Effect of ball-milling time and surfactant content for fabrication of 0.85(Bi0.5Na0.5)TiO3:0.15BaTiO3 green ceramics by electrophoretic deposition

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We fabricated thick and dense green ceramics consisting of the powders of (Bi0.5Na0.5)TiO3 (BNT) and hexagonal BaTiO3 (BT) with a molar ratio of 0.85:0.15 by electrophoretic deposition (EPD) in the suspension of isopropanol of 200 ml with the mixed powders of 20 g, and investigated the effect of the ball-milling time and the surfactant (polyethyleneimine, PEI) content for the suspension on the deposition weight and density of the green ceramics. When the ball-milling time was changed from 2 to 30 h with the PEI content of 0.2 g, the deposition weight was maximized at the ball-milling time of 15 h while the density monotonically increased with increasing ball-milling time for the EPD process of 1 h. When the PEI content was increased from 0.1 g to 0.2 and 0.3 g at the ball-milling time of 20 h, the deposit weight and density were increased. At the PEI content of 0.3 g, after the first EPD process was carried out and the cathode where the green ceramics were deposited was replaced without changing the suspension, the second green ceramics could be fabricated for the suspension ball-milled for 20 h, but not for the suspension ball-milled for 3 h. These results were explained by the size of the powders and the amount of PEI attached to the powders.

Key-words : Electrophoretic deposition, Lead-free piezoelectric ceramic, BNT–BT, Polyethyleneimine

1. Introduction

Lead-free piezoelectric materials have attracted worldwide attention, because most of currently utilized piezoelectric materials contains toxic lead.1) (Bi0.5Na0.5)TiO3–BaTiO3 (BNT–BT) solid-solution is a representative lead-free piezoelectric system with a high Curie temperature of ~250°C at the composition of 0.85BNT–0.15BT.2,3) However, the piezoelectric constant $d_{33}$ was as low as ~140 pC/N.3) Therefore, it is important to increase the piezoelectric response for commercial application.

Among piezoelectric materials, Pb(Zn1/3Nb2/3)O3–PbTiO3 single crystals have the best piezoelectric performance ($d_{33}$ > 2,000 pC/N), which is attributed to specific crystallographic orientations and reduced domain size.4,5) Control of these in the lead-free BT ceramics increased the piezoelectric properties.6–8) Karaki et al. reported BT ceramics with a small grain size of ~1 µm had the enhanced piezoelectric performance of $d_{33} = 460$ pC/N due to reduced domain size,6) while Wada et al. reported the [110]-textured BT ceramics with a $d_{33}$ value of 788 pC/N.7) These values were larger than that of the randomly oriented ceramics with large grains ($d_{33} = 190$ pC/N).3)

To obtain fine-grained and textured lead-free piezoelectric ceramics, an electrophoretic deposition (EPD) method has been used under magnetic field.9–11) With this method, [111]-textured BT ceramics were successfully fabricated using hexagonal BT particles with large crystal anisotropy (c/a ~ 2.44) to facilitate magnetic alignment.8,9) However, BT ceramics have a low Curie temperature about 130°C, which limited high-temperature applications.1,6–8) In this study, as an initial step for fabricating [111]-textured BNT–BT ceramics by the EPD method, the green ceramics consisting of BNT and hexagonal BT powders were fabricated by the EPD method without using a magnetic field. The BNT:BT molar ratio was determined to be 0.85:0.15 because this composition has a higher Curie temperature, which coincided with a depolarization temperature ($T_D$), and it had a single phase tetragonal structure similar to that of BT ceramics.2,3) The deposition weight and relative density of the green ceramics were measured for investigating effect of the surfactant (Polyethyleneimine, PEI) content and the ball-milling time for the suspension of the powders with PEI.
2. Experimental procedure

Green ceramics consisting of BNT and hexagonal BT powders with the BNT:BT molar ratio of 0.85:0.15 (85BNT–15BT) were fabricated by an EPD method. The starting materials were BNT (Nippon Chemical Industry Co., Ltd., particle sizes ~500 nm) and a hexagonal BT powder. The hexagonal BT powder was prepared from pseudo-cubic BT powder (BT01, particle sizes ~100 nm, Sakai Chemical Industry Co., Ltd.) which was fired at 1500°C in a H₂ reduction atmosphere. The obtained hexagonal BT powder was post-annealed at 1000°C in air for oxidizing reduced Ti ions while maintaining the hexagonal structure.10 To prepare a fine hexagonal BT powder, ball-milling was conducted three times using zirconia balls with different ball sizes and ethanol. First, the powder was ball-milled for 20 h with 10 mm diameter zirconia balls. Second, the slurry from the first procedure was ball-milled with 3 mm diameter zirconia balls for 20 h. Finally, the obtained slurry was ball-milled with 1 mm diameter zirconia balls for 20 h. The slurry was subjected to centrifugation at 1000 rpm for 10 min to remove larger particles. The slurry was then dried at 90°C for 12 h in an oven.

