Transactions of the Materials Research Society of Japan 31[1] 47-50 (2006)

Crystal Growth and Electric-field-induced Strain in $Bi_{0.5}Na_{0.5}TiO_3$ Single Crystals

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Large $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) single crystals with 10 mm × 10 mm × 5 mm were successfully grown by a flux method using BNT powder and the mixed flux composed of Bi_2O_3 and NaF. Dielectric measurements show a dielectric-permittivity peak at 310°C, which is the result from the gradual phase transition from rhombohedral (*R*3*c*) to tetragonal (*P*4*bm*) structure. High-pressure oxygen annealing (750°C, 35 MPa) raised permittivity-peak temperature to 330°C. Leakage current measurements show that the annealing led to an increase in leakage current at room temperature by one order of magnitude, showing that the carrier of the leakage current is electron hole generated by the incorporation of oxygen at oxygen vacancies. Electric-field induced strain measurements along the $[100]_C$ reveal that the effective piezoelectric strain constant d_{33}^* was estimated to be 130 pm/V even in a multidomain state.
Key words: ferroelectrics, bismuth sodium titanate (BNT), single crystals, flux method

1. INTRODUCTION

Piezoelectric materials have been in commercial use for over 60 years as sensors, actuators and other electronic devices. The most widely used piezoelectric material is lead zirconium titanate (PZT), which contains a large amount of toxic lead. The illegal disposal of PZT-based devices is an urgent issue that must be addressed from environmental and industrial points of view. It is necessary to substitute lead-free materials for PZT in order to protect the environment and the ecosystem.

Since Smolenskii *et al.* reported that bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT), showed ferroelectric properties in 1961 [1], BNT has attracted a great deal of attention as a promising base material for a lead-free piezoelectric. BNT-based ceramics have been extensively investigated for use in both piezoelectric and pyroelectric applications, because of 1) ease of processing, *i.e.* no atmosphere control is necessary during processing and 2) good mechanical properties[2,3,4]. BNT has a rhombohedral structure with space group *R*3*c* at room temperature[5]. BNT is suggested to form a morphotropic phase boundary (MPB) with some other perovskite materials with tetragonal or orthorhombic symmetry, since superior piezoelectric properties are expected near the MPB composition. Recently, considerable efforts have been paid to improve the piezoelectric properties of BNT ceramics by forming solid solutions with other perovskite oxides such as $BaTiO_3$, $SrTiO_3$, $KNbO_3$ and so on [5,6,7,8].

Although there have been many reports on the BNT-based ceramics to date, few studies of BNT single crystals have been carried out[9,10], probably because of the difficulty of the crystal growth of BNT. The investigations on the single crystals are quite important for elucidating the fundamental properties as well as for establishing the material design for BNT-based materials. In this paper, we show that the flux method using the mixed flux composed of Bi_2O_3 and NaF is effective for obtaining large single crystals of BNT, and their dielectric, ferroelectric and piezoelectric properties are reported.

2. EXPERIMENTS

BNT ceramics were prepared by a conventional solid-state reaction. Powders of Bi_2O_3 and TiO_2 of 99.99% purity and Na_2CO_3 of 99.95% purity were used as starting raw materials. In order to compensate Na vaporization during heat treatments, excess powder of 20 at.% of Na_2CO_3 was added to the starting powder with the stoichiometric composition. These powders were mixed by ball milling for 1 h and calcined at 850°C for 4 h in an almina crucible.

