1. Introduction

Development of Pb-free ferroelectric and piezoelectric materials with sufficient properties has been strongly demanded from the environmental concerns associated with the toxicity in Pb-based perovskite oxides and the legislative restriction of Pb use in electronic devices in the European Union and a part of Asia. BaTiO3 (BTO), KNbO3, NaNbO3, LiTaO3, LiNbO3, and their related materials have long history of research and development.\(^1\)-\(^13\) Recently, fine-grained BTO ceramics, thin films, and related multi-layered ceramic capacitor (MLCC) devices are on the hot topic in the ferroelectric and piezoelectric community in the world since they represented a large piezoelectric constant and strain displacement.\(^13\)-\(^13\) Not only these ferroelectric and piezoelectric materials, but also Bi-based perovskite oxides are already generating a lot of attention. Takenaka et al. have demonstrated that the Bi-based perovskite oxides such as (Bi,Na)TiO\(_3\) (BNT), Bi\(_4\)Ti\(_3\)O\(_{12}\) (BiT), and their related solid solutions are attractive piezoelectric materials\(^{14}-\(^{31}\)\) because of their large spontaneous polarization (P\(_s\)) and superior high-power properties\(^{19},^{20},^{27}\) owing to their high mechanical quality factor (Q\(_{m}\))\(^{19},^{26}-\(^{31}\)\) for the study of BNT, since its piezoelectric properties are lost or drastically deteriorated above the depolarization temperature (T\(_d\)) of around 185°C for BNT\(^{20},^{21}\) due to the structural phase transition from rhombohedral (R3c symmetry: ferroelectric) to tetragonal (P4bm symmetry: ferroelectric).\(^{31}\) The investigations of increasing the T\(_d\) for the solid solutions between the BNT and other perovskite materials have been paid attention to.\(^{17}-\(^{23}\)\) The use of BNT-based ferroelectrics as piezoelectric materials is considered to help the development of lead-free piezoelectric devices with suitable properties in a cost-effective manner.

