Effects of Eu$^{3+}$ Doping on Characteristics of (Bi$_{3.25}$Nd$_{0.75}$)Ti$_3$O$_{12}$ Nanoplates

Masafumi Kobune$^{1,2}$, Yausuku Kaneko$^1$, Ryo Kishimoto$^1$, Takuya Kugimiya$^1$, Satoshi Ueshima$^1$, Hiroshi Nishioka$^1$, Takeyuki Kikuchi$^1$, Hironori Fujisawa$^2$, Seiji Nakashima$^2$, Masaru Shimizu$^2$, Naoki Fukumuro$^1$, and Hitoshi Matsuda$^1$

$^1$Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, Himeji, Hyogo 671-2201, Japan
$^2$Department of Electrical Engineering and Computer Sciences, Graduate School of Engineering, University of Hyogo, Himeji, Hyogo 671-2201, Japan
E-mail: kobune@eng.u-hyogo.ac.jp

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a- and b-axis-oriented (Bi$_{3.25}$Nd$_{0.75}$Eu$_x$)Ti$_3$O$_{12}$ (BNEuT, $x = 0$–0.75) films of 3.0-μm thickness were fabricated on conductive Nb$_2$TiO$_3$(101) substrates containing 0.79 mass % Nb by high-temperature sputtering at 650°C, and their structural and ferroelectric characteristics were investigated. All the films had a mostly single-phase orthorhombic structure, with high degrees of a- and b-axis orientations of 99.0–99.8%. The lattice parameters (a-, b-, and c-axis lengths) and the calculated orthorhombic lattice distortion decreased monotonically with increasing Eu content. The microstructure of BNEuT films with $x = 0$–0.50 was nanoplate-like, whereas that of films with $x \geq 0.60$ was significantly more bulk-like. The real room-temperature remanent polarization ($P_r^*$), taking the porosity between the nanoplates into account, had a maximum value of $2P_r^* = 87 \mu$C/cm$^2$ at $x = 0.10$, which was approximately 1.3 times larger than that (65 $\mu$C/cm$^2$) of the nondoped BNT film. It is shown that lattice distortion caused by rotation of octahedra in the $a$–$b$ plane due to the Eu substitution plays a significant role in the improvement of ferroelectricity.

1. Introduction

In recent years, (Bi$_n$Nd$_m$)$_3$Ti$_3$O$_{12}$ (BNT),$^{1,4-6}$ Bi$_4$Ti$_3$O$_{12}$ (BIT),$^{3,5}$ SrBi$_2$Ta$_2$O$_9$ (SBT),$^{6,7}$ and SrBi$_2$Nb$_2$O$_9$ (SBN),$^{8-10}$ which are members of the bismuth layer-structured ferroelectric (BLSF) family, have attracted much attention as promising alternatives to lead zirconium titanate (PZT)$^{1,12}$ for ferro- and piezoelectric applications. In our previous studies,$^{13,14}$ we have succeeded in fabricating heteroepitaxially grown (Bi$_{3.25}$Nd$_{0.75}$)Ti$_3$O$_{12}$ (BNT-0.75) nanoplates with a- and b-axis orientations by high-temperature sputtering using conductive Nb$_2$TiO$_3$(101) substrates with 0.79 mass % Nb, and confirmed their ferroelectric properties. This was made possible by controlling the difference in linear expansion coefficients and the long-range lattice matching between the BNT film and the Nb$_2$TiO$_3$(101) substrate. It is known that Aurivillius phases are layered compounds with the general formula (Bi$_2$O$_2$)$_{2n}$+$\beta$(A$_m$-1B$_m$On+1)$_2$-, where $n = 1$–8, and that they consist of a Bi$_2$O$_2$ layer intergrown with a perovskite block containing multiple BO$_6$ octahedral layers with A sites ($m \geq 2$).$^{15,16}$ BNT-0.75 consists of a (Bi$_2$O$_2$)$_2$- layer and a (Bi$_{3.25}$Nd$_{0.75}$)Ti$_3$O$_{12}$- perovskite block, and the latter is further composed of triple TiO$_6$ octahedral layers containing two A (Bi$^{3+}$ and Nd$^{3+}$) sites. Since the appearance of ferroelectricity in this BNT crystal is mainly attributable to the rotation and tilting of the TiO$_6$ octahedra described above,$^{17,18}$ spontaneous polarization ($P_s$) can be enhanced by increasing the amount of distortion of the TiO$_6$ octahedra. One method of increasing $P_s$ is to change the ferroelectric distortion by substituting Eu$^{3+}$ ions, which have a smaller radius ($r_{Eu} = 0.0947$ nm for 6-fold coordination) than ($r_{Nd} = 0.0983$ nm for 6-fold coordination) Nd$^{3+}$ ions, for A-site (Nd$^{3+}$) ions in the (Bi$_{3.25}$Nd$_{0.75}$)Ti$_3$O$_{12}$- layer of the BNT structure.