In order to prepare 85BNT–15BT green ceramic using an EPD process, the BNT and hexagonal BT powders were weighed according to the chemical formula and anhydrous iso-propanol was added. Then, PEI (molecular weight > 10,000) at different contents of 0.1, 0.2, and 0.3 g were added as surfactant and cationic polyelectrolyte to the slurry.12 Finally, ball-milling was carried out with 3 mm diameter zirconia balls for different duration of 2–30 h to prepare dispersed suspensions. After ball-milling, a powder per medium concentration was adjusted to a powder of 20 g per iso-propanol of 200 ml (100 g/l). The EPD process was carried out under an electric field of 75 V/cm using a pair of Palladium (Pd) electrodes (the electrode area was 25 mm × 25 mm) immersed in the suspensions. Deposited green ceramics were dried at room temperature in air and then PEI was removed by annealing at 600°C for 2 h.

The deposition weight of the green ceramics was measured before the PEI burn-out. The relative density was measured using an Archimedes method after the PEI burn-out. Microstructures of the green ceramics were observed by field emission scanning electron microscopy (FE-SEM, JSM-6500F, JEOL). The zeta potential and particle sizes of the BNT and hexagonal BT powders and PEI-added BNT–BT suspensions were measured by laser Doppler velocimetry (Zetasizer Nano-ZS, Malvern). For this, the concentration of the PEI-added BNT–BT suspensions (100 g/l) was diluted to 0.1 g/l.

3. Results and discussion

To obtain thick and dense green ceramics by the EPD process, high zeta potential particles are required for achieving high mobility under the electric field and preventing flocculation. Table 1 lists zeta potential and pH of the suspensions of the BNT and hexagonal BT powders and the PEI-added BNT–BT powder in iso-propanol medium. The suspension of the PEI-added BNT–BT powder was ball-milled for 20 h and the PEI-added BNT–BT powder in iso-propanol medium. Here, the suspension of the PEI-added BNT–BT powder was ball-milled for 20 h. Both the BNT and hexagonal BT powders showed negative zeta potential and the absolute values were small. This suggested that the suspension was near an isoelectric point.13,14 This low zeta potential was not appropriate for the EPD process because it was difficult to retain the deflocculated suspensions with high mobility under the electric field. Since the EPD suspension of the concentration of 100 g/l without the surfactant settled quickly, it was clear that the surfactant was important to prepare a well-dispersed suspension. PEI is a representative cationic polyelectrolyte and PEI-adsorbed particles were deflocculated by the electrostatic repulsion due to the positive charge of PEI and the steric repulsion because of the adsorbed polymer layers.15 In this experiment, the particle charge of the PEI-adsorbed 85BNT–15BT suspensions was mainly determined by the adsorbed PEI on the particles: for example, a 0.2 g PEI-added suspension with the BNT and BT powders showed a high positive charge (zeta potential of about 61.8 mV) which was appropriate for the EPD process. It was confirmed that the PEI-added particles were deposited on the negative electrode during the EPD process because of the positive charge of PEI.

