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Grain-orientation control of $Bi_5FeTi_3O_{15}$ ceramics prepared by magnetic-field-assisted electrophoretic deposition

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Magnetic-field-assisted electrophoretic deposition (*B*-assisted EPD) method has been applied for synthesizing *a*(*b*)-axis-oriented $Bi_5FeTi_3O_{15}$ ceramics, and the effects of the *B*-assisted EPD on grain orientation and microstructures have been investigated. The sintering at 1100 °C of the green compact obtained by the *B*-assisted EPD led to dense ceramics with a high relative sintered density of 98 %. X-ray diffraction analysis shows that the *a*(*b*)-axis-orientation degree of the grain oriented ceramics evaluated by the Lotgering method was 45 %.
Key words: Bismuth layer-structured ferroelectric, Grain orientation, Magnetic field, electrophoretic deposition

1. INTRODUCTION

Much attention has been paid to bismuth layer-structured ferroelectrics (BLSFs) from the technological and scientific points of view because of their high Curie temperature (T_C) [1, 2] and relatively large spontaneous polarization (P_s) [3, 4-6]. In the crystal structure, perovskite blocks composed of m layers of BO_6 octahedra with A-site cations are sandwiched between Bi_2O_2 layers. The entire displacement of the perovskite blocks with respects to the Bi_2O_2 layers induces ferroelectric Ps which appears mainly along the *a*-axis [3]. This layered structure results in a strong anisotropy of the ferroelectric and piezoelectric properties of BLSFs. Strenuous efforts have been devoted to prepare grain-oriented (GO) ceramics of $Bi_4Ti_3O_{12}$ (BiT) and related materials by hot forging [7-9] and templated grain growth method [10-13]. These methods using the anisotropy of grain growth allow us to obtain GO-BLSFs ceramics. Recently, colloidal processing taking advantage of high magnetic field [14-16] has been developed to obtain GO-ceramics not only of alumina [14, 15, 17] and titania [18, 19] but also of BLSFs [16, 20-23]. In this processing, a magnetic field (*B*) of 10~12 T is applied to particles dispersed in a colloidal suspension. The interaction between the anisotropic magnetic susceptibility ($\Delta\chi$) of the particles and *B* leads to a magnetic torque (*F*) [17, 24], which is a driving force for the alignment of the particles along a specific crystallographic orientation.

Here, we report the B-assisted electrophoretic deposition (*B*-assisted EPD) for synthesizing $Bi_5FeTi_3O_{15}$ (BFT) ceramics. For the *B*-assisted EPD, we perform EPD under a high *B* in the suspension in which the particles are uniaxially aligned by *F*, leading to GO-green compacts. A degree of grain orientation is greatly enhanced by grain growth and densification of the compacts during sintering [14]. The *B*-assisted EPD [14] is an active method for synthesizing GO-green compacts in a short period of time of several tens minutes compared with the slip casting method.

EXPERIMENTAL

BFT powder was synthesized by solid-state reaction using Bi_2O_3 (99.9999%), TiO_2 (99.99%) and Fe_2O_3 (99.99%). These raw materials were weighted with a composition of $Bi_5FeTi_3O_{15}$. In order to investigate a calcination temperature at which single-phase BFT is formed, the mixture was calcined at different temperatures from 800 to 1000 °C for 2 h in air. The optimized calcination temperature for BFT powder was determined to be 900 °C.

For obtaining green compacts by the B-assisted EPD, we dispersed the calcined powder homogeneously in ethanol with phosphoric ester and polyethylenimine using magnetic stirrer with the help of an ultrasonic horn. EPD was conducted for 60 mm in a magnetic field of 12 T using a pair of facing Pd electrodes with an electrode spacing of 20 mm by applying an electric voltage of 200 V. In this processing, both electric and magnetic fields were applied along a vertical line, and the particles were deposited onto the bottom electrode. After the deposited bulk was drawn out from the suspension outside the magnet and carefully dried for 1 week under no magnetic field. The dried compacts were sintered at 1100 °C for 2 h in air. For comparison, randomly-oriented (RO) BFT ceramics were prepared by conventional solid-state reaction using the same powder used for the EPD processing. The powders were pressed into disks followed by cold isostatic pressing and then sintered at 1100 °C for 2 h in air. The density was determined by the Archimedes method.

