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Mechanisms of Texture Development in Bismuth Layer-Structured Ferroelectrics Prepared by Templated Grain Growth

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Abstract. The mechanism for texture development in bismuth layer-structured ferroelectrics prepared by the templated grain growth method was examined using template and matrix grains with different chemical compositions. The template particles used were platelike $Bi_4Ti_3O_{12}$ and $Ba_6Ti_{17}O_{40}$ for $SrBi_4Ti_4O_{15}$-matrix composites and platelike $Ba_6Ti_{17}O_{40}$ and $Sr_3Ti_2O_7$ for $BaBi_4Ti_4O_{15}$-matrix. The ⟨001⟩-texture developed in all composites examined. The origins of texture development were the growth of matrix grains to be platelike and the formation of face-to-face contact between the template and matrix grains and also between matrix grains.

Keywords: bismuth layer-structured ferroelectrics, crystallographic texture, templated grain growth method, texture engineering

1. Introduction

Bismuth layer-structured ferroelectrics (BLSFs), such as $SrBi_4Ti_4O_{15}$ (SBT) and $BaBi_4Ti_4O_{15}$ (BBT), are the candidate materials for lead-free piezoelectric ceramics. The problem of BLSFs is the smaller properties of a polycrystalline ceramic than those of a single crystal, because of the anisotropy in piezoelectric coefficients [1]. In this respect, crystallographically textured ceramics have been prepared to improve electrical properties. The templated grain growth (TGG) method is one of the convenient techniques to develop the crystallographic texture [1]. In this method, a slurry containing equiaxed particles and particles with shape anisotropy (matrix and template particles, respectively) are tape-cast to form a green compact, in which template particles are aligned in a specific direction. Sintering of the compact results in the formation of textured ceramic. The growth of template grains at the expense of matrix grains has been proposed for the origin of texture development [2].

In our previous study on the fabrication of textured SBT by the TGG method [3], we found a microstructure composed of two regions as shown in Fig. 1. One was a group of large grains with a large aspect ratio and another was composed of small grains with a small aspect ratio. The grains in the former regions developed extensive texture by forming face-to-face contact, and the latter regions contained misaligned grains. This microstructure suggests that a mechanism other than the growth of template grains operates to develop the former regions, as pointed out in Ref. [1].

This work has been planed to examine the possibility if a mechanism other than the growth of template grains operates in the texture development of BLSFs. Ordinarily, the material with the same chemical composition was used for the template and matrix grains in the TGG method. In this case, the distinction of growth behavior between template and matrix grains is difficult, and the contribution of matrix grains to the texture development has been ignored. In the present work, the template and matrix grains with the different chemical compositions were used to clearly observe the growth behavior of template and matrix grains. Platelike $Bi_4Ti_3O_{12}$ (BIT), $Ba_6Ti_{17}O_{40}$ (B6T17), and $Sr_3Ti_2O_7$ (S3T2) particles were used as template grains and equiaxed BBT and SBT were used as matrix grains.

2. Experimental Procedure

Chemically pure $SrCO_3$, $BaCO_3$, Bi_2O_3 and TiO_2 were used as raw materials. Platelike BIT, B6T17 and

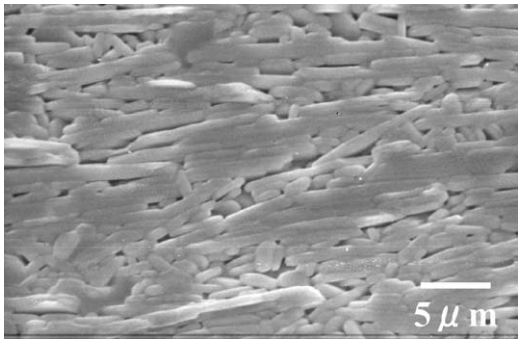

Fig. 1. Microstructure of SBT prepared by TGG method, sintered at 1200°C for 10 h.

