Polarization and piezoelectric properties of high-quality (Bi,Na)TiO₃ crystals grown by high-oxygen-pressure flux method

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Crystal growth at a high P_{O_2} (oxygen pressure) is developed for Bi_{0.5}Na_{0.5}TiO₃ single crystals based on defect chemistry at high temperatures. Bi_{0.5}Na_{0.5}TiO₃ crystals grown at $P_{O_2} = 1$ MPa show a saturated remanent polarization of 44 $\mu\text{C}/\text{cm}^2$ along $[110]_{\text{cubic}}$, suggesting a spontaneous polarization of 54 $\mu\text{C}/\text{cm}^2$ along $[111]_{\text{cubic}}$ (polar direction) of rhombohedral Bi_{0.5}Na_{0.5}TiO₃. High- P_{O_2} heat treatments are demonstrated to be suitable for fabricating high-quality and high-performance ferroelectric and piezoelectric devices using Bi_{0.5}Na_{0.5}TiO₃ crystals

Key words: ferroelectrics, piezoelectrics, single crystal, lead free, perovskite

1. INTRODUCTION

Pb(Zr,Ti)O₃ and related Pb-based perovskite oxides have been widely used as the ferroelectric and piezoelectric material of sensors, transducers, actuators and non-volatile memories. Since the use of Pb(Zr,Ti)O₃ in electronic materials would be restricted in the near future due to the toxicity of lead, the development of lead-free ferroelectric and piezoelectric materials with sufficient properties has been strongly demanded from the environmental and economical points of view. Recently, lead-free perovskite ferroelectrics of BaTiO₃ (BT)-based materials¹⁻³⁾, (Bi, K, Na)TiO₃⁴⁻⁷⁾, (K, Na)NbO₃ (KNN)⁸⁻¹⁰⁾ and layered ferroelectrics of SrBi₂Ta₂O₉¹¹⁻¹⁴⁾, Bi₄Ti₃O₁₂ (BiT)¹⁵⁻¹⁸⁾, CaBi₄Ti₄O₁₅¹⁹⁻²²⁾ and their derivatives²³⁻²⁵⁾ have attracted a great deal of attention as alternative materials of Pb(Zr,Ti)O₃.

KNN⁸⁻¹⁰⁾ has been recognized as a promising lead-free material, because of its high Curie temperature (T_C) of 420 °C and superior piezoelectric properties. KNN shows a consecutive structural phase transitions from cubic to tetragonal around 420 °C and tetragonal to orthorhombic around 200 °C. BT has recognized as cost-effective lead-free piezoelectric materials. Recent investigations^{1,2,26)} have demonstrated that fine-grained BT ceramics with a grain size of ~100 nm show a large piezoelectric strain constant (d_{33}), in which engineered domain configurations^{26,27)} probably enhance the piezoelectric properties. However, T_C of BT is as low as 135 °C, and furthermore fine-grained BT ceramics exhibit a tetragonal-orthorhombic transition temperature around room temperature.³⁾ Since the temperature dependence of materials properties becomes marked near phase-transition temperature, the phase transition near room temperature constitutes an obstacle to the practical applications of BT.

Pioneering works by Takenaka *et al.*⁴⁻⁶⁾ have demonstrated that (Bi,Na)TiO₃ (BNT) is an attractive piezoelectric material because of a high T_C of 320 °C and a large spontaneous polarization. One of the problems to be overcome is that depolarization temperature (T_d), i.e., piezoelectric activities disappear or are markedly reduced over T_d , lies around 200 °C for BNT^{7,28,29)} due to the structural phase transition from

rhombohedral ($R3c$ symmetry: ferroelectric) to tetragonal ($P4bm$ symmetry: ferriferroelectric).²⁸⁾ Recent investigations have focused on increasing T_d for the solid solutions of BNT with other perovskite materials.^{7,29)} It is considered that the use of BNT-based ferroelectrics for piezoelectric materials opens up the possibility of lead-free piezoelectric devices in views of properties and cost-effectiveness.