Constituent phase, crystal structure, and grain orientation of the sintered ceramics were analyzed by x-ray diffraction (XRD). The degree of *a*(*b*)-axis orientation was evaluated by the Lotgering method. Microstructures were observed by scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Figure 1 shows an SEM image for grinded BFT particles used for preparing GO-ceramics. The particles

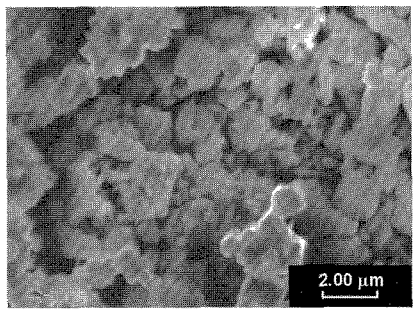

Fig. 1. A SEM image for ground BTF particle after calcination.

have an elongated or plate-like shape with a grain size of several microns (1-4 μm). Figure 2 represents the XRD patterns measured on the surface of BFT ceramics. All of the XRD peaks can be assigned to BLSF (m = 4). Compared with the RO-ceramics [Fig. 2 (a)], the green compacts obtained by the B-assisted EPD [Fig. 2 (b)] exhibited a slightly high intensity ratio of 200/020 to 119. The degree of $a(b)$-axis orientation was estimated to be 6 % for the green compacts, demonstrating that the alignment of the particles in the suspension induced by the B application remains even in the green compacts.

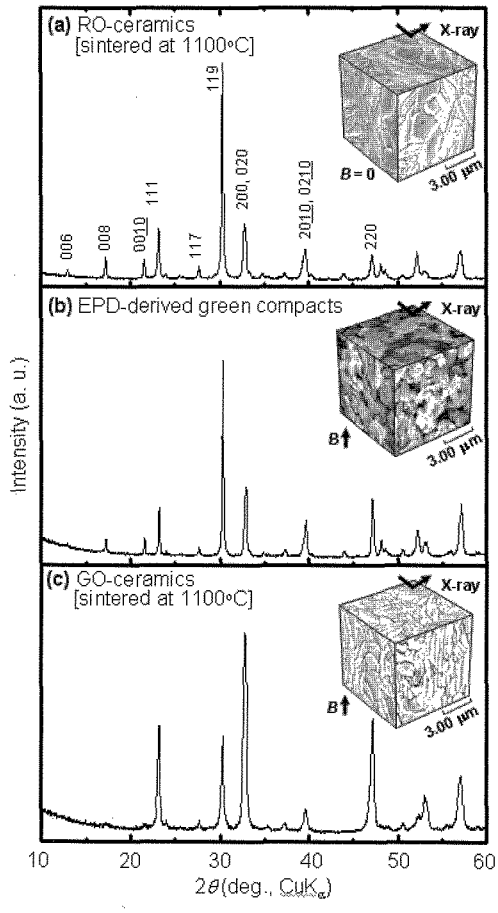

Fig. 2 . XRD patterns of BTF ceramics measured on the surfaces of the bulk samples for (a) randomly-oriented (RO)-ceramics, (b) EPD-derived green compacts and (c) GO-ceramics with schematic 3D microstructure produced from SEM images.

Since the surface normal of the compacts is corresponding to the direction of B, the $a(b)$-axis orientation along B is established for BFT particles, which agrees well with GO-ceramics of BiT [21, 23] and $CaBi_4Ti_4O_{15}$ (m = 4) [20] prepared by the slip casting under B.

