Influence of tetragonality on crystal orientation induced by a strong magnetic field and on the piezoelectric properties of the (Bi$_{0.5}$, Na$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ ceramic system

Satoshi TANAKA$^{1,3}$, Keisuke SANO$^1$, Tomohiro HARADA$^2$, Hiroyuki SHIMIZU$^2$ and Yutaka DOSHIDA$^3$

1 Department of Materials Science and Technology, Nagaoka University of Technology, 1603–1 Kamitomioka, Nagaoka, Niigata 940–2188, Japan
2 R & D Center, Taiyo Yuden Co. Ltd, 5602–1 Nakamurota-machi, Takaiki, Gunma 370–3347, Japan
3 Division of Electrical and Electronic Engineering, Department of Innovative Engineering, Ashikaga University, 268–1 Omae-cho, Ashikaga, Tochigi 326–8558, Japan

Crystal-oriented (Bi$_{0.5}$, Na$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ (BNBT) ($x = 0.1–0.25$) ceramics with a perovskite crystal structure were prepared by colloidal processing in a strong rotating magnetic field with the aim of improving their piezoelectric properties. The advantages of increasing the amount of Ba in these ceramics are twofold; specifically, this will lead to anisotropic crystal lattices and it will also increase the tetragonality. The crystal-oriented BNBT ($x = 0.1–0.25$) ceramics were prepared by using a rotating magnetic field to orient the $a$- and $c$-axes of the crystal in the powder compact. The degree of orientation also increased with the tetragonality. The phase transformation that occurred above Curie temperature during sintering redistributed the $c$-axis-oriented structure along both the $a$- and $c$-axes. Again, the $c$-axis orientation was enhanced by electrical field polarization. The piezoelectric $d_{33}$ constant, which depends on the Ba content, achieved a maximum value of 122 pC N$^{-1}$ at a Ba content of 15 mol%.

Key-words : Crystal-oriented ceramics, Perovskite, Piezoelectric ceramics, Ferroelectric ceramics, Barium titanate, Tetragonality, Magnetic field orientation

1. Introduction

(Bi$_{0.5}$, Na$_{0.5}$)TiO$_3$-based ferroelectric ceramics are one of the most promising candidates for lead-free piezoelectric materials currently under investigation.1)–3) These ceramics have a perovskite crystal structure and form a solid solution with other alkaline or alkaline-earth cations, and improvements in their properties are possible by means of the preparation of solid solutions.3)–19) Takenaka et al.4)–15) have reported extensively on systematic studies of the (Bi$_{0.5}$, Na$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ (BNBT) ceramic system. In this system, BNBT has a morphotropic phase boundary (MPB, $x = 0.06–0.07$) with a rhombohedral and tetragonal crystal structure, in which comparably large displacements can be achieved both by polarization and phase transformations.2)16),17)

Another strategy for improving the properties of such material is to adjust the orientation of the grains in BNBT ceramics.3)20) Yilmaz et al.3) reported on the c-axis orientation of BNBT ($x < 0.065$) following templated grain growth achieved by using tabular SrTiO$_3$ template particles. The piezoelectric coefficient $d_{33}$ was 500 pC N$^{-1}$, and this value was driven by the high electric fields. In contrast, our approach to obtain an optimal crystal orientation entailed colloidal processing in a strong magnetic field.21)–24) In this approach, particles with anisotropic crystal structures are oriented along a direction even though they are spherical particles. The direction of the grains is governed by the interaction between their anisotropic magnetic susceptibility and the strong magnetic field. For a diamagnetic material, the crystal direction with the highest susceptibility orients itself in the direction normal to the applied magnetic field. Applying a rotating magnetic field (RMF) in the horizontal plane of the particles gathers the magnetic susceptibility of all the particles along a single direction.35),36) The merits of this method are that special template particles are unnecessary, and thus densification can be achieved easily. To date, we have fabricated crystal-oriented ceramic BNBT ($x = 0.15$) (hereafter, BNBT15) materials and improved the piezoelectric properties.37) Although the component BNBT does not exhibit good properties compared to the MPB phase, it has a higher depolarization temperature than the MPB composition, which is preferable for potential commercial applications.
The objective of this study was to produce crystal-oriented BNBT ($x = 0.10$–$0.25$) ceramics by colloidal processing in a magnetic field, and to show the influence of the Ba content on the orientation and improvement of their piezoelectric properties. In this regard, an appropriate amount of Ba would be expected to preferably result in crystal system anisotropy with a tetragonal crystal structure.

