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Effect of matrix particle size on texture development in $SrBi_4Ti_4O_{15}$ made by templated grain growth

Toshio Kimura · Chihiro Miyazaki

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Abstract Textured $SrBi_4Ti_4O_{15}$ (SBT) ceramics were fabricated by the templated grain growth process to examine the effect of matrix particle size on texture development and densification. Texture was developed by the shape change of matrix grains from equiaxed to platelike and the alignment of their plate face parallel to that of template grains. The matrix particle size determined the number of platelike matrix grains with right orientation, and an increase in the matrix particle size increased the number of misoriented grains. Misoriented grains formed large pores, resulting in a low sintered density. It was concluded that small matrix particles were favorable for preparing dense, highly textured SBT ceramics.

Keywords Crystallographic texture · Templated grain growth · Microstructure · Strontium bismuth titanate

1 Introduction

One of the candidates for lead-free piezoelectric ceramics is a compound belonging to the family of bismuth layer-structured ferroelectrics (BLSFs) [1, 2]. Because the crystal structure of BLSF is highly anisotropic, the properties of polycrystalline ceramics prepared by the conventional sintering method are lower than those of single crystals, and texturing is necessary for practical use [3]; the properties of piezoelectric ceramics are strongly dependent on the microstructure, and are enhanced by the development of texture in polycrystalline ceramics [4–6].

The templated grain growth (TGG) process is one of the most convenient methods of preparing textured BLSF ceramics [7–10]. A green compact is made from a mixture of large, platelike template particles and small, equiaxed matrix particles. The template particles are aligned in the green compact by a method such as tape casting and extrusion. Dense, highly textured ceramics are obtained by sintering the green compact. Because the presence of two kinds of particles with quite different powder characteristics makes green compacts highly inhomogeneous, close attention must be paid to design and control the microstructure of sintered compacts.

It has been proposed that texture development in TGG-processed α-Al_2O_3 is controlled directly by the growth of the template grains [11, 12]. Recently, it has been found that texture development in $BaBi_4Ti_4O_{15}$ is caused by the shape change of matrix grains from equiaxed to platelike and the simultaneous alignment of their plate faces parallel to those of template grains [10]. The purposes of this study are to investigate the origin of texture development in $SrBi_4Ti_4O_{15}$ (SBT) made by the TGG process and to examine the effect of the matrix particle size on texture development to find out the conditions for preparing highly textured ceramics.

2 Experimental

Platelike SBT particles for templates were prepared by molten salt synthesis [13]; a mixture of $SrCO_3$, Bi_2O_3, and TiO_2 (a molar ratio of 1:2:4) was heated at 1,100 °C for 1 h in the presence of KCl. Figure 1 shows the photomicrograph of obtained particles. The powder particles had a

T. Kimura (✉) · C. Miyazaki
School of Integrated Design Engineering,
Graduate School of Science and Technology,
Keio University, 3-14-1 Hiyoshi,
Kohoku-ku, Yokohama 223-8522, Japan
e-mail: kimura@applc.keio.ac.jp

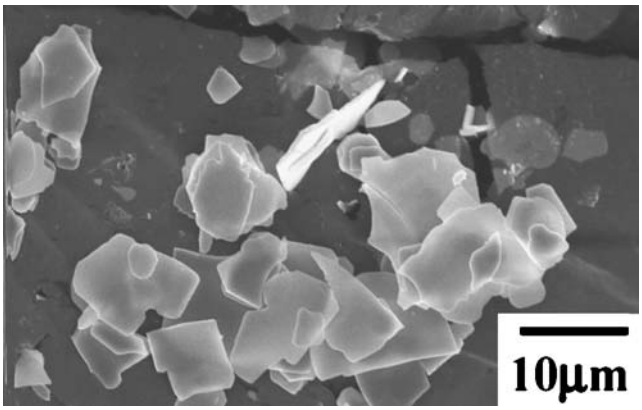

Fig. 1 SEM photograph of $SrBi_4Ti_4O_{15}$ particles prepared by molten salt synthesis

platelike shape with a diameter of about 10 μm and a thickness of about 0.4 μm. Four kinds of matrix SBT particles were prepared by conventional solid-state reaction and ball milling. The name, preparation conditions, and particle size are shown in Table 1. The average particle size and its distribution were determined based on the observation with a scanning electron microscope (SEM). About 300 particles were counted. The particle shape was almost equiaxed. The formation of SBT was completed in S2 and L, but S1 and M contained a small amount of intermediate compounds ($Bi_4Ti_3O_{12}$ and $SrTiO_3$).