Defects in ferroelectric materials markedly affect their leakage current, ferroelectric, and piezoelectric properties. The control of polarization states is the underlying principle of ferroelectric and piezoelectric devices. Polarization switching is achieved through the nucleation of domains and subsequent domain wall motions by the application of an electric field. The leakage current arising from defects, however, interferes with the polarization switching of Bi-based ferroelectrics.\(^{33}-\(^{35}\)\) In addition, oxygen vacancies are known to obstruct polarization switching,\(^{36},^{37}\) resulting in a reduction in remanent polarization (P\(_r\)) by the clamping of the domain walls. The leakage current and clamping of the domain walls by oxygen vacancies make ferroelectric materials unsuitable for practical applications.\(^{38}-\(^{40}\)\) Therefore, materials design based on defect chemistry is essential for fabricating high-quality Bi-based devices with superior ferroelectric and piezoelectric properties. It is advantageous to investigate single crystals in order to study the influences of defects on the properties of ferroelectric materials since these properties are unaffected by the microstructure and grain size of the materials. Based on this standpoint, high-P\(_{02}\) (partial oxygen pressure) crystal growth in order to suppress Bi vaporization is demonstrated to be effective for enhancing the polarization and piezoelectric properties of BNT and BiT single crystals.\(^{41}-\(^{43}\)\) Whereas the Bi-based ferroelectric single crystals grown in high-P\(_{02}\) of approximately 1 MPa represented highly superior
leakage current and ferroelectric properties compared with those of single crystals grown in air, it is also of great difficulty to deposit high quality Bi based ferroelectric thin films with sufficient properties since a number of ferroelectric oxides thin film synthesis methods, such as sputtering, pulsed laser deposition (PLD) method and metal organic chemical vapor deposition (MOCVD) method, are high vacuum processes. B. H. Park et al. inferred from X-ray photoemission spectroscopy (XPS) analysis for the Bi-Ti-O thin films annealed under P02 of 10−5 torr that oxygen vacancies were found at both the (Bi2O3)x and the (Bi2Ti3O12)y perovskite layers. They demonstrated to improve the polarization properties of BiT thin films by some Bi ions substituted near the Ti-O octahedron layers with the La ions in order to reduce the oxygen vacancy at perovskite layer. They represented the larger polarization property for the Bi1.25La0.75Ti3O12 (LBT) films than that of BiT films, although the La substitution causes intrinsic ferroelectricity to gradually deteriorate. Additionally, T. Watanabe et al. achieved to exhibit better ferroelectric properties for the Nd substituted BiT thin films than those of LBT thin films. In a ceramic processing based on solid-state reaction, BNT and BiT have been sintered at a high temperature of around 1200°C to obtain dense ceramics. Such a high-temperature treatment induces a vaporization of Bi with a high vapor pressure, which leads to a formation of vacancies of Bi and oxygen. The polarization and piezoelectric properties of BNT and BiT ceramics sintered at high temperatures are influenced to some extent by leakage current and clamping of domain walls. Noguchi et al. demonstrated that V doping for BiT was effective for a decrease in oxygen vacancies and significantly reduce the influence of domain clamping, which was responsible for a large P and E. Also Nagata reported the influence of oxygen vacancies on ferroelectric and piezoelectric properties for the Nd substituted BiT and BNT ceramics with the excess Bi2O3 fabricated by conventional solid phase reaction and hot-press method. Not only lanthanoid substitution, but also V, Bi2O3 addition and low temperature sintering by use of the hot-press method, but also an aerosol deposition (AD) method is expected to be useful for obtaining stoichiometric Bi-based ferroelectric materials with sufficient properties. The AD method, which is based on a room temperature impact consolidation (RTIC) phenomena, is attracting attention because it can form thick ceramic layers at a room temperature. The use of AD method has been already reported for the fabrication of the Pb(Zr, Ti)O3 (PZT) and its application as a component in a piezoelectric actuator. Fully dense BTO ceramic films on resin substrates were also successfully fabricated by the AD and they were investigated taking into consideration their possible application to low temperature co-fired ceramics (LTCC). While the AD method can provide the fully dense ceramics at a room temperature, the crystallite size of the as-deposited AD films is too small to exhibit good ferroelectric properties. However, the crystallite size can be controlled by a low temperature annealing under a variety of atmosphere (such as high-P02 and vaporized Bi atmosphere), which leads to a suppressing the Bi vaporization.

In this study, high-P02 flux method and use of the AD method have been demonstrated to be effective for the obtaining high quality BNT single crystals and polycrystalline ceramics. BNT single crystals were grown by the high-P02 flux method and their polarization and piezoelectric properties were investigated along [100], [110], and [111]), where “c” denote cubic notation used in this paper throughout. Strain measurements of rhombohedral BNT crystals suggest that the polarization reversal along [111] is achieved by non-180° P rotation. The values of P obtained along these three directions provide a value of P of 55–60 μC/cm² for rhombohedral BNT at 25°C, and then, a maximum P of 48–52 μC/cm² are estimated for the BNT polycrystalline ceramics, where Pmax poly is complete electric poling for rhombohedral polycrystalline ferroelectrics can be obtained directly from the analytical formula of √3/2 x P. The AD method supplied the fully dense BNT polycrystalline films. A heat treatment of 500°C detached the BNT polycrystalline films from the substrates. The annealed self-supported BNT polycrystalline ceramic films indicated a superior leakage current density (J) and well-saturated hysteresis loops with a large P of 40 μC/cm², which were better quality than those of the sintered bulks.