2. Experimental procedure

\((\text{Bi}_{0.5}, \text{Na}_{0.5})_{1-x}\text{Ba}_{x}\text{TiO}_3\) (BNBT, \(x = 0.1, 0.125, 0.15,\) and 0.25) powders were synthesized by employing a solid-state reaction. First, reagent-grade \(\text{Bi}_2\text{O}_3, \text{Na}_2\text{CO}_3,\) \(\text{BaCO}_3,\) and \(\text{TiO}_2\) were weighed according to their compositions. After mixing them, BNBT powders were synthesized by heating at 1100°C for 3 h in air.

The synthesized BNBT powders were dispersed in isopropyl alcohol (2-propanol) with poly(ethyleneimine), (PEI), as a dispersant, and a slurry with 35 vol% solid content was prepared by ball milling for 5 h. The amount of PEI used was 1.0 wt% in relative to the weight of BNBT powder. The slurry (3 mL) was poured into a 25-mm-diameter and 20-mm-depth cylindrical container for the preparation of a green compact. To form a powder compact in the RMF, the container was rotated horizontally at 30 rpm in the static horizontal magnetic field (10 T) of a superconducting magnet (TM10VH10, TOSHIBA, Japan) at room temperature, until the slurry was fully dried (Fig. 1). The sample thickness after drying was controlled to be approximately 3.0 mm. Another portion of the slurry was dried in the absence of the magnetic field to prepare a reference sample. The powder compact was subjected to cold isostatic pressing at 200 MPa. The samples were then sintered in air for 1 h at 1130°C in a furnace.

The crystal structure and particle orientation in the powders were characterized by powder X-ray diffraction (XRD) analysis (Ultima-IV, RIGAKU, Japan) over the 2\(\theta\) range of 20–70°. Cu was used as the X-ray source. To estimate the lattice parameters \(a\) and \(c\), diffraction angle values of 200 and 002, respectively, were used. A small amount of Si powder was included in the BNBT powder as an internal standard. The specific surface area of BNBT powders was measured with a Brunauer–Emmett–Teller specific surface meter (Flowsorb 2010, Micromeritics) by using nitrogen as an adsorbing gas. The relative density of the samples was measured by using the Archimedes’ method and their microstructures were observed with scanning electron microscopy. The polarization \((P)\) curve at room temperature was measured as a function of the electric field \((E)\) by using a commercial apparatus (Type-5/1, TOYO Corp., Tokyo, Japan). The sample shape was a square flat plate; each side had a length of 4 mm, and the thickness of the plate was 0.5 mm. Gold electrodes with a thickness of 200 nm were sputtered onto the samples. The measurements were conducted at a frequency of 0.5 Hz. The samples in silicone oil at 100°C were poled for 10 min parallel to the rotation axis for the green compact under an electric field of 6.0 kV/mm. The piezoelectric constant \(d_{33}\) was measured with a \(d_{33}\) meter (ZJ-6B, Institute of Acoustics, Chinese Academy of Sciences).

3. Results and discussion

The particles that were prepared (see Fig. 2) had an average diameter of 0.5 \(\mu\)m and a specific surface area of 3.3 \(\text{m}^2\)g\(^{-1}\). Figure 3 shows the XRD patterns of the prepared powder, and crystal phase of the powder was identified as a tetragonal crystal phase.\(^{17}\) The lattice parameters \(a\) and \(c\) along the \(a\)-axis and \(c\)-axis were calculated using
the 200 and 002 diffraction angle values, (Fig. 4), respectively, and the data yielded a c/a ratio of 1.016–1.023. The magnitude of the c/a parameter increased with the increasing amount of Ba. The slurry of BNBT particles showed slight shear-thinning, and their behavior was almost Newtonian. These results demonstrate that the particles were well dispersed in the slurry.

**Figure 5** shows the XRD patterns of the polished horizontal planes for the powder compact and sintered specimens formed with and without the magnetic field.

The Miller index was identified with ICDD database (PDF 00-063-0735). For powder compact subjected to the RMF, the peaks from the c-planes of the crystal, such as the 001 and 002 ones, were intense. Peaks arising from a-planes, such as the 100 and 200 peaks, were also observed. In addition, their intensities were higher than those for the
powder compacts formed without RMF. These results indicate that the c-plane was preferentially oriented to the rotating axis, but the a-plane was oriented simultaneously in the rotating axis. Thus, we can conclude that many particles consisted of multiple domains or crystals. For the sintered specimens, at a temperature higher than the Curie temperature, the c-plane and a-plane became a-planes in the cubic structure that arose from the phase transformation from tetragonal to cubic. As the crystal structure returned to a tetragonal arrangement during cooling to room temperature, the c- and a-planes became a-planes formed in a 1:2 ratio. For samples formed in RMF, it is noteworthy that an oriented structure was maintained during and after sintering. Additionally, the intensities from the c-plane and a-plane were enhanced, whereas those of the other planes decreased with sintering in almost all samples except for BNBT10. It is possible that grains oriented to the a- and c-axis in the BNBT12.5, BNBT15, and BNBT25 ceramics preferentially grew by incorporating other grains during sintering. Although there were a few exceptions, the results showed that c- and a-axis-oriented BNBT10-25 polycrystalline ceramics were produced by using a RMF and subsequent sintering.