Mixtures containing 20 vol.% template and 80 vol.% matrix particles were mixed with a solvent (60 vol.% toluene–40 vol.% ethanol), a binder (poly(vinyl butyral)), and a plasticizer (di-*n*-butylphtalate) for 2 h using a ball mill to prepare slurries (solid: solvent: binder: plasticizer= 1.00: 4.88: 0.66: 0.66 by volume). The slurries were tape cast by a doctor blade technique. The height of the blade was 0.3 mm and the casting speed was 4.0 cm/s. The cast sheets were cut, laminated and pressed at 80 °C and 50 MPa for 3 min to form laminated compacts with a thickness of about 2 mm. The compacts were heated at 500 °C for 2 h to burn out binder and then sintered at 900–1,200 °C for 10 h. The specimens containing the S2, S1, M, and L matrix particles will be refer to as specimens S2, S1, M, and L, respectively. The bulk density of sintered compacts was measured by the Archimedes method. A theoretical density of 7.448 g/cm^3 of SBT was used to calculate the relative density [14]. The crystalline phases and the degree of texture development were evaluated by X-ray diffraction (XRD) analysis using CuKα radiation. The Lotgering F factor was used to evaluate texture [15]; F=1 or 0 indicates that the compacts are completely textured or random, respectively. The diffraction lines between 2θ=20° and 60° were used for the evaluation. The microstructure was observed with SEM; polished and chemically etched sections were observed for dense specimens, and fractured surfaces were observed for porous specimens.

Table 1 Preparation conditions and particle size of matrix particles.

Specimens	S2	S1	M	L
Calcination temperature (°C)	1,000	850	900	1,000
Milling time (day)	4	1	1	1
Average particle size (μm)	0.32	0.48	0.83	1.5
Particle size range (μm)	0.2–0.8	0.3–1.0	0.5–1.5	1–2

3 Results and discussion

3.1 Effects of matrix particle size on texture development and densification

Figure 2 shows the XRD patterns of specimen S1 sintered at various temperatures for 10 h. All diffraction lines belong to SBT except for those at 30.1 and 32.4° in the 900 °C specimen; they are (117) of $Bi_4Ti_3O_{12}$ and (110) of $SrTiO_3$, respectively, and these intermediate phases were present in the matrix particles. The diffraction lines of intermediate phases disappeared at 1,000 °C, indicating the formation of single phase SBT. An increase in the intensity of (*00l*) lines and a decrease in that of other diffraction lines indicate the development of <001> texture.

Figure 3 shows the Lotgering F factor for all specimens examined, illustrating an increasing trend of the F factor with a decrease in the matrix particle size. The F factor of specimen S2 was the largest among the specimens examined and it reached more than 0.9 at 1,100 °C. For specimens S1 and M, an increasing trend of the F factor with an increase in sintering temperature was shown. For specimen L, the F