Defects in ferroelectric materials play an important role in their properties of leakage current, ferroelectric and piezoelectric properties. The control of polarization states is the underlying basis of ferroelectric and piezoelectric devices. Polarization switching is achieved through nucleation of domains and subsequent domain-wall motion by applying an electric field (E). Leakage current arising from defects, however, interferes with the polarization switching of Bi-based ferroelectrics.³⁰⁻³²⁾ In addition, oxygen vacancies are known to act as an obstacle to the polarization switching,^{33,34)} and a resultant remanent polarization (P_r) is reduced by the clamping of the domain walls by oxygen vacancies. The leakage current and domain clamping by oxygen vacancies make ferroelectric materials unsuitable for practical applications.³⁵⁻³⁸⁾ Thus, materials design based on defect chemistry is required to be established for fabricating high-quality Bi-based devices with superior piezoelectric properties. Investigations on single crystals seem advantageous to investigate the influences of defects on the properties of ferroelectric materials, in which microstructure and grain size does not affect the properties.

In this paper, high- P_{O_2} (oxygen pressure) crystal growth, the crystal growth at a high P_{O_2} is demonstrated to be effective for enhancing polarization and piezoelectric properties of BNT single crystals. It is proposed that high- P_{O_2} heat treatments are effective for fabricating high-quality and high-performance ferroelectric and piezoelectric devices using Bi-based ferroelectric oxides.

2. EXPERIMENTAL

BNT powder was prepared by a solid-state reaction. Raw materials of Bi₂O₃ (99.9999%), TiO₂ (99.99%) and

Na₂CO₃ (99.95%) were mixed with the stoichiometric composition by ball milling. The mixed powder was calcined at 800 °C for 4 h in air, which led to single-phase BNT powder. Single crystals of BNT were grown by a flux method. Crystal growth was performed at a P_{O_2} of 0.02 MPa (air), 0.1 MPa (O₂ gas flow with a flow rate of 100 ml/min) and 1 MPa. High- P_{O_2} crystal growth at 1 MPa was done using the pocketed-heat electronic furnace (HPF-1300, Crystal Systems Corp.) In this paper, P_{O_2} denotes oxygen pressure during crystal growth, while in TG analysis P_{O_2} expresses an oxygen partial pressure in the measurement system. The calcined powder of BNT mixed with Bi₂O₃-NaF flux was put in a platinum crucible. The mixture was soaked at 1250 °C for 20 h and then slowly cooled to 1150 °C at a rate of 2 °C/h. Yellowish transparent crystals with a size of 2×2×2 mm³ were obtained. Before electrical measurements, the crystals were annealed in air at 950 °C for 10 h to reduce oxygen vacancies as well as to release stress induced during crystal growth.

Resonator specimens were prepared by cutting the crystals into rectangular prisms with $0.6 \times 0.6 \times 1.6$ mm³, of which the long axis was parallel to [110]_{cubic}. These specimens were poled along the long axis under an E of 50 kV/mm for 10 min in a silicone oil at 148 °C. The resonance-antiresonance characteristics were measured using an impedance/grain phase analyzer, and effective electrochemical coupling coefficient of the length-extensional 33 vibration mode (k_{33}) was evaluated by the standard resonance method (JEITA EM-4501).

3. RESULTS AND DISCUSSION

Figure 1 shows the polarization-electric field (P - E) hysteresis loops at 25 °C along [110]_{cubic}. A polarization hysteresis was observed for the crystals (P_{O_2} = 0.02 MPa and 0.1 MPa). These crystals exhibited a remanent polarization (P_r) of approximately 22–24 $\mu\text{C}/\text{cm}^2$ and a coercive field (E_c) of 35–45 kV/cm. This value of P_r was higher than those reported previously.³⁹⁾ Note that the high- P_{O_2} -grown crystals (P_{O_2} = 1 MPa) show a well-saturated hysteresis loop with a P_r of 44 $\mu\text{C}/\text{cm}^2$ and an E_c of 39 kV/cm. These results demonstrate that crystal growth at a higher P_{O_2} of 1 MPa is effective for enhancing polarization switching in BNT crystals, as has also been reported for Bi₄Ti₃O₁₂ crystals.³⁸⁾ Assuming that polarization switching is completely accomplished for the crystals (P_{O_2} = 1 MPa), one can estimate the P_s value along the polar direction of [110]_{cubic} of 54 $\mu\text{C}/\text{cm}^2$ from the P_r value (44 $\mu\text{C}/\text{cm}^2$) along [110]_{cubic}.