2. BNT Single crystals grown in high oxygen partial pressure

(Bi0.5Na0.5)TiO3 (BNT) single crystals were grown by a high-P02 flux method and their polarization and piezoelectric properties were investigated along [100], [110], and [111]), the values of P obtained along these three directions provide a value of P of 55–60 μC/cm² at 25°C for rhombohedral BNT. BNT powder was prepared by a solid-state reaction. The raw materials, Bi2O3 (99.999%), TiO2 (99.999%), 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 yielded single-phase BNT powder. Single crystals of BNT were grown by a flux method. Crystal growth was performed at a high P02 of 1 MPa (under O2 gas flow at a flow rate of 2.5 l/min at 0.1 MPa with a pulse pressure controller) in a pocketed-heat electronic furnace (Crystal Systems HPF-1300). Calcined BNT powder mixed with Bi2O3–NaF flux was placed in a platinum crucible. The mixture was soaked at 1250°C for 20h, slowly cooled to 1100°C at a rate of 2°C/h, and then furnace cooled to room temperature. Remaining flux was removed by washing it in hot nitric acid, and crystals were taken out from the flux. Yellowish transparent crystals with dimensions 10 × 10 × 10 mm³ were obtained. Before electrical measurements, the crystals were annealed in air at 950°C for 10h to reduce oxygen vacancies as well as to release stress induced during crystal growth. For the measurements of polarization hysteresis, leakage current and electric-field-induced strain (Toyo, FCE-1), the annealed crystals were cut into 0.1–0.2-mm-thick plates, and gold electrodes were sputtered onto the cut surfaces. Figure 1 indicates the polarization properties of BNT single crystals measured at 1 Hz (25°C) along [100], [110], and [111]). Well-saturated hysteresis loops were observed along all three directions. The values of P were 31 μC/cm² along [100], 44 μC/cm² along [110], and 55 μC/cm² along [111]. Compared with a P of 22 μC/cm² along [100]), of BNT crystals grown in air, a large P was observed, because BNT crystals grown at a high-P02 obtained in this study have less oxygen vacancies and Bi vacancies. It has been reported that the strong attractive interaction between non-180° domain walls and oxygen vacancies is origin of the domain clamping, i.e., a low P for BiT single crystals. It is considered that the low value of P obtained for BNT crystals grown in air is attributed to the domain clamping of non-180° domain walls. The estimated P from these polarization properties for BNT crystals grown at a high P02 was approximately 55–60 μC/cm² at 25°C.

Figure 2 exhibits the bipolar and unipolar strain curves of BNT crystals measured at 1 Hz. Well-established butterfly strain loops are clearly observed for all specimens. The values of
maximum strain \((S)\) over the maximum \((E)\) \((S_{\text{max}}/E_{\text{max}})\) were determined to be 127 pm/V along \([100]\), and 63 pm/V along \([111]\), at 25°C. BNT crystals along \([111]\) indicated a large negative strain \((-0.33\%)\) at an \(E\) around \(E_c\) at 25°C. To investigate the influence of depolarization \((T_d)\) on the electric-field induced strain, the strain curves were measured at 180°C along \([100]\), and \([111]\), and compared with those at 25°C. As shown in Fig. 2. (a) (along \([100]\)), A strain value at a high \(E\) was larger at 180°C than that at 25°C. A strain jump due to polarization switching at around \(E_c\) slightly increased at 180°C compared with that at 25°C. The value of \(S_{\text{max}}/E_{\text{max}}\) (127 pm/V at 25°C) increased up to 217 pm/V at 180°C [Fig. 2(c)]. It is worth noting that the strain curves along \([111]\), were significantly different at between 25 and 180°C [Figs. 2(b) and 2(d)]. For the strain data at 25°C, a large negative strain was observed in the bipolar strain curve [Fig. 2(b)]. Since this takes place at around \(E_c\), the negative strain is considered to originate from polarization switching. A strain difference due to the polarization switching reaches \(-0.33\%\). A liner strain \((S_{\text{max}}/E_{\text{max}} = 63 \text{ pm/V})\) with respect to \(E\) in the unipolar strain curve [Fig. 2(d)] were observed at 25°C due to inverse piezoelectric effect. In contract, The bipolar strain at 180°C did not show a negative strain and exhibited a relatively large jump with a positive sign of approximately +0.17% [Fig. 2(b)]. Furthermore, the unipolar strain curve at 180°C [Fig. 2(d)] indicates a hysteresis with a strain jump at around 25 kV/cm, and its \(S_{\text{max}}/E_{\text{max}}\) value was 456 pm/V.

