Fabrication of (111)-oriented BaTiO$_3$ ceramics by high magnetic field electrophoretic deposition using hexagonal-tetragonal co-existing BaTiO$_3$ powder

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(111)-oriented BaTiO$_3$ (BT) ceramics were prepared by a high magnetic field assisted electrophoretic deposition method using hexagonal-tetragonal co-existing BT powders. With increasing the hexagonal content, the (111)-orientation factor increased, while piezoelectric strain constant $d_{33}$ increased up to the hexagonal content of 80% with attaining a maximum value of 627 pm V$^{-1}$ and then rapidly decreased. In contrast, the decreasing trend of $d_{33}$ with increasing hexagonal content in the randomly oriented ceramics was observed. These results were discussed with the degree of the orientation and the possible twin defects in the BT ceramics.

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Key-words: Barium titanate, Electrophoretic deposition, Crystalline oriented ceramics, High magnetic field, Piezoelectric properties

[Received January 20, 2020; Accepted March 23, 2020]

1. Introduction

The toxicity of lead and lead-oxide released from the lead-based piezoelectric materials has demanded the development of environment-friendly lead-free piezoelectric materials.$^1$ Barium titanate (BaTiO$_3$, BT) is a well-known prototype lead-free piezoelectric ceramics with a piezoelectric constant ($d_{33}$) of 191 pC/N.$^2$ It is well known that the piezoelectric response increases below a grain size of 10 µm and gets maximized at a grain size of $\approx$1 µm$^3$-$^5$ which is attributed to high domain wall density. Furthermore, a high $d_{33}$ of 788 pC/N$^6$ has been reported for the BT ceramics with its engineered domain configuration for grain orientation along the (110)-direction. It has been accounted that the piezoelectric properties can be strongly increased by texturing in off自发aneous polarization directions. These results have revitalized the possibility of further enhancement in fine-grained BT ceramics with a suitable engineered domain configuration. Here, the engineered domain configuration along the (110)-direction has only two equivalent domains whereas along the (111)-direction it has three equivalent domains,$^7$ which suggests that the one-more-equivalent domain in the (111)-direction may further enhance the piezoelectric properties. Thus, BT has still great potential for physics as a model lead-free piezoelectric material.

There are several techniques for producing grain-oriented ceramics such as templated grain growth (TGG)$^6$,$^8$ reactive templated grain growth (RTGG)$^9$ hot forging.$^{10}$ etc. Among many grain orientation techniques, high magnetic field-assisted slip casting (HM-SC)$^{11}$ and high magnetic field-assisted electrophoretic deposition (HM-EPD)$^{12,13}$ techniques are suitable for starting materials with fine spherical particles to achieve high grain orientation. But these methods require particles with anisotropic diamagnetic susceptibilities associated with asymmetric crystal structures, such as Al$_2$O$_3$, TiO$_2$, ZnO, etc.$^{14}$ When such particles are placed in a magnetic field, they rotate to minimize the system’s energy. This driving force is magnetic torque ($T$), which can be expressed as:$^{15}$

$$ T = \frac{\Delta \chi VB^2}{2\mu_0} \sin 2\theta $$  (1)

where $\Delta \chi$ is an anisotropic diamagnetic susceptibility, $V$ is the volume of each particle, $B$ is the applied magnetic field, $\mu_0$ is the permeability in a vacuum, and $\theta$ is the angle between easy magnetization axis in a crystal and applied magnetic field direction. Thus, BT has gained a renewed interest due to the possibility of enhancing its piezoelectric properties on the basis of its diamagnetic nature which helps for making texture ceramics with fine grain.$^{13,16}$ But, this Eq. (1) suggests that easy particle rotation needs large $\Delta \chi$, which can be achieved with a large lattice.

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$^\ddagger$ Preface for this article: DOI http://doi.org/10.2109/jcersj2.128.P8-1

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constant ratio $c/a$. Although this ratio for BT, being tetragonal at room temperature, has just 1.01. Recently, Watanabe et al.\textsuperscript{17)} reported the transformation of tetragonal BT into hexagonal BT ($c/a = 2.44$) by reduction in the hydrogen atmosphere. Also, (001)-oriented BT compacts were successfully fabricated by HM-SC and (111)-oriented tetragonal BT ceramics were obtained after sintering in air. Keeping all these things about BT in mind, Kobayashi et al.\textsuperscript{13)} fabricated (111)-oriented BT ceramics with a high degree of grain orientation by HM-EPD. However, their piezoelectric properties were not enhanced. It was suggested that (111) twins were formed in the BT ceramics at the transformation from the hexagonal phase to the tetragonal phase.\textsuperscript{17,18)} These twins might be acted as pinning sites for domain wall motion, and therefore resultant insufficient poling lowered the piezoelectric properties. However, the hexagonal phase of BT is required for imparting grain orientation in the HM-EPD method, and a higher extent of hexagonal content could be necessary for a high degree of orientation. With increasing the hexagonal content, the increase of twin concentration is expected. Thus, it is highly desirable to optimize the concentration of the hexagonal content in order to achieve a reasonably high degree of grain orientation with less twinning effect for enhanced piezoelectric properties.