Single crystals of BNT were grown by a flux method. Eprevier *et al.* have reported that large Bi_2WO_6 single crystals were obtained using Bi_2O_3-NaF mixed flux[11]. In this study, Bi_2O_3, NaF and B_2O_3 were used as flux for the growth of BNT crystals. The influence of flux composition on morphology, quality and size of the crystals obtained were investigated to obtain large and high-quality crystals. The temperature profiles for searching the optimum flux composition were as

follows: (1) heating from room temperature to 1200°C and dwelling for 5 h; (2) slow cooling to 1100°C at 20°C/h and then to room temperature. For dielectric and piezoelectric measurements, raw materials were melted at 1300°C for 20 h with the optimum composition and slowly cooled to 1200°C at a rate of 2°C/h. The crystals were annealed in air at 950°C for 24 h before electrical measurements. Some of the crystals were further annealed under high-pressure oxygen of 35 MPa at 750°C for 24 h. The structure of the crushed crystals was examined by X-ray diffraction (XRD) measurements. The XRD data were analyzed by the Rietveld method (the RIETAN2000 program[12]) on the basis of *R3c* rhombohedral symmetry. The composition of the BNT crystals was determined to be $Bi_{0.50}Na_{0.50}TiO_3$ by inductively coupled plasma (ICP) atomic emission spectroscopy.

For electrical measurements, the crystals were cut to be electric field (E) along $[100]_C$ direction, and then gold electrodes were sputtered on the $(100)_C$ faces. Polarization and piezoelectric properties were investigated with E // $[100]_C$.

3. RESULTS AND DISCUSSION

Although several flux compositions including B_2O_3 were attempted, BNT crystals were not obtained. Larger crystals were successfully grown using the mixed flux of Bi_2O_3 and NaF (2 mm × 2 mm × 2 mm) than those using Bi_2O_3 self flux (2 mm × 2 mm × 0.05 mm). The relation between Bi_2O_3-NaF flux composition and crystal size is listed in Table I. In this study, the optimum composition (weight ratio) of starting materials was determined to be 10 : 10 : 1 (BNT ceramics : Bi_2O_3 : NaF). Figure 1 shows the image of the BNT crystals melted at 1300°C. The change in dwelling temperature from 1200°C to 1300°C enabled us to obtain a larger crystal.

Figure 2 shows the XRD profile of BNT crystals. The Rietveld analysis indicates that the pattern observed fits

Table I. The relation between flux ratio and size of BNT crystals. The weight of BNT powder was fixed at 3 g (dwelling at 1200°C, cooling rate of 20°C/h).

Weight (Bi_2O_3 : NaF)	Size of the crystals (mm × mm × mm)
6.5 : 0.2	1 × 1 × 0.5
6.5 : 0.3	2 × 2 × 1
6.5 : 0.4	Not obtained.
1.5 : 0.3	Not obtained.
2.0 : 0.3	3 × 3 × 2
3.0 : 0.3	5 × 3 × 3
3.5 : 0.3	2 × 2 × 2
5.0 : 0.3	2 × 2 × 2

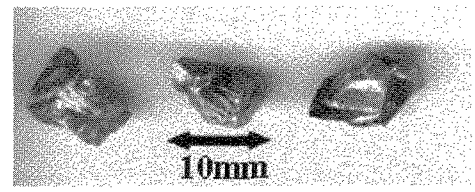


Fig. 1 BNT crystals melted at 1300°C.

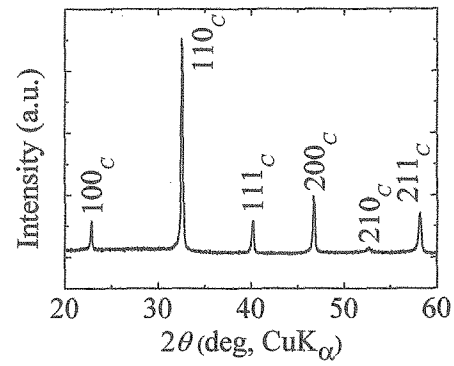
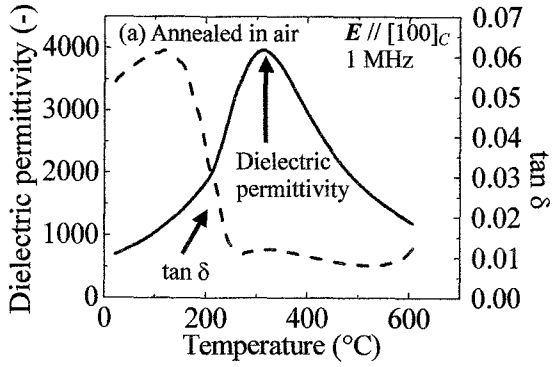