S3T2 were prepared by molten salt synthesis. The salt used and the reaction conditions were NaCl -KCl and 1130°C-1 h for BIT, NaCl and 1150°C-1 h for B6T17, and NaCl-KCl and 1200°C-1 h for S3T2. All products obtained by molten salt synthesis had platelike morphology. Equiaxed SBT and BBT particles were prepared by the conventional solid-state reaction at 950°C and 1000°C for 2 h, respectively. The reaction products were ground with a ball mill for 24 h using 15 mm^{Φ} ZrO_2 balls and for 24 h using 2 mm^{Φ} ZrO_2 balls. The average particle size of the ground powders was about 0.5 μm.

The combinations of template and matrix particles are shown in Table 1. The amount of template particles were 20 vol% of total solid. Slurries for tape casting were prepared by mixing powders, solvent (60 vol% toluene–40% ethanol), binder (poly-vinyl butyral), and plasticizer (di-*n*-butyl phthalate) using a ball mill for 2 h. Tape-cast sheets were cut, laminated and pressed at 80°C and 50 MPa for 3 min to form green compacts with a thickness of about 2 mm. The green compacts were heated in an oxygen atmosphere to 700°C and kept for 2 h to burn out organic ingredients, and then subjected to cold isostatic pressing (CIP) at 98 MPa for 2 min to increase green density. The compacts were sintered at various temperatures between 1000°C and 1200°C for desired soaking time. The crystalline phases and the degree of texture development were determined by X-ray diffraction (XRD) analysis using CuKα radiation on the major surface of the specimens. The Lotgering's F value was used to evaluate the texture [4];

$$F = (P - P_0)/(1 - P_0), \quad \text{where}$$
$$P = \Sigma I(001)/\Sigma I(hkl)$$
$$P_0 = \Sigma I_0(001)/\Sigma I_0(hkl),$$

and ΣI is the sum of the XRD peak intensities for the parallel plane of sintered specimens and ΣI_0 is the sum of peak intensities in the powder diffraction pattern. The intensity of the diffraction lines of matrix phase between $2\theta = 20^\circ$ and 60° was used for the calculation. The microstructure was observed at a fractured side face of the specimens with a scanning electron microscope (SEM). Some specimens for SEM were polished and thermally etched at 50°C below the sintering temperature for 15min. The density was measured by the Archimedes method.

Table 1. Powder mixtures for the preparation of specimens.

Name of specimens	Template particles	Matrix particles
BI-BB	BIT	BBT
B6-BB	B6T17	BBT
BI-SB	BIT	SBT
S3-SB	S3T2	SBT

3. Results and Discussion

3.1. Texture Development and Densification of BBT-Matrix Composites

Figure 2 shows the F value and relative density of the BI-BB and B6-BB specimens as a function of

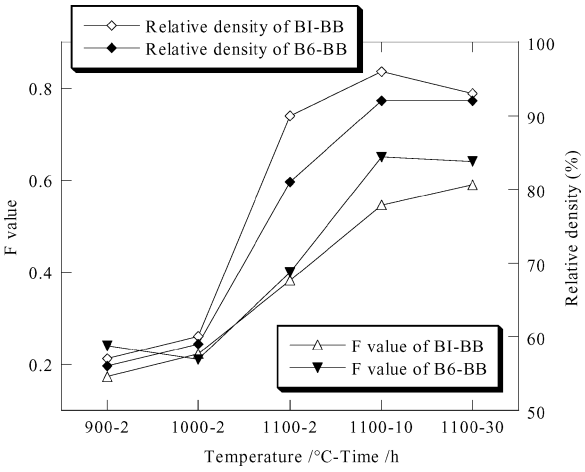

Fig. 2. Effect of sintering conditions on the F value and density of the B6-BB and BI-BB specimens.

temperature and soaking time. The texture development and densification behavior were similar in the BI-BB and B6-BB specimens. The maximum F values were 0.53 and 0.65 for the BI-BB and B6-BB specimens, respectively. These results indicate that the platelike grains with the chemical composition different from that of the matrix act as templates to give (001) texture for BBT, and BI and B6 with the different crystal structures had almost the same effect on the texture development. The origin of texture development will be discussed after examining the microstructures.