In this study, to limit the twinning effect, hexagonal-tetragonal co-existing BT powders with different ratios of hexagonal and tetragonal contents were used for the preparation of the (111)-oriented BT ceramics using the HM-EPD technique. And, the piezoelectric properties were evaluated to optimize the phase ratio of hexagonal content in hexagonal-tetragonal co-existing BT powders in an attempt for further improvement of the piezoelectric properties of BT ceramics.

2. Experimental procedure

BT powder (BT01, particle size $\approx 100\,\text{nm}$, Sakai Chemical Industry Co., Ltd.) was reduced under hydrogen atmosphere for 1 h at 1440, 1445, 1450, 1455, and 1456 °C to get hexagonal-tetragonal (Hex-Tet) co-existing BT powders, while reducing was done at 1500 °C for 1 h in order to make pure hexagonal (Hex) BT powder. The reduced powders were mildly oxidized in air at 1000 °C for an hour to oxidize Ti, while maintaining the hexagonal structure.\textsuperscript{17)} The degree of Hex-Tet ratios was estimated from the (103) hexagonal peak and (202) tetragonal peak of X-ray diffraction (XRD) patterns and compared with a calibration curve. The Hex-Tet co-existing BT powders reduced at 1440, 1445, 1450, 1455, 1456, and 1500 °C had the hexagonal content of about 30, 50, 70, 80, 90, and 100%, respectively. The obtained powders were then separately dispersed in dehydrated ethanol and ball milled with 10 mm zirconia balls along with dispersant (polyethyleneimine, PEI) for 72 h. The resultant slurries were sonicated for 10 min to get well-dispersed particles.

The green compacts of Hex-Tet co-existing BT particles were prepared by the electrophoretic deposition of the suspension in a high magnetic field. For this method, a pair of palladium (Pd) electrodes ($25 \times 15\,\text{mm}^2$) were immersed in the slurry which was placed in the center of the magnetic field of a superconducting magnet. Then, EPD was carried out by applying an electric field of 25 V cm$^{-1}$ between the electrodes for 1 h and a constant high magnetic field of 12 T was maintained throughout the process at room temperature. Here, the magnetic and electric fields were parallel with each other and perpendicular to the surface of the electrodes, so the Hex-Tet co-existing BT particles were deposited on the bottom electrode (cathode). More details about HM-EPD can be found elsewhere.\textsuperscript{12,19)} For comparison, the BT green compacts with 30, 70, and 90% hexagonal content were only prepared by the electrophoretic deposition method without the magnetic field. The obtained compacts were dried at room temperature for two weeks to prevent cracks’ formation. Hereafter, the green compacts with about 30, 50, 70, 80, 90, and 100% hexagonal phase are denoted by Hex30, Hex50, Hex70, Hex80, Hex90, and Hex100, respectively. The dispersants from the dried compacts were removed by heat treatment at 700 °C for 5 h and then the compacts with hexagonal content up to 90% were sintered at 1325 °C for 5 h in air. The BT compacts containing $\approx 100\%$ hexagonal phase were sintered at 1335 °C for 5 h in air.

The density of the sintered compacts was measured by Archimedes’ method using distilled water and the relative density was calculated using the theoretical density of BT (6.02 g cm$^{-3}$). The crystal structure and the crystal orientation of the polished surface of the sintered ceramics were studied by XRD (Ultima IV, Rigaku) with Cu-K$\alpha$ radiation. A degree of the crystal orientation was estimated by the Lotgering method.\textsuperscript{20)} The microstructures of the ceramics were observed by scanning electron microscopy (SEM; JEOL JSM-6510, Japan). For this, the ceramics were mirror polished and post-annealed at 1100 °C for 4 h. The average grain size for smaller grains was estimated at higher magnification using the linear intercept method, while the grain size of larger grains was estimated by averaging the size of more than 30 such individual grains.\textsuperscript{5)}

For the measurement of electrical properties, sintered ceramics were cut and polished into plate sample with a dimension of $4 \times 1.5 \times 0.4 \,\text{mm}^3$. These samples were post-annealed at 1100 °C for 4 h to recover mechanical damage and stress from the sample.\textsuperscript{21)} Then, Au-electrodes were formed by sputtering on the top and bottom surfaces of the plate samples with the area $4 \times 1.5\,\text{mm}^2$ and heated at 300 °C for 15 min to improve adhesion. The frequency dependent of dielectric constants and losses was measured using an LCR meter (Wayne Kerr Electronics 6440B) over the range of 1 kHz–1 MHz. The ferroelectric and piezoelectric properties were investigated by polarization–electric field ($P–E$) and strain–electric field ($S–E$) hysteresis loops, which were measured at 0.1 Hz and room temperature using a ferroelectric character evaluation system.