Here, topics of mechanism of polarization reversal by applying an \(E\) in BNT single crystals are discussed. There are two possible mechanisms for the polarization reversal. One is that \(P_s\) vector rotates through the formation of ferroelastic domains (71 and 109° domains), which is denoted by non-180° \(P_s\) rotation. The other is that \(P_s\) vector is directly switched by 180°, which is called as 180° \(P_s\) switching. For non-180° \(P_s\) rotation, the value of strain induced by polarization reversal, \(S_{\text{non-180° } P_s \text{ rotation}}\) is determined mainly not by inverse piezoelectric effect but by the deformation of unit cell attributed to non-180° \(P_s\) rotation. \(S_{\text{non-180° } P_s \text{ rotation}}\) can be calculated from the structural data reported by Jones and Thomas.32 For 180° \(P_s\) switching, the value of strain induced by polarization switching, \(S_{180° P_s \text{ switching}}\) is dominated primarily by inverse piezoelectric effect, because unit cell does not deform by 180° \(P_s\) switching. \(S_{180° P_s \text{ switching}}\) can be estimated from effective strain constant, i.e., \(S_{\text{max}}/E_{\text{max}}\), obtained from strain measurements.

Here, topics of \(S_{\text{non-180° } P_s \text{ rotation}}\) along \([111]\) are discussed. \(S_{\text{non-180° } P_s \text{ rotation}}\) originates from rhombohedral distortion are discussed. A rhombohedral distortion results in a splitting of \(111_c\) peak into \(111_1\) and \(111_2\) and then the values of the lattice spacing of \(d(111_c)\) and \(d(111_c)\) become different. The crystal anisotropy and rhombohedral distortion in BNT crystals with \(R3c\) structure are shown in Fig. 3(a). Here, we define \(d(111_1)/d(111_c)\) as an indicator of rhombohedral distortion. Cubic structure gives

![Fig. 1. Polari...](image-url)
From these values, $S_{\text{non-180°}}$, induced by polarization reversal can be calculated by the following formula: $S_{\text{non-180°}} = \frac{d_{\text{111},c} - d_{\text{111},c}}{d_{\text{111},c}}$ [see Fig. 3(c)]. According to this equation, we can obtain a value of $S_{\text{non-180°}}$ of $-0.34\%$ at 20°C and $-0.18\%$ at 180°C. This calculated value of $S_{\text{non-180°}}$ agrees qualitatively with the strain data along [111], at 25°C, in which the strain difference around their $E_s$ is due to polarization reversal was $-0.33\%$. In addition, the $S_{\text{non-180°}}$ value of $-0.18\%$ (at 180°C) is in fairly good agreement with the strain data along [111], at 180°C. These results suggest that the polarization reversal in rhombohedral BNT when an $E$ is applied along [111], is achieved by non-180° (71° or 109°) $P_s$ rotation [see Figs. 3(b) and 3(c)].

Here, topics of the difference between the strain curves at 25 and 180°C along [111], are discussed. When a bipolar $E$ was applied [Fig. 2(b)], BNT crystals exhibited a negative strain at 25°C while the crystals showed a positive one at 180°C. In addition, for the unipolar strain curves [Fig. 2(d)], BNT crystals exhibits an almost no hysteresis at 25°C, whereas the strain curve at 180°C exhibited a large hysteresis with a strain jump. If the depolarization is negligible, i.e., the domain state established by applying an $E$ remains stable, a linear strain with respect to $E$ should be observed due to inverse piezoelectric effect, as observed for the unipolar strain for BNT crystals at 25°C.

One of the possible reasons for the large hysteresis in the strain curve observed at 180°C is related to depolarization because the measurement temperature (180°C) was higher than that of depolarization temperature (130–150°C). The structural analysis [32] indicates that any structural phase transition is not present at least below 230°C. This results show that the crystal symmetry at 180°C is $R3c$, which is the same as that at 25°C. These results suggest that $P_s$ do not decrease markedly with increasing temperature at least below 200°C and that the low value of $P_s$ at 180°C originate from depolarization, i.e., collapse of the domain state established by applying an $E$. It is considered that the depolarization state contains only 180° but also non-180° domains. Not that the change in non-180° domain state leads to a significant change in strain, as observed for Fig. 2(b). As shown in Fig. 2(d) for BNT crystals at 180°C, a large strain was established at a high $E$, whereas depolarization results in a marked decrease in strain with decreasing $E$. When an $E$ is applied to the positive direction, non-180° domains are reoriented along the $E$ direction, which yields a strain jump (increase) corresponding to the rhombohedral distortion $d_{\text{111},c}/d_{\text{111},c}$ as observed for Fig. 2(d). With decreasing $E$, depolarization occurs and the $P_s$ vectors in non-180° domains are aligned in the out-of-plane direction with respect to $E$. This depolarization of non-180° domains gives rise to a marked decrease in strain also according to $d_{\text{111},c}/d_{\text{111},c}$ with decreasing $E$. It is suggested that a large hysteresis with a strain jump observed for BNT crystals at 180°C is attributed to a reversible rotation of non-180° domains [30]. Recently, Y. Kitakata et al. investigated the behavior of non-180° $P_s$ rotation by use of high-energy synchrotron radiation X-ray diffraction (SR-XRD) and density functional theory (DFT) calculations. They revealed that the 71° $P_s$ rotation is the dominant pathway for the electric-field-induced polarization switching in the BNT crystals [30].

