Fabrication of crystal-oriented barium-bismuth titanate ceramics in high magnetic field and subsequent reaction sintering

Satoshi Tanaka¹, Yusuke Tomita¹, Ryoichi Furushima¹, Hiroyuki Shimizu², Yutaka Doshida² and Keizo Uematsu¹

¹Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 9402188, Japan
²R&D Centre, Taiyo Yuden Co. Ltd, Takasaki Gunma, Japan
E-mail: stanaka@vos.nagaokaut.ac.jp

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Abstract
High magnetic field was applied to fabricate novel lead-free piezoelectric ceramics with a textured structure. A compact of crystallographically oriented grains was prepared by dry forming in a high magnetic field from a mixed slurry of bismuth titanate and barium titanate powders. Bismuth titanate particles with a size of about 1 µm were used as the host material. In the forming process, the slurry was poured into a mold and set in a magnetic field of 10 T until completely dried. Bismuth titanate particles were highly oriented in the slurry under the magnetic field. The dried powder compact consisted of highly oriented bismuth titanate particles and randomly oriented barium titanate particles. Barium bismuth titanate ceramics with a- and b-axis orientations were successfully produced from the dried compact by sintering at temperatures above 1100 °C.

Keywords: magnetic field, lead-free piezoelectric ceramics, sintering, bismuth titanate

1. Introduction
Bismuth-layered structure ferroelectrics (BLSFs) have a very high potential as new functional materials of the new generation [1–6]. They are lead free and thus may replace the current PZT (PbₓZr₁₋ₓTiO₃) system. However, their highly anisotropic properties hinder the applications. The piezoelectric constants are very high only along the a- and b-axis, but not along the c-axis [4]. Therefore, to achieve high performance in applications, the crystals must be oriented to a specific direction. As-synthesized BLSF particles often exhibit platelike shapes with a well-developed c-face [7]. The c-face laminated texture can be easily produced with conventional fabrication techniques such as hot pressing and tape casting [4, 7–10]. However, a new method is needed to orient the c-axis normal to the lamination.

The fabrication method using a magnetic field can align crystal grains in ceramics to a designed direction [11–14]. The method has outstanding merits. Firstly, the direction of orientation can be controlled easily and freely by adjusting the direction of magnetic field. Secondly, fine spherical particles can be used. This makes the subsequent densification very easy. Particle orientation within a dense structure has been reported for alumina, titania, and zinc oxide, which have a very low magnetic susceptibility (<|10⁻⁶|), using magnetic field of 10 T [14–21]. Recently, we have reported the a- and b-axis-oriented bismuth titanate Bi₄Ti₃O₁₂ (BiT) ceramics [11, 22]. The optimum conditions for fabricating...
The objective of this study is to fabricate BaBi₄Ti₄O₁₅ (BBTi) ferroelectric ceramics by the two-step method involving particle alignment in the magnetic field and a subsequent reaction sintering. In the first step, a mixed slurry containing BiT and BaTiO₃ (BT) powders was set in the magnetic field. The powder compact has a- and b-axis-oriented BiT particles and randomly oriented BT particles. Barium bismuth titanate (BBTi) of a- and b-axis orientation can be obtained via the reaction sintering of BiT and BT,

\[ \text{Bi}_4\text{Ti}_3\text{O}_{12} + \text{BaTiO}_3 \rightarrow \text{BaBi}_4\text{Ti}_4\text{O}_{15}. \]  

The crystal direction of oriented BiT after sintering should be maintained as BaTiO₃ particles reacted topotaxically (i.e., preserving initial orientation) on oriented BiT, as shown in figure 1. Although Ba²⁺ is larger than Sr²⁺, the Ba²⁺ may diffuse into BiT particles.