3. Results and discussion

The sintered BT ceramics for all of the compositions exhibited relative densities of 95% or higher. Figure 1
shows the XRD patterns of the polished surfaces of sintered BT ceramics fabricated by EPD in a 12 T magnetic field using BT powders with different hexagonal contents. The magnetic field (12 T) and electric field (25 V cm\(^{-1}\)) were applied parallel to each other and perpendicular to the surface.

For Hex100, a large \(F_{111}\) of 91% was observed. Such a large \(F_{111}\) was also reported for (111)-oriented BT ceramics prepared with 100% hexagonal BT powder.\(^{13,17}\) The obtained (111)-orientation was due to the structural transformation from the (0001)-oriented 6H-type structure to the (111)-oriented 3C-type structure during sintering.\(^{17}\) For Hex90, the \(F_{111}\) was decreased to 44%. And further decrease in the hexagonal content in the Hex-Tet co-existing powders decreased the \(F_{111}\) (also see Fig. 2). This decreasing trend of \(F_{111}\) with decreasing the hexagonal content was expected because only the hexagonal powders responded to the magnetic field. Note that a strong (100) orientation was also observed for the Hex90-Hex30 samples. Watanabe et al.\(^{17}\) reported the existence of a similar double orientation for the BT ceramics prepared using 100% hexagonal content. However, the (100) orientation was completely suppressed by post-annealing of a reduced hexagonal BT powder at 1000 °C in air for 1 h. In this study, all compositions of the Hex-Tet co-existing BT powders were also post-annealed at 1000 °C in air for 1 h; however, this seemed to be insufficient to prevent the double orientation for the hexagonal ratios of less than 100%. Further investigation is required to suppress the (100) orientation.

Fig. 1. XRD patterns of the polished surfaces of sintered BT ceramics fabricated by HM-EPD using hexagonal-tetragonal co-existing BT powders with different hexagonal contents. The magnetic field (12 T) and electric field (25 V cm\(^{-1}\)) were applied parallel to each other and perpendicular to the surface.

Fig. 2. The degree of (111)-orientation as a function of hexagonal contents of BT ceramics prepared by the HM-EPD. [Note: 100% hexagonal sample was sintered at 1335 °C and all others were sintered at 1325 °C for 5 h in air.]

Fig. 3. (a) SEM image of the polished surface of (111)-oriented BT ceramics with hexagonal content of 50%. The ceramic was mirror polished and annealed at 1000 °C for 4 h in air. The SEM image on the inset shows the microstructure of smaller grains of the ceramic. (b) Grain size as a function of hexagonal contents of the HM-EPD samples and the inset shows the percentage area covered by small grains of the ceramics.

Microstructures for the ceramics fabricated with the different hexagonal content powders were observed by SEM. Figure 3(a) shows a representative SEM image for the hexagonal content of 50%. A bimodal microstructure
was observed for all of the studied compositions. Such a bimodal microstructure is often observed for stoichiometric and Ti-rich compositions. The variation in the size of larger and smaller grains as a function of hexagonal contents is plotted in Fig. 3(b). The smaller grains were about 2–3 μm and the larger grains were 50–70 μm, and they were not strongly dependent on the hexagonal content. However, the fraction of area covered by the larger and smaller grains were different as a function of hexagonal content. The percentage area covered by the small grains is shown in the inset of Fig. 3(b). The area covered by the small grains was 67 ± 2% for the 50–90% hexagonal content samples. On the other hand, the areas of the 30 and 100% hexagonal content samples were larger than the value; that is, 75 and 90%, respectively. The grain size of EPD samples without a magnetic field was also bimodal and comparable with those of the HM-EPD samples with the same ratios.

Figure 4 shows the hexagonal content dependence of the dielectric constant and loss tangent of the HM-EPD samples measured at 1 kHz and room temperature. The largest dielectric constant was observed at the 100% hexagonal content. This was attributed to the large \( F_{111} \) of 91%, as a larger dielectric constant is expected in the off-polar directions such as \( \{110\} \) and \( \{111\} \) for BaTiO\(_3\). Besides the large \( \{111\} \)-orientation, the large area of the small grains with a large dielectric constant due to the grain size effect also counted for the largest dielectric constant. Meanwhile, the largest dielectric constant may also be, at least partially, attributed to its largest dielectric loss factor. At the 50–90% hexagonal content, the dielectric constant was decreased and not strongly dependent on the hexagonal content. For \( \{110\} \)-oriented BaTiO\(_3\) ceramics, it was reported that the dielectric constant did not increase with increasing the degree of \( \{110\} \)-orientation before the degree did not reach 80%. The degrees the \( \{111\} \)-orientation of the 50–90% hexagonal content samples were as low as 3–44%, and therefore much improvement in the degree was necessary to see a \( \{111\} \)-orientation dependence. The dielectric constant of the 30% hexagonal content was larger than those of the ceramics prepared using hexagonal content of 50–90%. This was due to the large area (≈75%) covered by small grains. The dielectric loss was below 3% for all of the HM-EPD samples.