Fig. 2 XRD profile of the crushed powder of BNT crystals.

fairly well to the calculated one (R_{wp} = 10.8%, S = 1.29). The lattice parameters were determined to be $a(b)$ = 0.551 610(6) nm, c = 1.35 6209(1) nm, which agree well with the crystals data reported by Jones *et al.*[13].

Figure 3(a) and 3(b) show dielectric properties of BNT crystals annealed in air and in high pressure O_2 at a frequency of 1 MHz on cooling (E // $[100]_C$), respectively. The temperature of the permittivity peak, T_m, of the BNT crystals annealed in air was 310°C. This T_m value is consistent with the previous report of BNT crystals[10]. The dielectric permittivity at room temperature was 710, which is comparable to that of BNT crystals[10] and ceramics[14]. Jones *et al.*[13] have reported a detailed structural phase transition in BNT; low-temperature *R3c* rhombohedral, intermediate *P4bm* tetragonal and high-temperature *P-3m* cubic. These phase transitions gradually take place through the coexisting temperature region. Around 310°C, *R3c* rhombohedral and *P4bm* tetragonal coexist and their volume fraction is almost the same at 310°C. It is suggested that the dielectric permittivity peak at T_m is the result from the gradual rhombohedral/tetragonal transition. Jones *et al.*[13] have also shown that the tetragonal/cubic coexistence region lies from 500°C to 540°C, and the phase above 540 °C is cubic. A dielectric anomaly was not observed around 540 °C in this study. The T_m of the BNT crystals annealed in high pressure O_2 was 330°C, which is almost the same as that of BNT annealed in air. The high-pressure oxygen annealing led



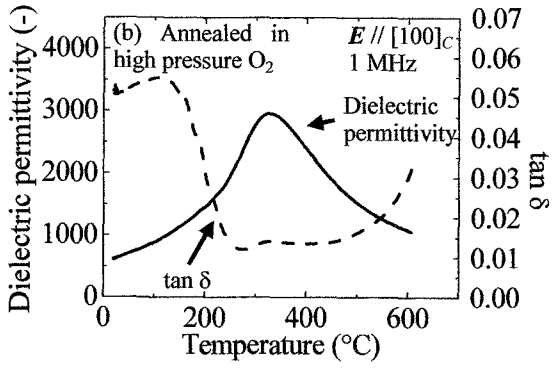


Fig. 3 Dielectric properties of crystals
(a) annealed in air
(b) annealed in high pressure O_2.

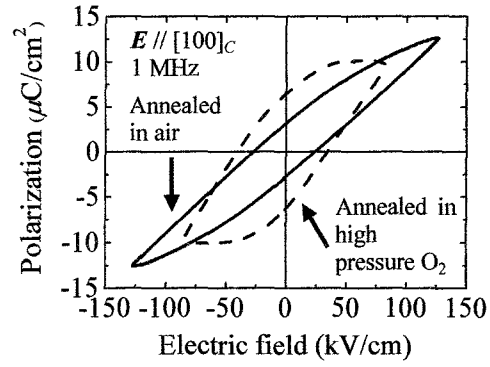


Fig. 4 *P-E* hyseresis loops of crystals.