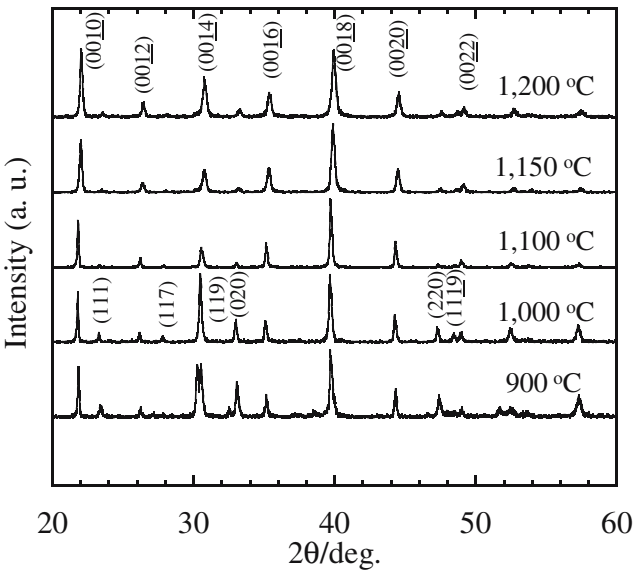

Fig. 2 XRD patterns of specimen S1 heated at various temperatures for 10 h

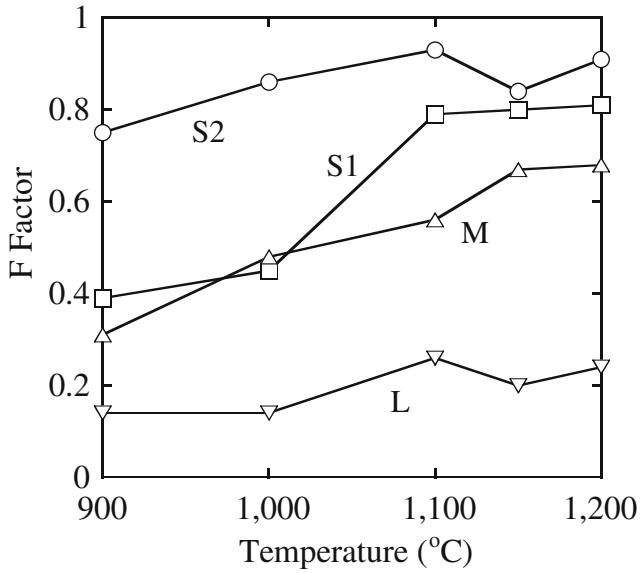

Fig. 3 Effect of sintering temperature on texture development

factor did not increase with an increase in sintering temperature and it was small (0.24) even at 1,200 °C.

Figure 4 shows the relative density of all specimens. The densification started at 1,000 °C for all specimens. The densification behavior was almost the same for specimens L, M and S1, but specimen S2 densified at a temperature 100 °C lower than the other specimens. Specimens L and S2 had the lowest and highest density, respectively, and the latter reached 90% of the theoretical value at 1,200 °C.

3.2 Effects of matrix particle size on microstructure development

The previous work on microstructure development in TGG-processed $BaBi_4Ti_4O_{15}$ showed that texture development