The degrees of orientation were calculated semi-quantitatively by using the Lotgering method as follows:38)

\[
F = \frac{P - P_0}{1 - P_0},
\]

where \( P_0 = \Sigma[I_0(h00) + I_0(00l)]/\Sigma I_0(hkl) \), \( P = \Sigma[I(h00) + I(00l)]/\Sigma I(hkl) \), and in turn \( I \) and \( I_0 \) are the intensities of the diffraction peaks of XRD patterns in the samples prepared with and without the magnetic field, respectively. Here, intensities of the h00 planes are included because polarization causes the 90° domain rotation away from the a-axis. All the diffraction peaks in the range of 20–70° were used for this calculation. Figure 6 shows the Lotgering factor of the powder compacts and sintered ceramics. This factor increased with the increasing amount of Ba, which corresponded to the change in tetragonality. The Lotgering factors of the sintered samples also increased with the tetragonality. Interestingly, the increasing slope indicates that the oriented structure was maintained and enhanced after sintering.

Figure 7 shows the microstructures of the powder compacts formed with and without the magnetic field and sintered samples of BNBT25, for which the grains were both oriented and non-oriented, respectively. The sintering temperature of the ceramics was 1130°C. The relative density of both samples (oriented and non-oriented) was 98% at this temperature. Fine equiaxed particles \( \sim 0.5 \mu m \) in size were observed in both of the powder compacts for both samples, the same as for BNBT15.37) After sintering, the grains \( \sim 3 \mu m \) in size in the sintered samples of BNBT25 had an equiaxed shape, even though the tetragonality of these samples was the highest among all samples. The microstructure observed here for BNBT was considerably different from that observed for crystal-oriented tungsten bronze materials in a previous study,26) in which the longer grains were oriented parallel to the rotation axis of the magnetic field. Therefore, the anisotropy of the crystal system affects the microstructure in crystal-oriented ceramics.

Figure 8 presents the ferroelectric properties of the oriented and non-oriented BNBT15 and BNBT25 ceramics. P–E hysteresis loops were visible for the samples prepared with [Figs. 8(a) and 8(c)] and without [Figs. 8(b) and 8(d)] the RMF. For BNBT15, the P–E loops became more extended as the applied electric field increased; in particular, a well-developed P–E loop was visible in the data for the c- and a-axis oriented samples at lower electric fields. At an applied electric field of 60 kV cm\(^{-1}\), saturation polarizations of \( \sim 39 \) and \( \sim 31 \mu C cm^{-2} \) were measured in the oriented and non-oriented samples, respectively. The remnant polarization \( P_r \) of 30 \( \mu C cm^{-2} \) measured for the oriented sample was slightly higher than the 25 \( \mu C cm^{-2} \) value obtained for the non-oriented sample. At a lower electric field of 40 kV cm\(^{-1}\), the \( P_r \) of 21 \( \mu C cm^{-2} \) measured for the oriented sample was much higher than the 10 \( \mu C cm^{-2} \) obtained for the non-oriented sample. At

![Fig. 6](image-url)  

**Fig. 6.** Lotgering factor of the powder compact and sintered ceramics plotted as a function of the tetragonality. (a) Powder compact and (b) sintered ceramics.

![Fig. 7](image-url)  

**Fig. 7.** Microstructures of the powder compact and ceramics BNBT25. Powder compact prepared (a) with the magnetic field and (b) without the magnetic field; (c) sintered ceramics of (a), and (d) sintered ceramics of (b).
60 kV cm\(^{-1}\), the coercive electric field \(E_c\) of 24 kV cm\(^{-1}\) obtained for the oriented BNBT15 was lower than the 28 kV cm\(^{-1}\) measured for the non-oriented sample. This reduction in \(E_c\) shows that 180° domain switching along the \(c\)-axis and 90° domain rotation away from the \(a\)-axis were more readily achieved in the oriented BNBT15 than in the non-oriented BNBT15.\(^{37}\) For BNBT25, at an applied electric field of 60 kV cm\(^{-1}\), saturation polarizations and remnant polarization were \(\sim\)28 and 24 \(\mu\)C cm\(^{-2}\) for both samples, respectively. The \(E_c\) values were measured as \(\sim\)32 and \(\sim\)35 kV cm\(^{-1}\) in the oriented and non-oriented samples, respectively. At a lower electric field of 40 kV cm\(^{-1}\), the \(P_r\) of 16 \(\mu\)C cm\(^{-2}\) for the oriented sample was higher than the 7.5 \(\mu\)C cm\(^{-2}\) value obtained for the non-oriented sample. Although the effect of orientation on \(P-E\) hysteresis appeared for BNBT25, the remnant polarization decreased with increasing the amount of Ba.