Figure 2 indicates the leakage current properties measured at 25 °C along [110]_{cubic}. The leakage current density (J) of the crystals (P_{O_2} = 0.02 MPa) was of the order of 10^{-7} A/cm. It is worthy of note that higher P_{O_2} during crystal growth led to a marked decrease in J . An extremely low J of the order of 10^{-9} A/cm was found for the crystals (P_{O_2} = 1 MPa). The increase in P_{O_2} from 0.02 MPa to 1 MPa suppressed J by approximately two orders of magnitude.

Figure 3 (a) shows the electric-field-induced strain of BNT crystals measured at 25 °C. Before measurements, a unipolar E of 100 kV/cm was applied to the crystals at 25 °C for poling treatments. Apparent strain data were not obtained for the crystals (P_{O_2} = 0.02 MPa), probably

Fig.1 Polarization hysteresis loops measured at 25 °C at a frequency of 1 Hz along [110]_{cubic} of the crystals grown at a P_{O_2} of 0.02 MPa, 0.1 MPa and 1 MPa.

Fig. 2 Leakage current densities as a function of applied E along [110]_{cubic} of the crystals grown at a P_{O_2} of 0.02 MPa, 0.1 MPa and 1 MPa.

Fig. 3 (a) Unipolar and (b) bipolar electric-field-induced strain measured at 25 °C at a frequency of 1 Hz along [110]_{cubic} of the crystals grown at 0.1 MPa and at 1 MPa.

due to insufficient poling (multidomain state, which is discussed later). The crystals ($P_{O_2} = 0.1$ MPa and 1 MPa) showed a linear strain with respect to E . It is found that the rotation of non-180° domains makes a minor contribution to the strain properties, which is evident from the small hysteresis in the strain curves. The maximum strain over the maximum E ($S_{\max}/E_{\max}$) was determined to be 96 pm/V ($P_{O_2} = 0.1$ MPa) and 133 pm/V ($P_{O_2} = 0.1$ MPa). These results show that the piezoelectric strain properties are improved for the crystals grown at a higher P_{O_2} . Figure 3(b) exhibits the bipolar strain properties (25°C). Although the crystals ($P_{O_2} = 0.1$ MPa) did not show an apparent strain jump due to polarization switching, a well-established butterfly strain loop was clearly observed for the crystals ($P_{O_2} = 0.1$ MPa). The $S_{\max}/E_{\max}$ value obtained from the butterfly strain loop was 132 pm/V, which is in good agreement with the unipolar value (133 pm/V).

Figure 4 illustrates the frequency dependences of impedance and phase for the prism-shaped crystals grown at $P_{O_2} = 1$ MPa. The poling treatment ($E = 50$ kV/mm for 10 min at 148 °C) led to a phase maximum ($\theta_{\max}$) of 86 deg, which was slightly smaller than 90 deg. The smaller value of $\theta_{\max}$ than 90 deg is caused by an insufficient poling treatment, i.e. domain switching along the poling direction was not completely established due to a difficulty of P_s rotation and/or switching along $[110]_{\text{cubic}}$. The crystals ($P_{O_2} = 1$ MPa) had a k_{33} of 54 %. The measurements reveal a relative dielectric permittivity under zero elastic stress of 591. An effective piezoelectric strain constant (d_{33}) determined by the resonance-antiresonance method was 131 pm/V, which agrees well with the $S_{\max}/E_{\max}$ of 133 pm/V determined by the unipolar strain measurements. These results lead to the conclusion that high- P_{O_2} crystal growth is advantageous to enhanced ferroelectric and piezoelectric properties as well as to reduced leakage current of BNT crystals.