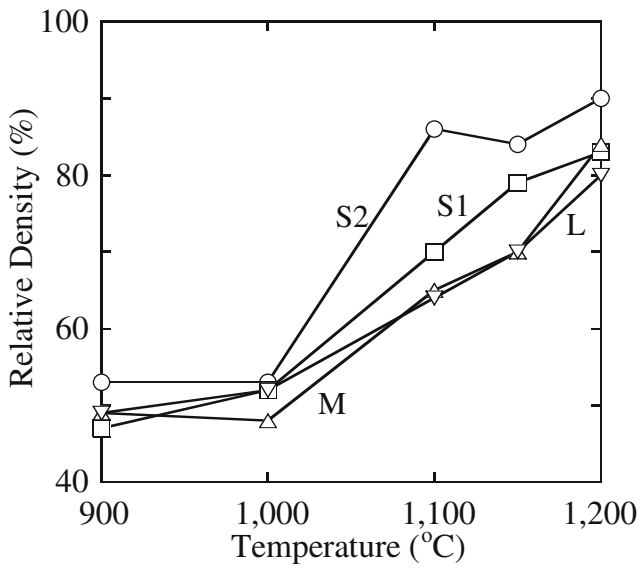

Fig. 4 Effect of sintering temperature on the density

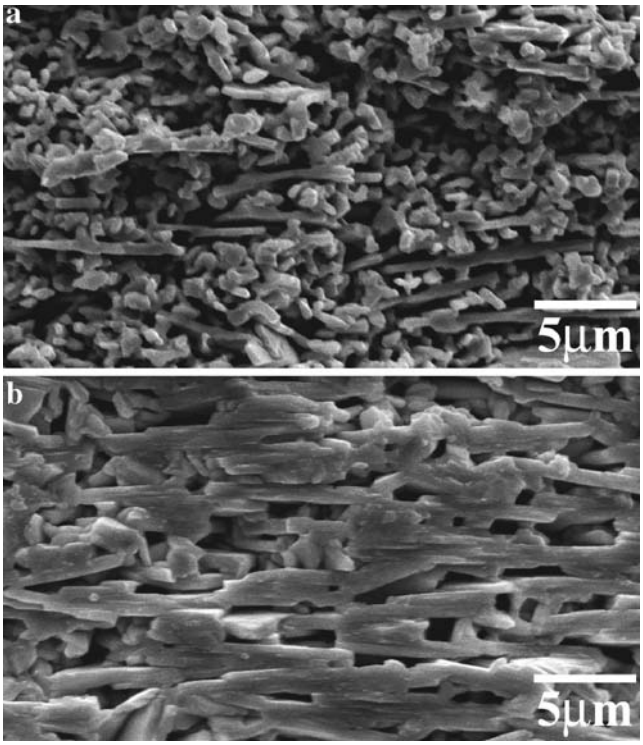

Fig. 5 Microstructures of specimen S1 sintered at **a** 1,000 °C and **b** 1,100 °C for 10 h

was caused not by the growth of template grains but by the shape change of matrix grains; the equiaxed matrix grains changed their shape to be platelike, and simultaneously,

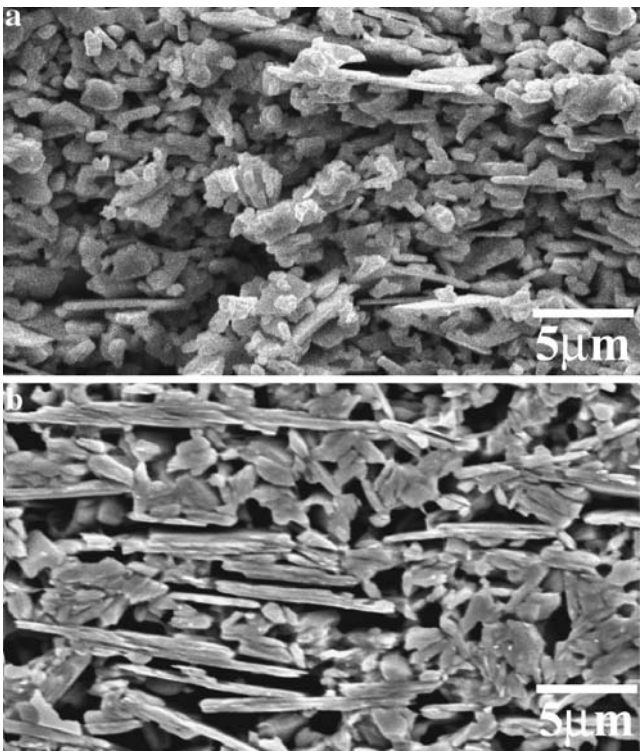

Fig. 6 Microstructures of specimen *L* sintered at **a** 1,000 °C and **b** 1,150 °C for 10 h

