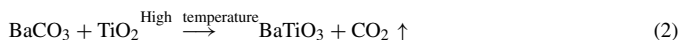
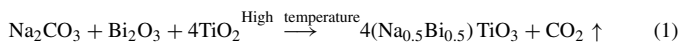
Single crystals provide the opportunity to conveniently investigate the physical properties as a function of crystallographic orientations and find the optimum crystallographic cuts for practical applications. Up to now, many growth methods have been tried to obtain NBT-based crystals, including Czochralski 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.

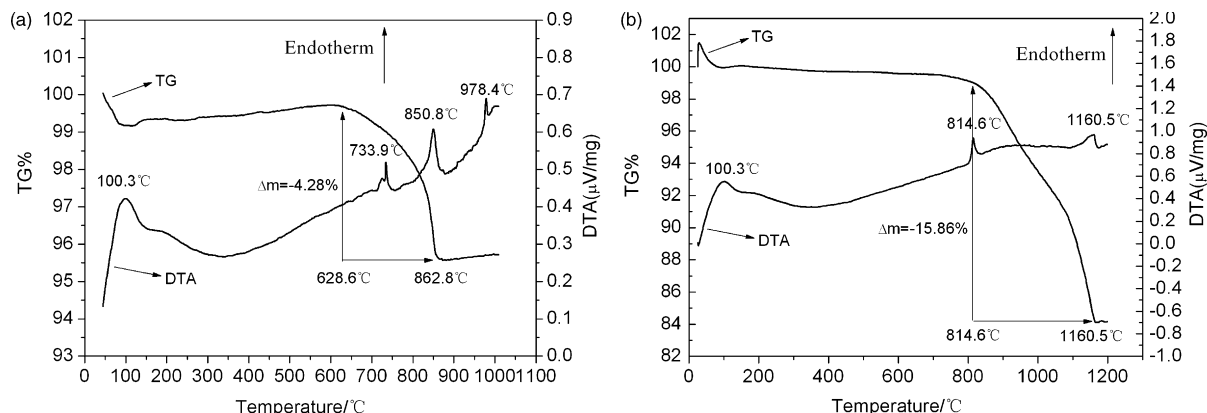


Fig. 1. TG–DTA curves for mixture powder of (a) $\text{Na}_2\text{CO}_3 + \text{Bi}_2\text{O}_3 + 4\text{TiO}_2$ and (b) $\text{BaCO}_3 + \text{TiO}_2$.

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