In the present study, the fabrication of a- and b-axis-oriented (Bi$_{3.25}$Nd$_{0.75}$Eu$_x$)Ti$_3$O$_{12}$ (BNEuT, $x = 0$–0.75) nanoplates heteroepitaxially grown on conductive Nb$_2$TiO$_3$ substrates was attempted by systematically substituting Eu$^{3+}$ ions for Nd$^{3+}$ ions in the BNT crystal structure. By focusing attention on the orthorhombic lattice distortion [orthorhombicity, $2(a-b)/(a+b)$]$^{19,20}$ which is one of the lattice distortions significant for the appearance of ferroelectricity that is closely related to the rotation of TiO$_6$ octahedra in the $a$–$b$ plane, the effects of Eu$^{3+}$ doping on the structural and ferroelectric characteristics of the resulting BNEuT nanoplates are discussed.

2. Experimental Procedure

Reagent-grade Bi$_2$O$_3$, Nd$_2$O$_3$, TiO$_2$, and Eu$_2$O$_3$ were used as starting materials. Powders for the sputtering target, in proportions appropriate for the compositions calculated using Eq. (1), were uniformly mixed for 30 min in an alumina mortar. After calcining the mixtures in air at 750°C for 3 h, the calcined powders, together with the excess Bi$_2$O$_3$ indicated in Eq. (1), were ground for 30 min in the same mortar. Compacted powder targets were fabricated by filling and pressing the ground powders at 40 MPa in a shallow 0.1-m-diameter Cu dish.

(Bi$_{3.25}$Nd$_{0.75}$Eu$_x$)Ti$_3$O$_{12}$ + 0.49Bi$_2$O$_3$, $x = 0$–0.75. (1) Using these targets, 3.0-μm-thick BNEuT films were deposited at 650°C on conductive rutile phase Nb$_2$TiO$_3$(101) substrates containing 0.79 mass % Nb by RF magnetron sputtering. The crystalline phases and orientations of the films were evaluated using an X-ray diffraction (XRD) system (Bruker AXS D8-μ-HR). The degree of a- and b-axis orientations $\alpha_{(h00)/(0k0)}$ for the BNEuT films is defined as

$$\alpha_{(h00)/(0k0)} = \frac{\sum I_{(h00)/(0k0)}}{\sum I_{(hkl)}} \times 100\%,$$

where $I_{(h00)/(0k0)}$ and $I_{(hkl)}$ represent the XRD intensities of the (h00)/(0k0) and (hkl) reflections, respectively. Component (Eu content) analyses and surface microstructural observations of the films were carried out using a field emission scanning electron microscopy (FE-SEM; JEOL JSM-7001FA) system equipped with an energy dispersive X-ray spectrometer (EDS). Cross-sectional observations of the microstructure of the BNEuT film and the interface
between the film and the Nb:TiO$_2$ substrate were carried out using a transmission electron microscopy (TEM; JEOL JEM-2100) system equipped with a selected area electron diffraction (SAED) system. To form ohmic contacts for electrical measurements, RF sputtering was carried out to deposit an approximately 30-nm-thick Ti film on the back side of the substrate and Pt electrodes on the top surface of the BNEuT film; this was carried out without heating the substrate. The specimens for ferroelectric measurements thus had the structure Pt/BNEuT/Nb:TiO$_2$(101)/Ti. Here, to evaluate the real remanent polarization $2P_r^*$, the porosity between the nanoplates was determined from surface FE-SEM images using an image analysis system. Polarization-electric field ($P$–$E$) hysteresis loops were measured using a ferroelectric film testing system (Radiant RT66A).