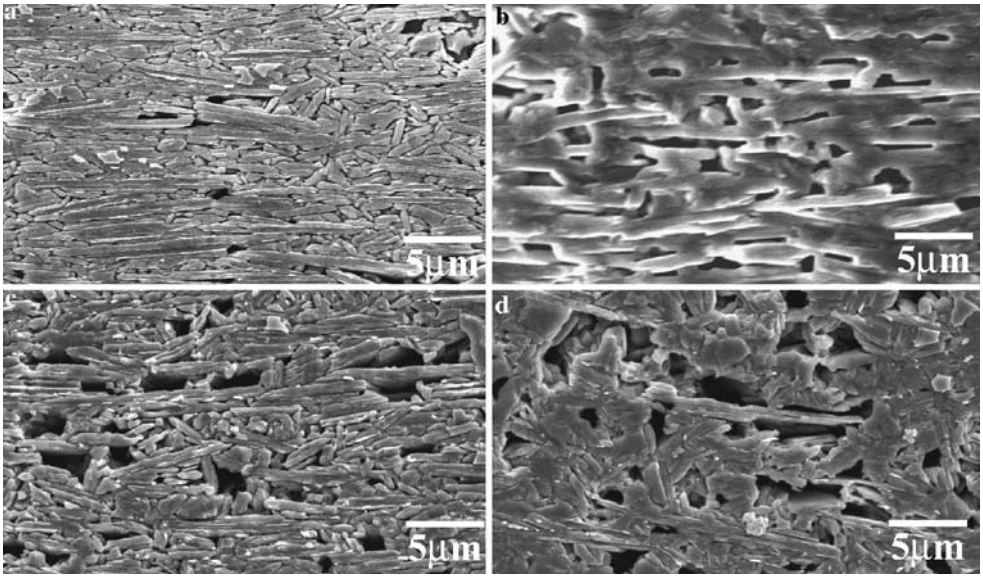

Fig. 7 Microstructures of specimens **a** S2, **b** S1, **c** M, and **d** L sintered at 1, 200 °C for 10 h

their plate faces aligned parallel to those of template grains [10]. The same characteristics of microstructure development were also observed in SBT. Figure 5 shows the microstructures of specimen S1 sintered at 1,000 and 1,100 °C for 10 h. The microstructure change between 1,000 and 1,100 °C indicates the shape change of matrix grains from equiaxed to platelike and the alignment of their plate faces parallel to those of template grains. The same microstructure change was observed in specimen S2.

Figure 6 shows the microstructures of specimen L sintered at 1,000 and 1,150 °C for 10 h. The matrix grains changed their shape from equiaxed to platelike, but newly formed platelike grains hardly aligned parallel to each other. The formation of misoriented platelike matrix grains was responsible for a small degree of orientation (Fig. 3). This microstructure change suggests the conditions for obtaining highly textured SBT; they are (1) the matrix grains just surrounding template grains become platelike with their plate faces parallel to those of template grains and (2) the matrix grains not contacting to template grains become platelike with their plate faces parallel to those of matrix gains which have already become platelike with right orientation. The fulfillment of these conditions is determined by the matrix particle size.

Figure 7 shows the microstructures of specimens sintered at 1,200 °C for 10 h. The microstructures were composed of platelike grains with a bimodal size distribution. Large and small grains originated from template and matrix particles, respectively. The lack of the extensive growth of template grains in all specimens and the presence of small platelike grains with alignment parallel to template grains in specimens S1 and S2 indicate that the texture is developed not by the growth of template grains but by the morphological change in the matrix grains.

The microstructures contained two kinds of large pores adjacent to large template grains and to misoriented matrix grains. The former pores are formed by the hindrance in densification by large grains in a compact with a bimodal size distribution [16, 17]. This hindrance is not avoidable in the TGG process and sintering at relatively high temperatures for a long duration is required to obtain dense ceramics. The latter pores were caused by misoriented grains forming a card house structure [18], and were responsible for a low density of specimens M and L (Fig. 4). These pores are avoidable by reducing the number of misoriented grains as shown in specimens S1 and S2.

4 Conclusion

Textured SBT ceramics were prepared by the TGG process and the effect of matrix particle size on microstructure development was examined. Texture was developed by the shape change of matrix particles to form platelike grains with their plate faces parallel to those of template grains. The matrix particle size determines the direction of plate faces and small matrix particles are favorable for the texture formation. The misoriented matrix grains form large pores and reduce density. Therefore, small matrix particles are favorable for preparing dense, highly textured SBT ceramics.

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