3.2. *Microstructure Development in BBT-Matrix Composites*

The microstructures of the B6-BB and BI-BB specimens are shown in Figs. 3 and 4, respectively. The matrix BBT particles grew to platelike grains, and the sintered compacts were composed of large and small platelike grains, which were template BIT and B6T17 and matrix (BBT) grains, respectively. The growth of template grains was not observed. The platelike matrix grains had a tendency to align their plate-face parallel to the plate-face of template grains. This grain alignment was not observed in the specimen without template grains. Therefore, the origin of texture development is the grain alignment assisted by the template grains.

The course of grain alignment can be deduced from Fig. 3. At first, the matrix grains grow to be platelike and those just around platelike templates attach to the template grains, and have a tendency to form face-to-face contact to reduce surface area at a neck region (Fig. 3(a)). A group of matrix grains attaching to a template and having the same orientation as the template will be called colony A. The matrix grains located between template grains form a group of grains with face-to-face contact (colony B), but the orientation is random. Pores are located between colonies at this stage (Fig. 3(a)). Next step is the formation of face-to-face contact between colonies A and B. Because the mass of colony A plus template is larger than that of colony B, the formation of face-to-face contact rotates colony B to align their plate-face parallel to the plate-face of the template (Fig. 3(b)). The fact that the F value did not increase after the completion of densification (Fig. 2, 1100°C-30 h) indicates that large pores between colonies assist the rotation of colonies B. Thus, the alignment of matrix grains advances from just around the template grains to the matrix interior (Fig. 3(c)).

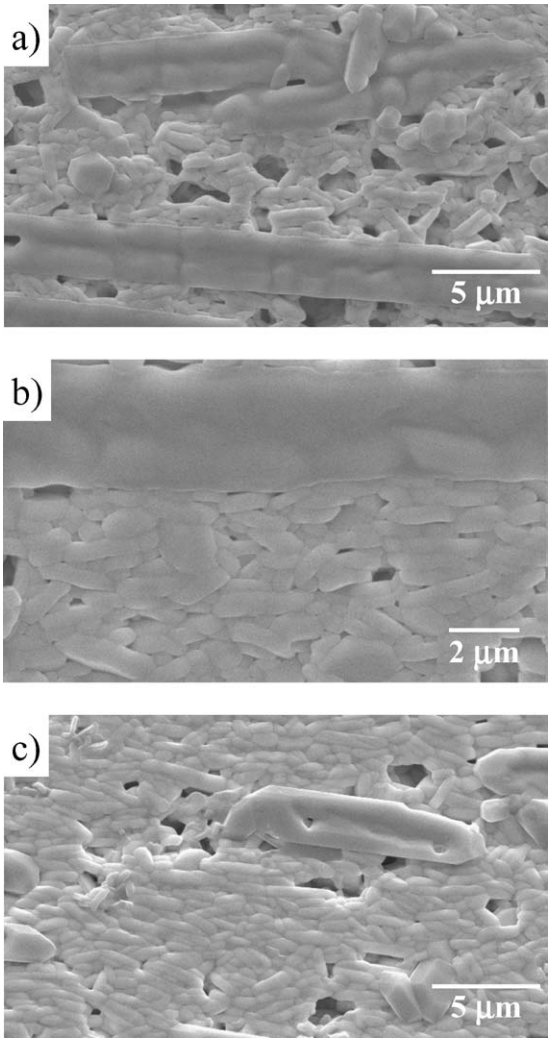

Fig. 3. Microstructures of B6-BB specimens heated at (a) 1100°C for 2 h, (b) 1100°C for 10 h, and (c) 1100°C for 30 h.

Probably, the same mechanism of texture development operated in both BI-BB and B6-BB specimens because of a similar texture development (Fig. 2). BIT and BBT have a similar crystal structure, and the growth of template BIT grains at the expense of the matrix BBT grains is one of the possible mechanisms of texture development as observed in a PMN-PT specimen using $BaTiO_3$ and $SrTiO_3$ templates. In the present case (Fig. 4), however, grain boundaries existed between BIT and BBT grains, indicating that the growth of template grains was not the origin of texture development.