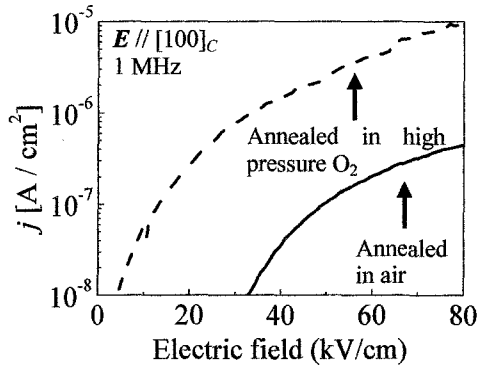


Fig. 5 Leakage current density of crystals.

to a decrease in dielectric permittivity from 710 to 620. Figure 4 shows the polarization hysteresis loop of the crystals annealed in air and in high pressure O_2 along the $[100]_C$. Although the electric field is much higher than the E_c value reported for BNT ceramics [1], a saturated polarization hysteresis was not obtained, probably due to the pinning of domain walls by defects. After annealing in high pressure O_2, the hysteresis became less saturated, probably due to the higher leakage current. Figure 5 shows the leakage current density of crystals along the $[100]_C$. The annealing in high pressure O_2 yielded a higher leakage current density by one order of magnitude. This result is direct evidence that the carriers of the BNT crystals are electron holes. It is well known that bismuth evaporates easily from crystal lattice during heating. The following Bi vaporization is considered to occur during crystal growth.

$$Bi_2O_3 = 2Bi(gas) + \frac{3}{2}O_2 + 2V_{Bi}''' + 3V\ddot{o} \qquad (1)$$

Here V_{Bi}''' and Vö are bismuth vacancies with three negative effective charges and oxygen vacancies with two positive effective charges, respectively. Equation (1) indicates that the generation of Bi vacancies is accompanied by Vö for maintaining charge neutrality. The resultant Vö causes the oxide-ion conduction in BNT at high temperatures. The electron holes, which is the origin of leakage current for BNT crystals, is induced by incorporation of oxygen in the gas phase into the lattice as expressed by

$$\frac{1}{2}O_2 + V\ddot{o} = Oo^* + 2h^{\cdot}, \qquad (2)$$

where Oo^* is lattice oxygen. The results shown in Figure 5 indicate that the reaction for generating electron holes is dominant for the BNT crystals.

Figure 6 shows the electric-field-induced strain of BNT crystals annealed in air (***E*** // $[100]_C$) at a frequency of 1 Hz. The effective piezoelectric strain constant (d_{33}^*) was estimated to be 130 pm/V from the slope. Even though this crystal was not in a fully poled state, the relatively high d_{33}^* was obtained, suggesting that an improvement of the quality of the BNT crystals leads to a significant enhancement of the piezoelectric properties.

4. CONCLUSIONS

Large BNT single crystals were obtained by a flux method using the mixed flux composed of Bi_2O_3 and NaF. The Rietveld analysis showed that the crystals have the rhombohedral *R*3*c* structure. Dielectric measurements showed that the T_m of the BNT crystals

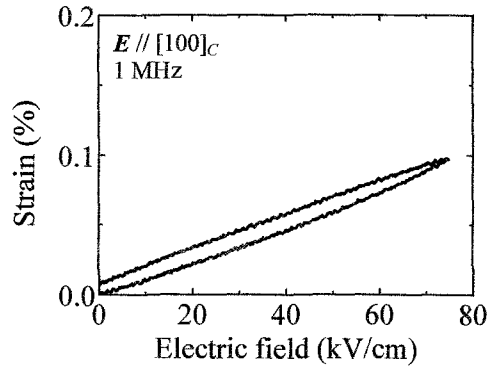


Fig. 6 Strain vs. electric field for BNT crystals.

was 310°C, which was assigned to the gradual phase transition from rhombohedral (*R*3*c*) to tetragonal (*P*4*bm*) phase. The oxygen annealing experiments revealed that the carrier of leakage current is electron hole generated by the incorporation of oxygen at oxygen vacancies. BNT crystals did not show a saturated polarization hysteresis, while the d_{33}^* value of the crystals was estimated to be 130 pm/V.

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(Received December 10, 2005; Accepted January 31, 2006)