Fabrication of Textured Ceramics Using Mn and Nb-doped Hexagonal BaTiO₃ by an Electrophoretic Deposition in a High Magnetic Field

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(111)-oriented Mn and Nb-doped barium titanate (BaTiO₃, BT) ceramics with fine grains were fabricated with an electrophoretic deposition (EPD) method in a high magnetic field and a topotactic phase transition. Initially, accumulations of (0001)-oriented hexagonal Ba(Ti_{0.95}Mn_{0.05})O₃ particles added with 2.5 mol%-Nb₂O₅ powder were prepared by the EPD method in the high magnetic field of 12 T. Then, the (111)-oriented, Mn and Nb-doped pseudo-cubic BT ceramics with fine grains of ~0.4 μm in diameter were obtained via the topotactic phase transition, with the degree of the (111) orientation being as high as 79 %. The piezoelectric properties of the oriented ceramics were also studied.

Key words: ferroelectric, barium titanate, grain-orientation, electrophoretic deposition, magnetic orientation.

1. INTRODUCTION

Barium titanate (BaTiO₃, BT) is a representative lead-free piezoelectric material. There are two major approaches to improving the piezoelectric properties. One is preparation of fine-grained BT ceramics [1-6]. It has been reported that the piezoelectric and dielectric properties of BT ceramics were maximized when the grain size was ~ 1 μm [4-6]. A high d_{33} value of 460 pC/N was obtained for fine-grained BT ceramics whose average grain size was 1.6 μm [1]. This value was higher than that of BT ceramics with larger grains (> 10 μm) (191 pC/N) [7]. The increased piezoelectric response has been attributed to an increased domain wall density in the small grains for BT ceramics. The other is preparation of crystallographically oriented BT ceramics [8-10]. At room temperature, BT has a tetragonal symmetry with a spontaneous polarization along the <001> directions. During application of an electric field to tetragonal BT in the directions which is not the spontaneous direction, such as [110] and [111], the polarization direction were rotated to the directions of the applied field and finally a monoclinic (or orthorhombic) phase with <110> polarization directions and a rhombohedral phase with <111> polarization directions can be induced, respectively, which results in a large piezoelectric response. This was demonstrated for (110)-oriented BT ceramics with a high d_{33} value of 788 pC/N [8]. An increased piezoelectric response was also reported for a (111)-cut tetragonal BT single crystal [11]. Therefore, a very high d_{33} value can be expected for oriented BT ceramics with the fine grains.

The well-known fabrication methods of oriented ceramics are templated grain growth (TGG), reactive TGG (RTGG), and hot forging [8,9,12,13]. However, large plate-like particles are needed in TGG and RTGG

methods thus the grain size of the resultant ceramics becomes large. Fabricating fine-grained ceramics by hot forging is also difficult because the shape of the particles must be anisotropic. In contrast, small particles can be used in the electrophoretic deposition (EPD) method in a high magnetic field if the particles are diamagnetically anisotropic [14,15]. The magnetic torque, T which aligns diamagnetic particles, is expressed as the following equation [16]:

$$T = \Delta\chi V \frac{B^2}{2\mu_0} \sin 2\theta \quad (1),$$

where $\Delta\chi$ is diamagnetic anisotropy, V is particle volume, B is magnetic flux density, μ_0 is magnetic permeability in vacuum, and θ is an angle between a magnetic field and an easier magnetization axis of the particle. T is driving force of rotation of the particle and it increases with increasing $\Delta\chi$. If the particle has large crystallographic anisotropy, it has a large $\Delta\chi$. Hence, large crystallographic anisotropy is advantageous for orientation. BT is a diamagnetic material and the crystal system is tetragonal at room temperature and the ratio of lattice parameters c to a (c/a) is 1.01. Since this value is rather small, tetragonal BT particles cannot be aligned along a high magnetic field easily [17]. On the other hand, hexagonal BT has a large c/a of 2.44. Actually, oriented BT ceramics were fabricated using hexagonal BT particles by slip-casting in a high magnetic field [10]. Then (0001)-oriented 6-H type hexagonal BT was transformed to (111)-oriented 3-C type (tetragonal or cubic) BT ceramics via sintering. This change of the orientation occurred, because [0001] direction of 6-H type hexagonal BT is the same as [111] direction of 3-C type BT.

The hexagonal phase is stable at high temperature >1430°C for undoped BT prepared in air [18]. This high temperature needs to be lowered in order to avoid undesirable grain growth of the BT particles. In previous study, it was demonstrated that the hexagonal phase could be stabilized at room temperature by doping transition elements [19-21]. Ba(Ti_{0.95}Mn_{0.05})O₃, Mn-doped BT, is transformed to a hexagonal form at the lower temperature of 1250°C. Moreover, the hexagonal Mn-doped BT can be transformed to 3-C type BT when it additionally reacted with Nb₂O₅ at 1250°C. Hence, we considered that fine-grained 3-C type Mn and Nb-doped BT ceramics can be obtained using these hexagonal BT particles.