2. Experimental procedure

2.1. Sample preparation

Bismuth titanate Bi₄Ti₃O₁₂ powders, which were prepared via the solid reaction of Bi₂O₃ and TiO₂ at 950 °C, were used as raw material [22]. The average particle size was nominally 1.0 µm, and the specific surface area, measured by the BET method, was 2.5 m² g⁻¹. BaTiO₃ particles (Sakai Chemical, Japan) were 0.3 and 0.5 µm in diameter (figure 2). A mixed slurry was prepared by ball milling with a dispersant for 24 h with a powder volume fraction of 30 vol%. The slurry (5 cm³) in a shallow plastic container was placed horizontally in a superconducting magnet (bore: 100 mm, TM-10VH10, TOSHIBA, Japan). The container was continually exposed to a magnetic field (10 T) for 1 day at room temperature until the slurry has completely dried. Reference samples were dried without magnetic field. The dried powder compacts were heated at 5 °C min⁻¹ from 1000–1150 °C and held at that temperature for 1 h before cooling to room temperature. The orientations of particles in the powder compact and sintered bodies were determined by analyzing x-ray diffraction (XRD) patterns with the Lotgering method. Mass density was measured with the Archimedes method using distilled water as the immersion liquid. The specimen was polished and thermally etched for 1 h to examine the microstructure by scanning electron microscopy (SEM).

2.2. Testing of cation diffusion

The diffusion of cations such as Bi³⁺ and Ba²⁺ into another material was studied by a diffusion test. Each sintered body was made by dry pressing from BiT and BT powders. The pressure was about 50 MPa. Each BiT and BT powder compact was heated at 1200 and 1350 °C, respectively. After machining and polishing to a 5 × 5 × 2 mm³ size, each sample was stacked and heated at 1100 °C for 0–24 h. The cross section at the interface was observed and analyzed for Ba and Bi concentrations with SEM combined with energy dispersive x-ray analysis (SEM-EDX).
Figure 2. Raw powders used in this study; (a) synthesized BiT, (b) barium titanate (particle size 0.3 μm) and (c) barium titanate (0.5 μm).

3. Results

Figure 2 shows bismuth titanate (BiT) and barium titanate (BT) powders. The size of BiT particles ranged between 0.5 and 2 μm; their shapes were irregular but not platelike. The two kinds of BT powders with particle size of 0.3 and 0.5 μm shown in the figure were nearly spherical and had a mono-disperse size distribution. The crystal structure of BT at room temperature is a tetragonal, similar to a cubic system.

The diameter ratios of BiT/BT were 3 and 5. Particle ratio may affect the reaction.

Figure 3 shows the diffusion of Ba\(^{2+}\) and Bi\(^{3+}\) after 16 h at 1100 °C. The cations had different distributions. Ba\(^{2+}\) diffused 0.6 mm, further than Bi\(^{3+}\) ions (0.1 mm). This indicated that more of the material BaBi\(_4\)Ti\(_4\)O\(_{15}\) (BBTi) was generated on the BiT side. Ba\(^{2+}\) content was constant at 0.0–0.5 mm inside BiT. The ratio of Ba\(^{2+}\) to Bi\(^{3+}\) was about 1–4, in agreement with the stoichiometry of BaBi\(_4\)Ti\(_4\)O\(_{15}\).

Figure 4 shows XRD patterns of the powder compact dried with or without magnetic field. All the peaks derived from BiT and BT were detected in both XRD patterns. The intensity of some peaks of BiT changed in the sample prepared in magnetic field. The strongest reflection of BiT is 117; intensity of this reflection decreased for the sample prepared in magnetic field. Instead of the 117 peak, 200, 220 and 400 reflections, which were derived from the a and b faces, strengthened. The a- and b-axis of BiT particles in the compact prepared in magnetic field were oriented to the field. For BT, all reflections were similar and independent of the magnetic field.