BNT single crystals exhibited a saturated polarization hysteresis with $P_s$ of 31 µC/cm² along [100], 44 µC/cm² along [110], and 54 µC/cm² along [111]. These results show that spontaneous polarization of BNT is approximately 55–60 µC/cm².
Strain measurements of rhombohedral BNT crystals suggest that the polarization reversal along [111], is achieved by non-180° $P_r$ rotation.

3. BNT polycrystalline ceramics prepared by using AD method

The $P_{r,max.poly}$ of 48–52 $\mu$C/cm$^2$ was obtained for the BNT polycrystalline ceramics from the $P_r$ of the high quality BNT single crystal. In this study, self-supported BNT polycrystalline films were prepared by the AD method with heat treatment, and their ferroelectric and leakage current properties were investigated. It is well-known that there are two kinds of process for preparing the self-supported thick films by the AD method. Use of the polycarbonate substrates is simplicity and beneficial idea.66 The ceramic thick films can be deposited on the polycarbonate substrates by the AD method because of the room temperature process. We can obtain self supported ceramic films after the substrates are burned in air. The other is applied for the difference of the thermal expansion coefficient between the films and substrates materials.11 If the magnitude of interfacial stress is higher than the adhesion strength between the film and the substrate during heat treatment, the difference of the thermal expansion detaches the films from the substrate. We chose the latter in this study. Measurements of polarization and leakage current properties for the annealed self-supported BTN polycrystalline films with thickness of around 20 $\mu$m suggest that applied AD method is proposed to be effective for obtaining good stoichiometric Bi-based ferroelectric polycrystalline ceramics.

The starting BNT powder was synthesized by a solid-state reaction using $\text{Bi}_2\text{O}_3$, $\text{TiO}_2$ (purity $\geq 99.99\%$) and $\text{Na}_2\text{CO}_3$ (purity $> 99\%$). These materials were weighed with a composition of $\text{Bi}_2\text{O}_3$/$\text{Na}_2\text{TiO}_3$. They were thoroughly mixed by planetary ball milling for 1 h in ethanol. The mixed powder was calcined in an alumina crucible at 800°C for 4 h in air prior to deposition. Scanning electron microscopy (SEM) observation indicated that obtained starting powder had spherically-shaped particles with the size of 0.1–1.0 $\mu$m, and included a small amount of aggregate with the size of 1–5 $\mu$m. BNT films with thickness of around 20 $\mu$m were deposited on the SrTiO$_3$ single crystal substrates deposited by the AD method. The pressure of the deposition chamber was around 200 Pa for all deposition experiments. The nozzle had an orifice size of 10 mm × 400 $\mu$m, total $\text{N}_2$ gas flow rate was about 4–6 l/min, and the distance between the nozzle and substrate was from 2.5 to 10 mm. A heat treatment of 500°C for 30 min or 1000°C for 60 min in air detaches BNT thick films from the SrTiO$_3$ single crystal substrates [Fig. 4(a)]. Some of self-supported BNT polycrystalline films detached at 500°C were heat-treated at 1100°C for 60 min in the BNT starting raw powder in order to promote grain growth [Fig. 4(b)]. The self-supported BNT polycrystalline films after grain growth were annealed at 700°C for 30 min in the air [Fig. 4(c)]. For comparison, sintered bulks of BNT were prepared by a conventional solid-state reaction using the same starting raw powder of the AD method. The starting raw powders were pressed into disks followed by cold isostatic pressing and then sintered at 1200°C for 4 h in the BNT starting raw powder. This process provides dense BNT ceramics with a relative density of 97% and 15 mm high. The BNT sintered bulks were cut into 100-$\mu$m-thick plates. Constitution phase, crystal structure and crystallite size measurement were analyzed by X-ray diffraction (XRD). Microstructure observation and measurement for the thickness of the self-supported films and the plates fabricated from the BNT sintered bulk were performed by the SEM. For the measurements of polarization hysteresis and leakage current properties, Au dots of 0.5 × 0.5 $\text{mm}^2$ were sputtered onto both surfaces of the self-supported AD films and the plates prepared from central part of the BNT sintered bulks.