In this study, we prepared accumulations which of (0001)-oriented hexagonal Mn-doped BT and Nb₂O₅ powders by an EPD method in a high magnetic field of 12T, and then (111)-oriented 3-C type Mn and Nb-doped BT ceramics with fine grains were obtained by sintering the accumulations. The degree of the preferential orientation of the accumulations and ceramics, grain size of the ceramics, and the piezoelectric properties were investigated. In addition, 3-C type Mn and Nb-doped BT ceramics were prepared from accumulations deposited by a slip-casting method in the high magnetic field and the properties were compared.

2. EXPERIMENTAL

Powders of barium titanate (Nippon Chemical Industrial Co., Ltd.), 5 mol%-MnO₂ and 5 mol%-BaCO₃ were well mixed and calcined at 1250°C for 5 h to synthesize hexagonal Mn-doped BT, Ba(Ti_{0.95}Mn_{0.05})O₃. The slurry of the hexagonal Mn-doped BT particles was prepared with dehydrated ethanol and a dispersant (polyethyleneimine). In order to transform hexagonal Mn-doped BT to 3-C type Mn-doped BT via sintering, an equivalent amount of Nb to Mn was premixed into the slurry in a form of Nb₂O₅ powder in order to reduce oxygen vacancies which hinder the phase transition. Then, the slurry was ball-milled for 20 h. The slurry was placed in the superconducting magnet, and then a high magnetic field of 12T was applied to the slurry to align each particle. A magnetic field was maintained during the EPD. A pair of palladium electrodes was immersed in the slurry. Then, the constant voltage of 50V was applied parallel to a magnetic field, so that the hexagonal particles were deposited on the electrode. As a result, the accumulations of (0001)-oriented hexagonal Ba(Ti_{0.95}Mn_{0.05})O₃ with an additive of 2.5 mol%-Nb₂O₅ were obtained. Slip-casting-derived accumulations of Mn-doped BT and Nb₂O₅ powders were prepared as described elsewhere [17]. After the dispersant was burned out, the accumulations were sintered at 1250°C for 5 h. Then, the (111)-oriented 3-C type Mn and Nb-doped BT ceramics were obtained. In addition, the randomly oriented Mn and Nb-doped BT samples were fabricated by the EPD method without the magnetic field.

The relative density of these samples was measured by an Archimedes method. The crystal structure and degree of the orientation of the accumulations and ceramics were measured by XRD (Rigaku UltimaIV, Cu Kα, 40kV, 30mA). The degree of (0001)-orientation

(F_{0001}) for the accumulations and the degree of (111)-orientation (F_{111}) for the ceramics were calculated from the XRD data in the 2θ range from 20 to 80° by the Lotgering method. The microstructures of these samples were observed by a field-emission scanning electron microscope (FESEM, Hitachi S-4500). In order to measure the grain size of the ceramics, the ceramics were mirror-polished using colloidal silica (mastermet2, particle size of 0.02 μm, Buehler) and then thermally etched at 1100°C for 10 min. To characterize the piezoelectric properties, gold electrodes were sputtered on the top and bottom surfaces of polished ceramics. Then the samples were cut into a size of 4.0 × 1.5 × 0.4 mm³. The piezoelectric properties, polarization-electric field (P - E) hysteresis and strain-electric field (S - E) hysteresis curves were measured at room temperature and 0.1 Hz using a ferroelectric character evaluation system with the ac field amplitude of 80 kV/cm.

3 RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the accumulations of Mn-doped BT and Nb₂O₅ powders prepared by the EPD method with and without the high magnetic field and the powder as a reference. The strong 0004, 0006, and 0008 peaks were observed for the accumulations prepared in the high magnetic field, which confirmed that a magnetic field was effective to induce the (0001)-orientation. F_{0001} for the (0001)-oriented accumulations was calculated to be 40 %. In previous study, the accumulations have been prepared by a slip-casting in a high magnetic field [10]. We also prepared the accumulations by the slip-casting method in 12T, then F_{0001} of the accumulations was 24 %. We considered that aggregation of the particles resulted in the decreasing of the F_{0001} of the accumulations prepared by the slip-casting method in the high magnetic field. Preparation of the accumulations by the slip-casting method needed a long time, and hence the particles aggregated during the slip-casting. On the other hand, the particles were deposited faster in the EPD method. Therefore, we improved the (0001)-orientation for the hexagonal accumulations by the EPD method in the high magnetic field.