3. Results and Discussion

Figure 1 shows the XRD profiles of 3.0-μm-thick BNEuT films with $x = 0$–0.75 deposited on Nb:TiO$_2$(101) substrates with 0.79 mass% Nb.

![Fig. 1. XRD profiles of 3.0-μm-thick BNEuT films with $x = 0$–0.75 deposited on Nb:TiO$_2$(101) substrates with 0.79 mass% Nb.](image)

Figure 2 shows X-ray pole figure plots for (a) Nb:TiO$_2$(200) between the film and the Nb:TiO$_2$ substrate were carried out using a transmission electron microscopy (TEM; JEOL JEM-2100) system equipped with a selected area electron diffraction (SAED) system. To form ohmic contacts for electrical measurements, RF sputtering was carried out to deposit an approximately 30-nm-thick Ti film on the back side of the substrate and Pt electrodes on the top surface of the BNEuT film; this was carried out without heating the substrate. The specimens for ferroelectric measurements thus had the structure Pt/BNEuT/Nb:TiO$_2$(101)/Ti. Here, to evaluate the real remanent polarization $2P_r^*$, the porosity between the nanoplates was determined from surface FE-SEM images using an image analysis system. Polarization-electric field ($P$–$E$) hysteresis loops were measured using a ferroelectric film testing system (Radiant RT66A).

![Fig. 2. XRD pole figure plots of (a) Nb:TiO$_2$(200) and (b) BNEuT(026) for a BNEuT film with $x = 0.10$, and (c) Nb:TiO$_2$(200) and (d) BNEuT(026) for a BNEuT film with $x = 0.60$ deposited on the Nb:TiO$_2$(101) substrates.](image)
Fig. 5(a)–5(c) show typical surface FE-SEM images of BNEuT films with \( x = 0, 0.10, \) and 0.75, respectively, and Fig. 5(d) shows the porosity between nanoplates in BNEuT films with \( x = 0–0.75 \) as a function of Eu content.

As can be seen, for \( 0 \leq x \leq 0.50 \) [Figs. 5(a) and 5(b)], the films exhibit a nanoplate-like microstructure with the plates aligned along the [001]/[010] direction. However, for \( 0.50 < x \leq 0.75 \), the films begin to appear more bulk-like in areas such as those indicated by the dashed lines in Fig. 5(c). The nanoplate thicknesses in the [001] direction are estimated to be 80–125 nm (\( x = 0 \)), 70–130 nm (\( x = 0.10 \)), 80–140 nm (\( x = 0.20 \)), 75–145 nm (\( x = 0.30 \)), 80–160 nm (\( x = 0.40 \)), 85–165 nm (\( x = 0.50 \)), 80–190 nm (\( x = 0.60 \)), and 115–230 nm (\( x = 0.75 \)). The increase in thickness for \( x \geq 0.60 \) can be attributed to significant grain growth along the [001] direction, as locally observed in Fig. 5(c). To determine the \( P_r \) value accurately, it is necessary to determine the porosity and calculate the effective area of the Pt top electrodes. The porosities between the nanoplates are almost constant at 20–27\% in the range of \( x = 0–0.50 \), whereas they decrease from 18 to 11\% owing to significant grain growth along the [001] direction in the range of \( x = 0.60–0.75 \) [Fig. 5(d)].