To find an optimum fabrication condition for the thick and dense green ceramics, the suspensions of the BNT and BT powders with 0.2 g of PEI were ball-milled for 2 to 30 h. The average particle sizes were measured using Zetasizer and were 558, 485, 452, 651, 612, and 1414 nm after 2, 10, 15, 20, 24, and 30 h ball-milling, respectively. SEM images of green ceramics fabricated by the EPD process are shown in Fig. 1. When the powders were ball-milled for 2–20 h, large particles were observed as indicated yellow arrows. On the other hands, large size particles were disappeared above 20 h ball-milling time. This was qualitatively consistent with the decrease in the average particle size measured by Zetasizer for the ball-milling time up to 15 h. Only fine particles were observed for the ball-milling time of 24 and 30 h. However, the average particle size measured by Zetasizer was increased. This was probably due to the aggregation of individual particles. Green ceramics fabricated using the suspensions are shown in Fig. 2(a). When the powders were ball-milled for 2 h, the weight and density of the green ceramics were as low as 1.97 g and 49.0%, respectively. As the ball-milling time increased, the weight increased up to the ball-milling time of 15 h and then decreased while the green
density monotonically increased [Fig. 2(c)]. To understand the decrease in the weight and the increase in the green density, the electric current during the EPD process was measured as a function of time at the electric field of 75 V/cm. Figure 2(b) shows the electric current behaviors with various ball-milling times. For the 2-h-ball-milling sample, the electric current was 2.4 mA when the EPD process was started. It rapidly decreased in the first 10 min. This was a typical EPD behavior, as the electric field between the electrodes was decreased by accumulation of insulating ceramic particles on the electrode.\(^{11,12}\) On the other hand, the electric current was not decreased rapidly for the samples with the 10 and 15 h ball-milling. It was assumed that PEI was acted as an additional conductive electrode between the electrode and the accumulated insulating particles.\(^{12}\) Therefore, the electric current was not rapidly decreased even though the ceramic particles were deposited on the cathode. For the sample with the 20-h-ball-milling, the electric current was decreased, and the current responses of the 24- and 30-h-ball-milling samples were further decreased and became similar to that of the 2-h-ball-milling sample. These results suggested that the deposition mechanism was changed by the ball-milling time. It was considered that this change was caused by the change in the degree of PEI adsorption on particle surfaces. It was supposed that the adsorption of PEI on the particle surfaces required sufficient time. That is, the ball milling of 2 h was so short that PEI could not fully cover the particles. Therefore, the deposition weight and the relative density were low. When the ball-milling time was increased to 10–15 h, the amount of PEI coated on the particles increased and thus the deposition weight increased. On the other hand, the ball milling time longer than 20 h decreased the deposition weight. This could be associated with the particle aggregation. It was considered that particle size was decreased and the surface area was increased with increasing ball-milling time, and thus the PEI sites were increased. Taking this into account, PEI did not fully cover individual particles which made an aggregation easily because of the lack of steric repulsion in each PEI adsorbed particle for example 1414 nm in the 30-h-ball-milled suspension. Therefore, the deposition weight was reduced for the longer ball-milling because of the decrease in the mobility of the aggregated particles while the relative density was kept constant because the amount of the adsorbed PEI on each individual particle surface was not changed in aggregated particles.

Since the amount of PEI attached to the particle surfaces seemed to be important for the deposition behavior, effect
of the PEI content for the EPD process was studied. Green ceramics fabricated by the 20 h ball-milling with various PEI contents are shown in Fig. 3(a). All of the green ceramics had deposition weights of about 2 g. The green ceramics with the low PEI content of 0.1 g had many cracks and the low relative density of 35.6%. On the other hand, the green ceramics with the 0.2 and 0.3 g PEI contents were denser and had the higher relative densities of about 54%. This result confirmed that a specific amount of PEI (0.2 g in this experiment) was needed for the preparation of thick and dense green ceramics. Figure 3(b) shows the deposition time dependence of the electric current. All of the EPD processes showed that the electric current decreased with increasing deposition time, and no significant differences were observed with the PEI contents.

To obtain thick and dense green ceramics effectively, two green ceramics were prepared by repeating the EPD process using the same suspension with the 0.3 g of PEI content. Here, after the first green ceramics were fabricated on the cathode, the cathode was removed from the suspension. Then, a new cathode was inserted and the second EPD process was performed. Here, effect of ball milling time (3 and 20 h) was studied. Figure 4(a) shows the first and second green ceramics fabricated by the 3- and 20-h-ball-milling.

The first green ceramics fabricated by both 3 and 20 h ball-milling had similar deposition weights and relative densities. On the other hand, the second green ceramics could not be fabricated by the 3 h ball-milling, while it could be fabricated by the 20-h-ball-milling. It was believed that the second green ceramics by the 3 h ball-milling could not be fabricated because most of the PEI-coated particles was used up for the fabrication of the first green ceramics. The increase in the ball-milling time from 3 to 20 h increased the number of PEI-coated particles, so that the second green ceramics could be fabricated by the 20 h ball-milling. Figure 4(b) shows the deposition time dependence of the electric current. For the 20 h ball-milling samples, the current values and deposition weights were consistent; the lighter first green ceramics were fabricated with the smaller electric current. On the other hand, the current behaviors for the 3 h ball-milling samples were confusing because some current was observed for the preparation of the second green ceramics, which were not obtained. This was probably occurred because of the flow of PEI (which was not attached to the particles) under the electric field.