Figure 5 represents the leakage current properties measured at 25°C for the sintered bulks, the self-supported BNT polycrystalline films detached at 1000°C [Fig. 4(a)] and the annealed BNT polycrystalline films [Fig. 4(c)]. Although both self-supported AD films indicated the superior insulating properties ($J \approx 10^{-8}$ $\text{A}/\text{cm}^2$ at 150 kHz/cm), the sintered bulks showed a relatively high $J$ of approximately $10^{-6}$ $\text{A}/\text{cm}^2$ at 150 kHz/cm.

Figure 6 illustrates polarization properties measured in 1 Hz at 25°C for the sintered bulks, the self-supported BNT polycrystalline films detached at 1000°C [Fig. 4(a)] and the annealed BNT polycrystalline films [Fig. 4(c)]. The sintered bulks exhibited a $P_r$ of 45 $\mu$C/cm$^2$ which was almost equal to estimated $P_{r,max.poly}$ and which was larger than those of self-supported BNT polycrystalline films detached at 1000°C ($P_r$, of 25 $\mu$C/cm$^2$) [Fig. 4(a)] and annealed BNT polycrystalline films [Fig. 4(c)] ($P_r$ of [Fig. 4(c)].

![Fig. 4](image-url) Schematic representation of the heat treatment process for the obtained BNT films prepared by AD method.
40 \mu C/cm^2), whereas $E_c$ of 69 kV/cm was confirmed for the sintered bulks, which were larger than those of the AD films (both $E_c$ of the AD films were 57 kV/cm). **Figure 7** represents $P_r$ saturation properties for the sintered bulks, the self-supported BNT polycrystalline films detached at 1000°C [Fig. 4(a)] and the annealed BNT polycrystalline films [Fig. 4(c)] shown in **Fig. 6**. Although both AD films indicated well-saturated $P_r$ properties, those of the sintered bulks were not saturated enough; these results suggest that the high $J$ of more than $10^{16}$ A/cm$^2$ at 150 kV/cm [Fig. 5] had an affected on the hysteresis loops of the sintered bulks [Fig. 6(a)]. Note that the annealed BNT polycrystalline films after grain growth at 1100°C in the starting raw powder [Fig. 4(c)] indicated the superior polarization and $P_r$ saturation properties, compared with self-supported BNT polycrystalline films detached at 1000°C [Fig. 4(a)].

Here, topics of advantageous effect of using the AD method are discussed. The heat treatment at 900°C or above certainly vaporize Bi.$^{41,61}$ The self-supported BNT polycrystalline films detached at 1000°C in air [Fig. 4(a)] exhibited an extremely low $J$ since the charge neutrality seemed to be satisfied only by $V_{BB'}$ and $V_0^-$, where $V_{BB'}$ and $V_0^-$ represent vacancies at Bi site and the O site, and dots represent negative charges. However, it is highly possible that the domain clamping of non-180° domain walls was induced by the formation of $V_0^-$ so that the self-supported BNT polycrystalline films could not represent large polarization properties. Resultant obtained films indicated well-saturated polarization properties due to their extremely low $J$ and the really small $P_t$ of 25 \mu C/cm$^2$, which was the almost half as large as the $P_{r, \text{max},\text{poly}}$. In contrast, the annealed self-supported BNT polycrystalline films after grain growth in the starting raw powder [Fig. 4(c)] exhibited good ferroelectric properties (the $P_r$ of 40 \mu C/cm$^2$ and superior $P_t$ saturation properties. While the low temperature sintering is effective for the suppression of the oxygen vacancies induced for the BNT ceramics as reported by Nagata,$^{49}$ the heat treatment of 1000°C in the air was not low enough to obtain sufficient ferroelectric properties for these thick films. Although the applied AD method with use of the heat treatment provided the fully dense self-supported stoichiometric BNT polycrystalline films below 500°C which is too low temperature to vaporize Bi, the crystallite size of the films was too small to represent good ferroelectric properties. Therefore, the grain growth of the self-supported BNT polycrystalline films was promoted at the low temperature under the localized vaporized Bi atmosphere by the starting raw powder coating. In fact, the