The \( P-E \) hysteresis loops of the HM-EPD samples are shown in Fig. 5(a). Under an electric field of 30 kV cm\(^{-1}\), well saturated typical ferroelectric \( P-E \) hysteresis loops were obtained for all of the samples prepared with different Hex-Tet co-existing BT powders, while the ceramics prepared using 100% hexagonal content exhibited slightly leaky behavior. The remanent polarization (\( P_r \)) and coercive field (\( E_c \)) evaluated from the bipolar \( P-E \) hysteresis loops are shown in Fig. 5(b). The \( P_r \) and \( E_c \) values were 12–14 μC cm\(^{-2}\) and 2–3 kV cm\(^{-1}\), respectively, and no strong dependence on the degree of the \( \{111\} \) orientation was observed. Because the \( \{111\} \) direction is an off-polar direction for BaTiO\(_3\), the increase in the \( \{111\} \)-orientation should decrease the remanent polarization. The difference between the expectation and the observed data could be attributed to the insufficient degrees of the \( \{111\} \)-orientation for the 50–90% hexagonal content samples and the leaker response of the 100% hexagonal content sample.

Figure 6(a) shows the unipolar \( S-E \) curves of the HM-EPD samples. The maximum strain increased with increas-
The dielectric constant should increase with increasing the degree of off-polar (111)-orientation. The observed weak dependence suggests that the polarization switching in more randomly oriented polarization of smaller hexagonal content samples was more difficult and the switching become easier with increasing the degree of (111)-orientation. Thus, the dependence was weakened. Also, despite from the large orientation factor (over 90%) for the BT ceramics prepared using 100% hexagonal content, the $d_{33}$ value was, however, lower than that of the ceramics prepared with the 80% hexagonal content. Thus, this result suggested that the orientation factor solely could not contribute to the enhancement of piezoelectric properties. This discrepancy could be caused by different concentrations of possible twin defects for the ceramics prepared using different ratios of hexagonal content as the twin defects are expected to be higher for the ceramics prepared using 100% hexagonal BT powders. After exceeding the hexagonal content of 80%, the effect of twin defects on piezoelectric degradation was found to be dominant. Meanwhile, the $d_{33}$ values for the randomly oriented samples (prepared without magnetic field) for Hex-Tet co-existing powders with different hexagonal contents are also plotted for comparison. The decreasing nature of $d_{33}$ of randomly oriented ceramics is attributed to increased possible twin defects concentration with hexagonal contents increment.

Based on these results, grain-orientation and twin defects are found to have an opposite impact on properties enhancement. Thus, samples with high degree of texturing along with maintaining lower extent of twin defect is crucial for higher piezoelectric properties. Besides, grain size also plays an important role on piezoelectric properties. The property is not enhanced as expected, it may be due to the bimodal microstructures of the ceramics, where, it is difficult to segregate the individual effect of larger and smaller grain. Thus, the observed effect is the average effect of coarse and fine grains. In the future, ball-milling technique as well as sintering conditions will be modified to achieve highly (111)-oriented BaTiO$_3$ ceramics with uniform microstructures and optimum grain size in order to increase the domain wall density and enhance the piezoelectric properties.

4. Conclusions

In this study, (111)-oriented BaTiO$_3$ ceramics were fabricated by electrophoretic deposition in a high magnetic field by different ratios of hexagonal-tetragonal co-existing BT powders. Mainly, the variation of orientation and piezoelectric strain constant $d_{33}$ with hexagonal contents were investigated. Both orientation and $d_{33}$ values were increased with increasing hexagonal contents, but $d_{33}$ started decreasing after 80%, which reinforces the hypothesis that twin dominates the grain-orientation-associated properties enhancement as hexagonal content increases. This study confirms that the piezoelectric properties could

\[ d_{33} = \frac{S_{\text{max}}}{E_{\text{max}}} \times 10^5 \]
be enhanced between 70 to 90% hexagonal contents if one could control the uniform microstructure below 10\(\mu\)m grain size with reasonably high orientation.

**Acknowledgements** We would like to thank the Graduate Program for Power Energy Professionals (PEP), Waseda University from the MEXT WISE Program for partial support of this work. We would also like to thank Sakai Chemical Industry Co., Ltd., for providing BT01 powder.

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