Fig. 1 The XRD patterns of the accumulations of Mn-doped BT and Nb₂O₅ powders prepared by the EPD method (a) in the high magnetic field of 12T, (b) without the high magnetic field, and (c) the hexagonal Mn and Nb-doped BT powder.

Figure 2 shows the XRD patterns of the EPD-derived accumulations and the sintered ceramics in the region of 2θ from 44 to 46°. When the accumulations were sintered, the 20-24 peak disappeared and the 002 peak of Mn and Nb-doped BT appeared. The 002 peak was broad and did not split, thus the resultant ceramics was considered to be pseudo-cubic BT.

The XRD patterns of the (111)-oriented and randomly oriented Mn and Nb-doped ceramics prepared from the EPD-derived accumulations, and the Mn and Nb-doped BT powder are shown in Fig. 3. Here, the randomly oriented Mn and Nb-doped BT ceramics were obtained via sintering the accumulations prepared by the EPD method without the magnetic field. For the oriented ceramics, the strong 111 peak was observed. F_{111} of the oriented ceramics was calculated to be 79 %. On the other hand, F_{111} of (111)-oriented Mn and Nb-doped BT ceramics fabricated in this study by the slip-casting in the high magnetic field was calculated to be 29 %. Thus, a higher (111) orientation was obtained by the EPD method compared to the slip-casting method.

Fig. 2 The XRD patterns from 44 to 46° of (a) Mn and Nb-doped pseudo-cubic BT ceramics and (b) the accumulations of Mn-doped BT and Nb_2O_5 powders prepared by the EPD method.

Fig. 3 The XRD patterns of (a) the (111)-oriented, Mn and Nb-doped BT ceramics fabricated by the EPD method in the high magnetic field of 12T, (b) the randomly oriented Mn and Nb-doped BT ceramics fabricated by the EPD method without the high magnetic field, and (c) the Mn and Nb-doped BT powder.

Figure 4 (a) shows SEM images of the accumulations of the (0001)-oriented Mn-doped BT and Nb_2O_5 powders prepared by the EPD method in the high magnetic field. The accumulations were found to consist of submicron particles. The relative density was 60.1 %. After sintering the accumulations, fine-grained ceramics were obtained and the microstructure is shown in Fig. 4 (b). The average grain size of the ceramics was 0.4 μm and the relative density was 91.2 %. Note that an exaggerated grain growth was not observed for the samples sintered at low temperature of 1250°C. For comparison, the relative density of the (0001)-oriented accumulations prepared by the slip-casting method were 54.1 % and the relative density of sintered ceramics was 84.8 %.

The S - E and P - E hysteresis curves of the (111)-oriented Mn and Nb-doped BT ceramics prepared by the EPD method are shown in Fig. 5. The electrostrictive S - E curve and unsaturated P - E curve were observed with the small induced strain and polarization. For the randomly oriented Mn and Nb-doped BT ceramics, similar S - E and P - E responses were observed. There are two possible reasons for the small dielectric and piezoelectric responses. One is the small grain size. It is known that the dielectric and piezoelectric properties of BT ceramics were maximized at the grain size of $\sim 1 \mu\text{m}$, but they decreased with decreasing grain size [4-6]. In this study, the grain size was 0.4 μm , therefore the grain size needed to be increased to $\sim 1 \mu\text{m}$. The other is the Mn and Nb doping. It was reported that codoping of 3 mol% of Mn and Nb to BaTiO_3 reduced Curie temperature of BaTiO_3 below 0°C and thus made it paraelectric [7]. However, the S - E and P - E responses were rather similar to diffuse

Fig. 5 (a) The S - E hysteresis curve and (b) The P - E hysteresis curve measured at 0.1Hz for the (111)-oriented pseudo-cubic Mn and Nb-doped BT ceramics prepared by the EPD method.

dielectrics used for capacitor application [22], as evidence by the opened P - E loop. This was supported by a temperature dependent dielectric constant measurement of the Mn and Nb-doped BT ceramics, which showed a diffused peak near 120°C with a reduced temperature dependence of the dielectric constant. Thus, it is believed that the Mn and Nb-doped BT ceramics in this study became diffuse dielectrics and thus the S - E and P - E responses were reduced. The latter one is critical to improving the piezoelectric properties with the Mn and Nb doping method. An alternative approach to preparing oriented BT ceramic can be annealing undoped BT powder in H₂ atmosphere [10]. By doing this, tetragonal phase of BT transforms to a hexagonal phase. Then, 3-C type (111) oriented BT ceramics can be obtained by sintering accumulations of oriented hexagonal BT powder in an oxidizing atmosphere to change the hexagonal phase to the tetragonal phase. In ref. [10], the hexagonal BT powder was accumulated by a slip-casting method. When the EPD method is used to prepare the oriented BT ceramics, a higher degree of the (111) orientation is expected, which leads an increased piezoelectric response.