Figure 5 shows the domain structure observed by optical microscope for the as-grown crystals ($P_{O_2} = 0.02$ MPa and 1 MPa). The lines observed in the crystals are the non-180° DWs with the 71°- or 190°- P_s configurations. The high- P_{O_2} -grown crystals ($P_{O_2} = 1$

Fig. 4 The frequency dependences of impedance and phase for the crystals grown at $P_{O_2} = 1$ MPa (25°C). The poling treatment was performed at an $E = 50$ kV/mm for 10 min at 148°C.

MPa) had a smaller number of the non-180° DWs were compared with the crystals ($P_{O_2} = 0.02$ MPa). During cooling from high-temperature paraelectric state to ferroelectric phase, the non-180° DWs as well as the 180° DWs are established. If $[VO^{\bullet}]$ (oxygen vacancy) is sufficiently low for the non-180° DWs to have a high mobility, the non-180° DWs disappear, because the elastic energy of the non-180° DWs increases the total energy of the crystals. For the crystals with a higher $[VO^{\bullet}]$, the mobility of the non-180° DWs becomes lower due to the interaction between the DWs and $VO^{\bullet}$. The non-180° DWs are stabilized by $VO^{\bullet}$, which is clearly seen in the crystals ($P_{O_2} = 0.02$ MPa) [Fig. 8 (a)]. When $[VO^{\bullet}]$ is higher, some of the non-180° DWs are clamped due to the strong interaction between the DWs and $VO^{\bullet}$. Therefore, the non-180° DWs lose their mobility even if a high E is applied to the crystals with high $[VO^{\bullet}]$. The crystals ($P_{O_2} = 0.02$ MPa) indicated a small P_r compared with the crystals ($P_{O_2} = 1$ MPa) [Fig. 1]. The value of P_r is proportional to the volume fraction of switchable domains by applying an E . The small P_r observed for the crystals ($P_{O_2} = 0.02$ MPa) indicates that a large number of the non-180° DWs are clamped by $VO^{\bullet}$ even though a high E of 90 kV/cm is applied to the crystals. It is concluded that the smaller value of P_r for the crystals ($P_{O_2} = 0.02$ MPa) is attributed to the strong interaction between the non-180° DWs and $VO^{\bullet}$.

Fig. 5 (a) The temperature profile employed for the thermogravimetric analysis and (b) the weight loss for BNT powder at a gas-flow rate of 100 ml/min. P_{O_2} indicates the oxygen partial pressure during the thermogravimetric analysis.

4. CONCLUSIONS

Single crystals of BNT were grown by flux method, and the effects of P_{O_2} during crystal growth on the properties were investigated in view of defects formed at high temperatures. BNT crystals grown at $P_{O_2} = 1$ MPa exhibited a well-saturated polarization hysteresis with a P_r of 44 $\mu\text{C}/\text{cm}^2$ along $[110]_{\text{cubic}}$. This value of P_r along $[110]_{\text{cubic}}$ suggests that the P_s value along $[111]_{\text{cubic}}$ (the polar direction) is as high as over 54 $\mu\text{C}/\text{cm}^2$. The crystals grown at $P_{O_2} = 1$ MPa exhibited a low leakage current density of $\sim 10^{-9}$ A/cm². A butterfly-like loop in strain curve was observed for the crystals ($P_{O_2} = 1$ MPa), and the $S_{\max}/E_{\max}$ value along $[110]_{\text{cubic}}$ estimated by the slope of unipolar strain was 133 pm/V. The resonance-antiresonance measurements reveal a k_{33} of 54 % and a d_{33} of 132 pm/V.

It is suggested that in ferroelectric state oxygen vacancies are stabilized near non-180° domain walls due to the attractive interaction between them. The depolarization field due to the spatial variation of P_s

vector in non-180° domain walls is attributed to the attractive interaction. Domain structure observations by optical microscope confirms that the crystals grown at a higher P_{O_2} had a smaller number of non-180° domain walls, which appears to originate from the lower concentration of oxygen vacancies. It is proposed that high-oxygen-pressure heat treatments are effective for fabricating high-quality and high-performance ferroelectric and piezoelectric devices using Bi-based ferroelectric oxides.

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