In the process of the B-assisted EPD, a high B of 12 T generated in a superconducting magnet is applied to the particles homogeneously dispersed in a stable colloidal suspension. An F [17, 24] is exerted to the particles as a result of the interaction between the $\Delta\chi$ and B. Even though the $|\Delta\chi|$ of BFT is assumed to be as small as 1 $\times$ 10^{-8} like BiT [16], the high value of B plays a critical role in F. Since F is proportional to B^2, F of the particles in B is expressed as

$$F = -\Delta\chi V B^2 \sin 2\phi / 2\mu_0 \quad (1)$$

where μ_0 is the permeability of vacuum, $\Delta\chi$ is the anisotropic magnetic susceptibility, V is the particle volume and ϕ is the angle between the axis with the largest magnetic susceptibility and B. Since the use of a high B offers a sufficiently high F acting upon the particles, the particles are aligned along a specific orientation with respect to B to minimize the system energy. Note that densification followed by grain growth during sintering at 1100 °C of the green compacts promotes the $a(b)$-axis orientation [see Fig. 2(c)]. For GO-ceramics after the sintering, the peaks of 200/020 and 220 became marked and the peak intensity of 119 decreased. The $a(b)$-axis orientation degree of GO-ceramics (45 %) was much higher than that of green compacts (6 %).

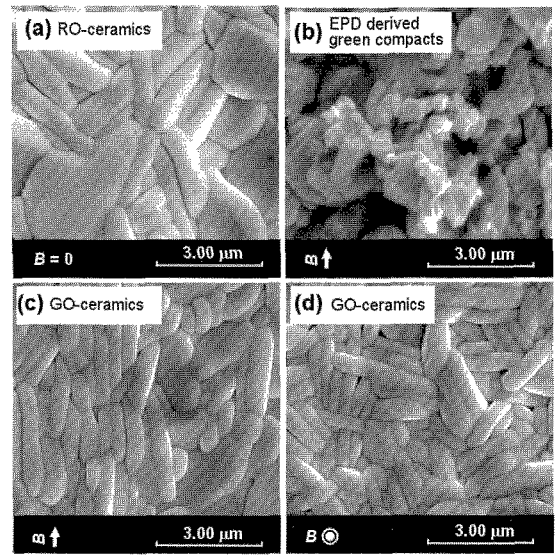

Fig. 3. SEM images of (a) RO-ceramics, (b) the cross-sectional surface of EPD-derived green compacts, (c) the cross-sectional surface of GO-ceramics and (d) the surface of GO-ceramics. The direction of B is depicted in arrows [Fig. 3(b) and (c)] and circles [Fig. 3 (d)].

Figure 3 shows the SEM images of (a) RO-ceramics, (b) the cross-sectional surface of EPD-derived green compacts, (c) the cross-sectional surface of

GO-ceramics and (d) the surface of GO-ceramics. The direction of *B* is indicated by arrows [Fig. 3(b) and (c)] and circles [Fig. 3 (d)]. Both ceramics synthesized by *B*-assisted EPD and fabricated by conventional solid-state reaction had a relative sintered density of 98 %. The grains of the ceramics sintered at 1100 °C have platelet shapes with a grain size of around 4 μm. These results suggest that the grain orientation in BFT ceramics proceeds via two states: the first state is the *a*(*b*)-axis alignment of the particles by *F* in the suspension [Fig. 2(b)] and this particle alignment is maintained in the green compacts obtained by EPD [Fig. 3(b)]; the second state is the enhancement of the *a*(*b*)-axis orientation of the grains by densification followed by grain growth during the sintering process [Fig. 3(c)].

CONCLUSIONS

B-assisted EPD method has been applied for synthesizing *a*(*b*)-axis-oriented $Bi_5FeTi_3O_{15}$ ceramics. Both ceramics sintered at 1100 °C obtained by the *B*-assisted EPD and conventional solid-state reaction had a relative sintered density of 98 %. The grains of GO- and RO-ceramics were a platelet shape with a grain size of around 4 μm. The degree of *a*(*b*)-axis orientation of the GO-ceramics evaluated by the Lotgering method was 45 %, which was much higher than that of green compacts (6 %).

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