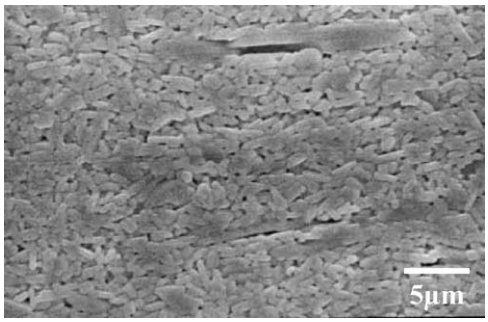

Fig. 4. Microstructure of BI-BB specimen heated at 1100°C for 10 h.

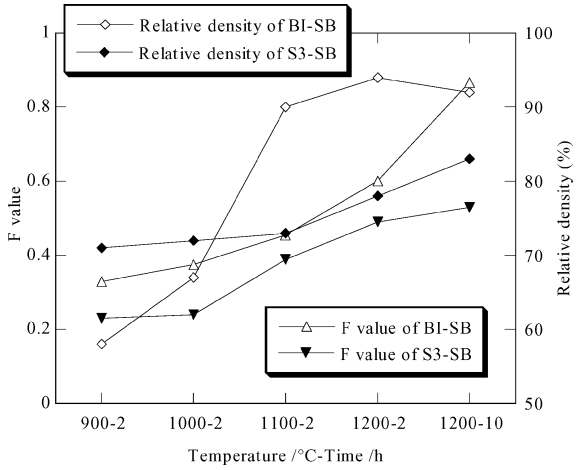

Fig. 5. Effect of sintering conditions on the F value and density of the S3-SB and BI-SB specimens.

3.3. Texture Development and Densification of SBT—Matrix Composite

Figure 5 shows the F value and relative density of the BI-SB and S3-SB specimens as a function of temperature and soaking time. In the SBT-matrix composites, the texture development was dependent on the chemical species of template grains; sintering at 1200°C for 10 h gave $F = 0.87$ and 0.53 for the BI-SB and S3-SB specimen, respectively.

3.4. Microstructure Development of SBT

The microstructures of the S3-SB and BI-SB specimens are shown in Figs. 6 and 7, respectively. The S3-SB specimen had microstructures similar to those of the BBT-matrix composites; the growth of template grains did not observed, and the matrix grains grew to be platelike and aligned their plate-face parallel to the plate-face of the template grains. The mechanism of the texture development might be the same as that operated in the BBT-matrix composites.

Extensive texture development was observed in the BI-SB specimen at 1200°C (Fig. 5). The microstructure at 1100°C was composed of large template grains and small matrix grains, which grew to be platelike and had the plate-face parallel to the plate-face of template grains (Fig. 7(a)). These microstructural characteristics were similar to those of the BBT-matrix composites and the S3-SB specimen. The large template grains disappeared at 1200°C, and the microstructure was composed of one kind of platelike grains (Figs. 7(b) and (c)). Probably, 1200°C was above the eutectic temperature between BIT and SBT, and BIT formed a liquid phase at 1200°C. The abrupt increase of density at 1100°C-2 h (Fig. 5) supports the probability of the formation of liquid phase.

The growth behavior of matrix grains was different in the S3-SB and BI-SB specimens. No appreciable grain growth was observed in the S3-SB specimen at 1200°C from 2 to 10 h, but grains grew extensively in the BI-SB specimen at the same conditions, for which

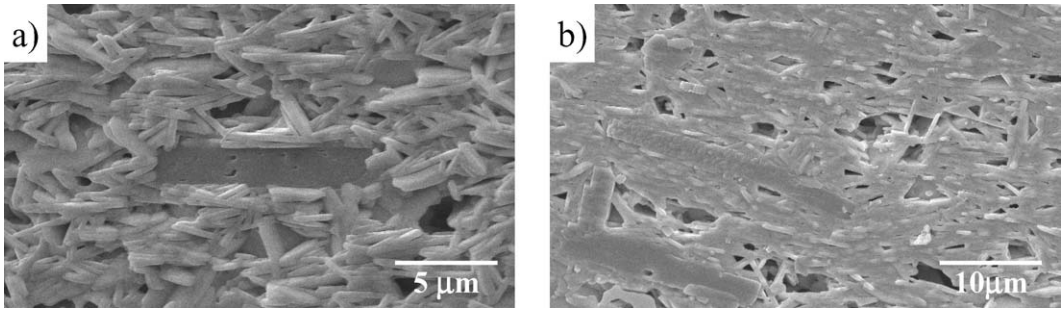

Fig. 6. Microstructures of S3-SB specimens heated at (a) 1200°C for 2 h and (b) 1200°C for 10 h.