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**Fig. 5.** Leakage current properties for sintered bulks, self-supported AD films detached at 1000°C [Fig. 4 (a)] and annealed self-supported AD films [Fig. 4 (c)].

**Fig. 6.** Polarization properties for (a) sintered bulks ($P_r = 45 \mu C/cm^2$, $E_c = 69 kV/cm$), (b) self-supported AD films detached at 1000°C [Fig. 4 (a)] ($P_r = 25 \mu C/cm^2$, $E_c = 57 kV/cm$) and (c) annealed self-supported AD films [Fig. 4 (c)] ($P_r = 44 \mu C/cm^2$, $E_c = 57 kV/cm$).

**Fig. 7.** $P_r$ saturation properties for sintered bulks, self-supported AD films detached at 1000°C [Fig. 4 (a)] and annealed self-supported AD films [Fig. 4 (c)].
applied AD method allows us to achieve a good balance between the low temperature heat-treatment and atmospheric control, as a synthesis of high quality stoichiometric (viz. precise compositionally-controlled) Bi-based polycrystalline ferroelectric ceramics. It is hard to combine the control between the low temperature process and atmosphere with obtaining the fully dense ceramics by the use of the other process (e.g. hot-press). Even so, it is considered that clamped domains which do not switch by applying a field are still present, and that the true value of $P_c$ for BNT polycrystalline ceramics is higher than $40 \mu C/cm^2$. Note that BNT single crystal showed an $E_c$ of 53 kV along [110], and 46 kV along [111].

BNT polycrystalline films with thickness of 20 μm were deposited on SrTiO₃ single crystal substrates by the AD method. The BNT polycrystalline films were detached from the substrate by a heat treatment of 500°C for 30 min or 1000°C for 60 min. The grain growth of the self-supported BNT polycrystalline films detached at 500°C for 30 min were performed in the BNT starting raw powder at 1100°C for 60 min, and then the self-supported BNT polycrystalline films after grain growth were annealed at 700°C for 60 min in the air. These annealed BNT polycrystalline films represented good ferroelectric and leakage current properties (the $P_c$ of 40 μC/cm², $E_c$ of 57 kV/cm, and $J_c$ of approximately $10^{-8} A/cm^2$ at 150 kV/cm), compared with the self-supported BNT polycrystalline films detached at 1000°C and the sintered bulks. These results suggest that the use of AD method is effective for obtaining good BNT polycrystalline ceramics.

4. Conclusions

BNT single crystals were grown by the high-$P_{02}$ flux method and their polarization and piezoelectric properties were investigated along [100], [110], and [111]. Strain measurements of rhombohedral BNT crystals suggest that the polarization reversal along [111], is achieved by non-180° $P_r$ rotation. The values of $P_r$ obtained along these three directions provide a value of $P_r$ of 55–60 μC/cm² for rhombohedral BNT. The AD method with use of heat treatment supplied the fully dense self-supported BNT polycrystalline films detached from substrates. The annealed self-supported BNT ceramic films indicated a superior low $J_c$ of approximately $10^{-8} A/cm^2$ at 150 kV/cm which was lower than that of sintered bulks as well as well-saturated hysteresis loops with a large $P_r$ of 40 μC/cm² which was near value of $P_{max,poly}$ (48–52 μC/cm²). The high-$P_{02}$ flux method and the applied AD method have been demonstrated to be effective for obtaining high quality BNT single crystals and polycrystalline ceramics.

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