A cross-sectional TEM image and four SAED patterns for an \( x = 0.10 \) BNEuT nanoplate epitaxially grown on the Nb:TiO\(_2\) substrate are shown in Fig. 6(a). As shown in the figure, the cross-sectional TEM image in a direction perpendicular to the c-axis of the film indicates a peculiar shape of the around 100-nm-thick nanoplates. The four insets show SAED patterns obtained from the upper, middle, and lower parts of the BNEuT, and from the Nb:TiO\(_2\) substrate, and demonstrate that the BNEuT nanoplate grew with a heteroepitaxial relationship to the underlying Nb:TiO\(_2\) substrate. Figure 6(b) shows (A) a cross-sectional TEM image and two lattice images of (B) an intermediate region of the BNEuT nanoplate and (C) the interface region between the BNEuT nanoplate and the Nb:TiO\(_2\) substrate in the \( x = 0.10 \) BNEuT/Nb:TiO\(_2\) structure. The microstructure shown in Fig. 6(b)-(A) consists of \( \oplus \) BNEuT nanoplates, \( \ominus \) a BNEuT seed layer with a thickness in the range of 10–30 nm, and \( \Xi \) the Nb:TiO\(_2\) substrate. A stacked structure along the c-axis consisting of a bismuth oxide layer and a perovskite block can clearly be observed in Figs. 6(b)-(B) and 6(b)-(C). Although the lattice image in Fig. 6(b)-(C) exhibits a slight misalignment between the atomic planes in the BNEuT layer and substrate, that in Fig. 6(b)-(B) shows good long-range lattice matching between a single unit cell in the BNEuT layer and seven lattice units in the underlying Nb:TiO\(_2\) crystal.\(^{1,22–25}\) Since the c-axis length in this BNEuT film and the b-axis length in the substrate are respectively 3.2824 and 0.4592 nm, their ratio is close to seven (approximately 7.15), which is the reason why the epitaxial growth of the BNEuT nanoplates is possible.
Therefore, the epitaxial growth of the BNEuT nanoplates described above originates from this consistency.

Figure 7 shows the variations in the remanent polarization \( P_r \) and coercive field \( E_c \) of 3.0-\( \mu \)m-thick BNEuT films as a function of Eu content. The inset indicates the ferroelectric hysteresis loop of the BNEuT film with \( x = 0.10 \). Open and solid circles indicate the measured \( 2P_r \) values and the real \( 2P_r^* \) values taking the porosity between the nanoplates into account, respectively.

Fig. 7. Variations in remanent polarization (\( P_r \)) and coercive field (\( E_c \)) of 3.0-\( \mu \)m-thick BNEuT films as a function of Eu content. The inset indicates the ferroelectric hysteresis loop of the BNEuT film with \( x = 0.10 \). Open and solid circles indicate the measured \( 2P_r \) values and the real \( 2P_r^* \) values taking the porosity between the nanoplates into account, respectively.

4. Conclusions

- \( a \)- and \( b \)-axis-oriented (Bi\(_{12.25}\)Nd\(_{0.75}\)Eu\(_x\))\( \mathrm{Ti}_3\mathrm{O}_12 \) (BNEuT, \( x = 0-0.75 \)) films of 3.0-\( \mu \)m thickness were fabricated on conductive Nb:TiO\(_2\)(101) substrates containing 0.79 mass % Nb by high-temperature sputtering at 650-\( ^\circ \)C, and their structural and ferroelectric characteristics were investigated. The results can be summarized as follows.

1. All the films had a mostly single-phase orthorhombic structure, with high degrees of \( a \)- and \( b \)-axis orientations of 99.0-99.8\%.
(2) The lattice parameters (a-, b-, and c-axis lengths) and the calculated orthorhombic lattice distortion decreased monotonically with increasing Eu content.

(3) The microstructure of BNEuT films with $x = 0$–0.50 was nanoplate-like, whereas that of films with $x \geq 0.60$ was significantly more bulk-like.

(4) The real room-temperature remanent polarization $(2P_r^\text{r})$, taking the porosity between the nanoplates into account, exhibited a maximum value of 87 μC/cm$^2$ at $x = 0.10$, which was approximately 1.3 times larger than that (65 μC/cm$^2$) of the nondoped BNT film.

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