Based on the above experiments, adsorption of PEI on the particle surfaces was important. For the low PEI content of 0.1 g, it was considered that particle surfaces were not fully covered with PEI as shown in Fig. 5(a). In this case, the driving force to migrate to the electrode was small and aggregation could be easily occurred due to incomplete steric repulsion and lack of the charge change from negative to positive on the particles surface, which led the low deposition weight and relative density. When the PEI content was large (0.3 g) but the ball-milling time was short (3 h), the particles were also not fully covered with PEI, as shown in Fig. 5(b). On the other hand, when the PEI content was large (0.3 g) and the ball-milling time was sufficiently long (20 h), the particles were fully covered with PEI, as in Fig. 5(c). This resulted in the high deposition weight and high relative density. Lastly, the green ceramic fabricated by the EPD method with the PEI...
content of 0.2 g and the ball-milling time of 20 h were sintered at 1125°C for 2 h. The piezoelectric constant $d_{33}$ evaluated by a $d_{33}$ meter was 70 pC/N. A further increase in the $d_{33}$ value is expected for ceramics whose the crystal orientation is aligned by a high magnetic field.

4. Conclusions

Lead-free 85BNT–15BT green ceramics were fabricated by the EPD process, and the effect of the PEI content and the ball-milling time was investigated. For the samples with the 0.2 g PEI content, the deposition weight was maximized at the ball-milling time of 15 h. It was found that the specific period of ball-milling enabled fabrication of thick and dense green ceramics. In short ball-milling time, particles were not fully covered with PEI while smaller particles with larger PEI sites could not accommodate a sufficient amount of PEI in long ball-milling time. The lack of PEI attached to the particles resulted in the reduced mobility under the electric field and flocculation, which reduced the deposition weight. On the other hand, the green ceramic density was monotonically increased with ball-milling time due to the increase of the amount of adsorbed PEI contents on the particle surfaces.

The amount of PEI added to the suspension also affected the quality of the green ceramics. For the 20 h ball-milled samples, the PEI content of 0.1 g was not sufficient and those of 0.2 and 0.3 g were necessary to obtain the higher densities. And, the powder ball-milled for 20 h with the 0.3 g PEI content allowed the second EPD process.

Under the optimum fabrication conditions, the green ceramics fabricated from the EPD process showed the high deposition weights over 2 g and the relative densities over 50% which were comparable to those of conventionally prepared green ceramics. The EPD process has advantages such as the high possibility of mass production and the use of a magnetic alignment technique. We believe that [111]-orientation textured BNT–BT ceramics could be fabricated using an EPD process under a high magnetic field.

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References

1) B. Jaffe, W. R. Cook, Jr. and H. Jaffe, “Piezoelectric ceramics” Ed. by J. R. Roberts and P. Popper, Academic Press London and New York (1971) pp. 53–181.
2) T. Takenaka, K. Maruyama and K. Sakata, \textit{Jpn. J. Appl. Phys.}, 30, 2236–2239 (1991).
3) Y. S. Sung, J. M. Kim, J. H. Cho, T. K. Song, M. H. Kim and T. G. Park, \textit{Appl. Phys. Lett.}, 96, 202901 (2010).
4) S.-E. Park and T. R. Shrouf, \textit{Mater. Res. Innov.}, 1, 20–25 (1997).
5) S.-E. Park and T. R. Shrouf, \textit{J. Appl. Phys.}, 82, 1804 (1997).
6) T. Karaki, K. Yan and M. Adachi, \textit{Jpn. J. Appl. Phys.}, 46, 7035–7038 (2007).
7) S. Wada, K. Takeda, T. Muraishi, H. Kakemoto, T. Tsurumi and T. Kimura, \textit{J. Appl. Phys.}, 46, 7039–7043 (2007).
8) E. Kobayashi, S. Ueno, K. Nakashima, N. Kumada, T. S. Suzuki, T. Uchikoshi, Y. Sakka, I. Fujii and S. Wada, \textit{Trans. Mater. Res. Soc. Jpn.}, 40, 223–226 (2015).
9) T. Sugiyama, M. Tahashi, K. Sassa and S. Asai, \textit{ISIJ Int.}, 43, 855–861 (2003).
10) T. Watanabe, M. Shimada, T. Aiba, H. Yabuta, K. Miura, K. Oka, M. Azuma, S. Wada and N. Kumada, \textit{Jpn. J. Appl. Phys.}, 50, 09ND01 (2011).
11) S. Okamura, T. Tsukamoto and N. Koura, \textit{Jpn. J. Appl. Phys.}, 32, 4182–4185 (1993).
12) I. Zhitomirsky, \textit{Adv. Colloid Interfac.}, 97, 279–317 (2002).
13) O. O. Van der Biest and L. J. Vandeperre, \textit{Annu. Rev. Mater. Sci.}, 29, 327–352 (1999).
14) M. C. Blanco-Lopez, B. Rand and F. L. Riley, \textit{J. Eur. Ceram. Soc.}, 17, 281–287 (1997).
15) M. C. Blanco-Lopez, B. Rand and F. L. Riley, \textit{J. Eur. Ceram. Soc.}, 20, 1587–1594 (2000).