**Figure 9** shows the XRD patterns obtained for the sintered samples before and after poling for the BNBT10, BNBT15, and BNBT25 ceramics. For all the samples, the \(c\)-plane peaks increased in intensity after poling. As in the previous study, poling led to domain-reorientations, that is, the domain along the \(c\)-axis developed from the polarization induced by the electric field. The domain along the \(c\)-axis developed because of the 180° domain switching along the \(c\)-axis direction, in addition, it developed from the 90° domain rotation away from the \(a\)-axis. Furthermore, it is possible that the reorientation from the \(a\)-to the \(c\)-axis (and therefore domain growth) was interrupted at some stage because of stress. Thus, the poling promoted the formation of \(c\)-axis oriented BNBT10 and BNBT15 ceramics. Poling-induced texture changes have also been reported for BNT systems.\(^{39}\)

**Figure 10** shows the relationship between the piezoelectric \(d_{33}\) constant, Lotgering factor, and tetragonality with increasing the amount of Ba. The piezoelectric \(d_{33}\) constant was enhanced by the orientation of BNBT samples in this study. The results showed that piezoelectric \(d_{33}\) constant of oriented BNBT ceramics reached a maximum value in the BNBT15 ceramics. As a result of crystal-orientation and poling, the piezoelectric \(d_{33}\) constant of the \(c\)-axis-oriented BNBT15 sample was 122 pC N\(^{-1}\), which represents an improvement in relation to value of 88 pC N\(^{-1}\) measured for the reference sample. This result can be ascribed to both the dependence of piezoelectric \(d_{33}\) constant on the composition of the ceramic samples in terms of the amount of Ba and the oriented structures of these ceramics. The piezoelectric \(d_{33}\) constant of oriented BNBT ceramics increased with the Lotgering factor which increased with the increasing tetragonality, and conversely, the piezoelectric \(d_{33}\) constant of non-oriented BNBT ceramics decreased with the amount of Ba in the samples.
This is the reason why the piezoelectric $d_{33}$ constant of oriented BNBT ceramics reached a maximum value for BNBT15 ceramics.

4. Conclusions

This study examined the influence of tetragonality on the crystal orientation induced by a strong magnetic field, and on the piezoelectric properties of the BNBT ($x = 0.1$–$0.25$) ceramic system. The substitution of Ba resulted in an increase in the tetragonality. The magnetic field was used to orient the $a$- and $c$-axes of the crystals of the BNBT particles in the powder compact. The Lotgering factor considering both the $h00$ and $00l$ phases also increased as the tetragonality increased. The phase transformation to the cubic phase, at a temperature above the Curie temperature during sintering, redistributed the $c$-axis-oriented structure such that it was oriented along both the $a$- and $c$-axes. Again, the $c$-axis orientation was enhanced by electrical field polarization. The piezoelectric $d_{33}$ constant of oriented BNBT ceramics increased with the Lotgering factor, which increased with the increasing tetragonality. Conversely, the piezoelectric $d_{33}$ constant of non-oriented BNBT ceramics decreased with the amount of Ba in the samples. As a result, the value of the piezoelectric $d_{33}$ constant of crystal-oriented BNBT ceramics prepared in magnetic field was maximum for BNBT15 ceramics.

Acknowledgements  This work was partially supported by Leading Industrial Technology Development Project Grant Funds of the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References


Fig. 9. XRD patterns for the horizontal planes of sintered samples formed with the magnetic field before and after poling for the (a) BNBT10, (b) BNBT15, and (c) BNBT25 ceramics. The XRD patterns were measured after removing Au.

Fig. 10. Relationship between the tetragonality and the piezoelectric constant as well as Lotgering factor; the tetragonality was derived from the amount of barium composition of ceramic samples. The piezoelectric constant data are for ceramics prepared (a) with the magnetic field and (b) without the magnetic field, and (c) shows the Lotgering factor for oriented ceramics.