Figure 5 shows the XRD patterns of sintered samples heated at 1100 °C. The diffraction angles for samples formed with and without magnetic field were the same as those of BBTi ceramics. The detected reflections of the sample formed with the magnetic field were 200, 220 and 400 of BBTi, i.e. BBTi crystals oriented to the a- and b-axis were produced. The crystal structure of BiT was maintained during
Figure 5. XRD patterns of sintered body heated at 1100 °C.

Figure 6. Change in the Lotgering factor with sintering temperature.

Figure 7. Microstructures of BaBi$_4$Ti$_4$O$_{15}$ ceramics fabricated with a magnetic field using (a) 0.3 µm and (b) 0.5 µm BT powders and (c) without magnetic field using 0.3 µm BT powder.

4. Discussion

Let us consider the effect of sintering on the crystal structure. Figure 3 shows that Ba$^{2+}$ diffused preferentially into BiT. This natural tendency played an important role in maintaining the $a$- and $b$-axis oriented structure of BiT to BBTi after reaction sintering. The retention of the structure indicates that this reaction sintering on the BiT side proceeded topotaxically, as illustrated in figure 1. The resemblance of the crystal structures of BBTi and BiT affects the reaction diffusion on the BiT side for this topotaxical reaction. The number of
perovskite layers $m$ in a crystal structure is 3 for BiT and 4 for BBTi. Unoriented BBTi, of course, should also be produced at the BT side, which shows random orientation.

Ba$^{2+}$ substitutes Bi$^{3+}$ in BiT for being a BBTi structure, although the reason for the rapid diffusion of Ba$^{2+}$ remains to be clarified. Charge neutrality might require that diffusion of 3 Ba$^{2+}$ ions into the BiT side causes diffusion of 2 Bi$^{3+}$ into the BT side. The sizes of Ba$^{2+}$ and Bi$^{3+}$ are also important for substitution from a comparison of Ba$^{2+}$ and Sr$^{2+}$ in a previous study.

The Lotgering factor of the sintered sample fabricated with 0.5 $\mu$m BaTiO$_3$ (BT), heated at 1120 $^\circ$C, was lower than that of the sample produced from 0.3 $\mu$m BT, as shown in figure 6. The result indicates that the sample sintered from 0.5 $\mu$m BT particles has a more random structure. The reaction sintering occurs at the interface of BiT and BT particles. The $a$- and $b$-axis oriented BiT structure is maintained by a preferential diffusion of Ba$^{2+}$ from BT to BiT. The size of oriented BBTi reflects the size of BiT particles (1.0 $\mu$m). Unoriented BBTi grains, however, are generated at the BT side; their size is smaller than BT grains (0.5 and 0.3 $\mu$m). Smaller random BBTi grains can be easily absorbed on to large oriented BBTi grains during the sintering. Some large random BBTi grains may survive the sintering. The size ratio of the host material BT to the guest material BBTi is important for the development of an oriented structure by grain growth.

5. Conclusion

$a$- and $b$-axis-oriented BaBi$_4$Ti$_4$O$_{15}$ ferroelectric ceramics were fabricated by alignment in magnetic field and subsequent reaction sintering. Bismuth titanate particles with a size of about 1 $\mu$m were the host material. Barium titanate, as a reaction additive, was used as the guest material. A well-dispersed slurry was prepared by mixing Bi$_4$Ti$_3$O$_{12}$ and BaTiO$_3$ powders. The ratio of particle size (Bi$_4$Ti$_3$O$_{12}$/BaTiO$_3$) was controlled. The slurry was poured into a mold and set in a magnetic field of 10 T until completely dried. Bi$_4$Ti$_3$O$_{12}$ particles in the slurry were highly oriented in a magnetic field, that is, the dried powder compact consisted of highly $a$- and $b$-axis-oriented Bi$_4$Ti$_3$O$_{12}$ particles and randomly oriented BaTiO$_3$ particles. Barium bismuth titanate BaBi$_4$Ti$_4$O$_{15}$ ceramics with an $a$- and $b$-axis orientation were successfully produced after sintering above 1120 $^\circ$C.

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