3. CONCLUSIONS

We fabricated the (111)-oriented 3-C type, Mn and Nb-doped BT ceramics with fine grains of ~0.4 μm in diameter by sintering the accumulations prepared by the EPD and slip-casting methods in the high magnetic field. It was found that the EPD method was more effective to increase the crystallographic orientation of the ceramics; the higher (111) orientation of $F_{111} = 79\%$ was obtained. The S - E and P - E responses of the oriented ceramics

were too small to see the effect of the orientation, which was attributed to the small grain size and the diffuse nature of the Mn and Nb-doped BT.

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REFERENCES

- [1] T. Karaki, K. Yan, T. Miyamoto, and M. Adachi, *Jpn. J. Appl. Phys.*, **46**, L97-L98 (2007).
- [2] T. Hoshina, K. Takizawa, J. Li, T. Kasama, H. Kakemoto, and T. Tsurumi, *Jpn. J. Appl. Phys.*, **47**, 7607-7611 (2008).
- [3] H. Takahashi, Y. Numamoto, J. Tani, and S. Tsurekawa, *Jpn. J. Appl. Phys.*, **45**, 7405-7408 (2006).
- [4] P. Zheng and J. L. Zhang, Y.Q. Tan, and C.L. Wang, *Acta Mater.*, **60**, 5022-5030 (2012).
- [5] G. Arlt, D. Hennings, and G. de With, *J. Appl. Phys.*, **58**, 1619-1625 (1985).
- [6] S. Shao, J. Zhang, Z. Zhang, P. Zheng, M. Zhao, J. Li, and C. Wang, *J. Phys. D: Appl. Phys.*, **42**, 189801-189801 (2009).
- [7] B. Jaffe, W. R. Cook Jr., H. Jaffe, "Piezoelectric ceramics", Academic Press, London, (1971), pp. 53-114.
- [8] S. Wada, K. Takeda, T. Muraishi, H. Kakemoto, T. Tsurumi, and T. Kimura, *Jpn. J. Appl. Phys.*, **46**, 7039-7043 (2007).
- [9] T. Sato, Y. Yoshida, and T. Kimura, *J. Am. Ceram. Soc.*, **90**, 3005-3008 (2007).
- [10] T. Watanabe, M. Shimada, T. Aiba, H. Yabuta, K. Miura, K. Oka, M. Azuma, S. Wada, and N. Kumada, *Jpn. J. Appl. Phys.*, **50**, 09ND01 (2011).
- [11] S. Wada, S. Suzuki, T. Noma, T. Suzuki, M. Osada, M. Kakihana, S.-E. Park, L. E. Cross, and T. R. Shrout, *Jpn. J. Appl. Phys.*, **38**, 5505-5511 (1999).
- [12] T. Kimura, M. H. Holmes, R. E. Newnham, *J. Am. Ceram. Soc.*, **65**, 223-226 (1982).
- [13] T. Takenaka, and K. Sakata, *Jpn. J. Appl. Phys.*, **19**, 31-39 (1980).
- [14] T. Uchikoshi, T. S. Suzuki, H. Okuyama, and Y. Sakka, *J. Mater. Sci.*, **39**, 861-865 (2004).
- [15] T. Uchikoshi, T. S. Suzuki, S. Iimura, F. Tang, and Y. Sakka, *J. Eur. Ceram. Soc.*, **26**, 559-563 (2006).
- [16] T. Sugiyama, M. Tahashi, K. Sassa, and S. Asai, *ISIJ Int.*, **43**, 855-861 (2003).
- [17] I. Fujii, T. Kita, K. Nakashima, T. Takei, N. Kumada, T. S. Suzuki, T. Uchikoshi, Y. Sakka, Y. Miwa, S. Kawada, M. Kimura, Y. Kuroiwa, and S. Wada, *Trans. Mat. Res. Soc. Japan*, **38**, 41-44 (2013).
- [18] K. W. Kirby, B. A. Wechsler, *J. Am. Ceram. Soc.*, **74**, 1841-1847 (1991).
- [19] H. T. Langhammer, T. Müller, R. Böttcher, V. Mueller, and H.-P. Abicht, *J. Eur. Ceram. Soc.*, **24**, 1489-1492 (2004).
- [20] A. Kirianov, N. Ozaki, H. Ohsato, N. Kohzu, and H. Kishi, *Jpn. J. Appl. Phys.*, **40**, 5619-5623 (2001).
- [21] J. a. Dawson, C. L. Freeman, L.-B. Ben, J. H. Harding, and D. C. Sinclair, *J. Appl. Phys.*, **109**, 084102 (2011).
- [22] T. Tsurumi, Y. Yamamoto, H. Kakemoto, and S. Wada, *J. Mater. Res.*, **17**, 755-759 (2002).

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