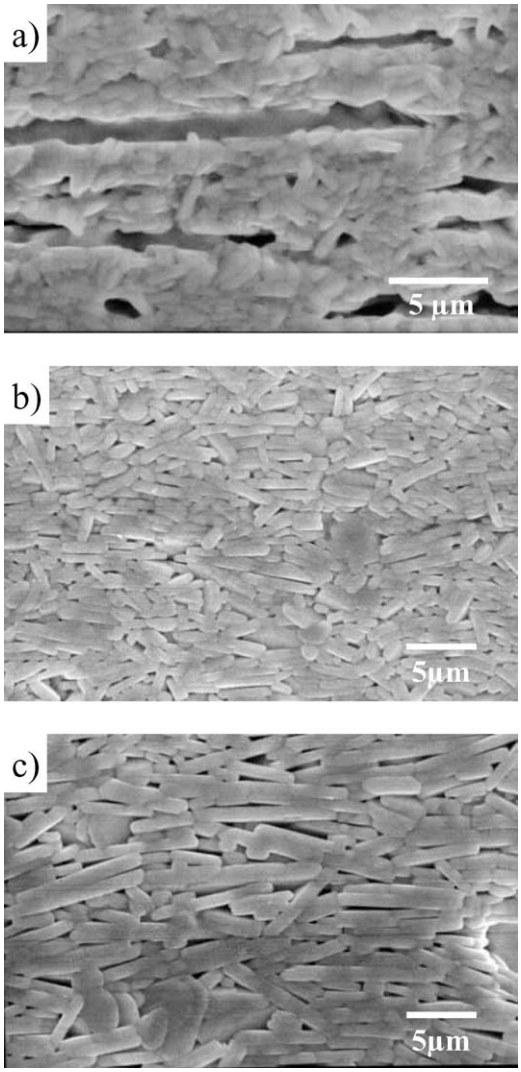

Fig. 7. Microstructures of BI-SB specimens heated at (a) 1100°C for 2 h, (b) 1200°C for 2 h, and (c) 1200°C for 10 h.

a liquid phase might be responsible. A part of matrix SBT grains aligned during heating up to the eutectic temperature, and the growth of these aligned grains at the expense of misaligned matrix grains developed the texture.

4. Conclusions

The texture development by the TGG method was examined using template grains with the composition different from that of matrix grains. The texture developed by the formation of face-to-face contact between template grains and matrix grains just surrounding the template grains and by advancing the aligned region from near template grains into the matrix interior. The experimental results for the BBT-matrix composites and the S3-SB specimen indicated that the texture development by the mechanism mentioned above increased the F value up to about 0.6. A further increase in the F value is caused by other mechanisms, such as growth of aligned grains at the expense of misaligned grains, as observed in the BI-SB specimens and textured BIT made by the TGG method [1].

References

1. J.A. Horn, S.C. Zhang, U. Selvaraj, G.L. Messing, and S. Trolier-McKinstry, *J. Am. Ceram. Soc.*, **82**, 921 (1999).
2. M.M. Seabaugh, G.L. Messing, and M.D. Vaudin, *J. Am. Ceram. Soc.*, **83**, 3109 (2000).
3. Y. Sakuma and T. Kimura, *J. Mater. Sci.*, submitted.
4. F.K.Lotgering, *J. Inorg. Nucl. Chem.*, **9**, 113 (1959).
5. S. Trolier-McKinstry, E. Sabolsky, S. Kwon, C. Duran, T. Yoshimura, J.-H. Park, Z. Zhang, and G.L. Messing, in *Piezoelectric Materials in Devices*, edited by N. Setter (EPFL Swiss Fedral Institute of Technology, Lausanne, 2002), p. 497.