Texture Development in Piezoelectric Ceramics by Templated Grain Growth using Heterotemplates

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Abstract

The mechanisms of texture development were examined in the <001>-textured bismuth layer-structured ferroelectrics (BLSF) prepared by the templated grain growth (TGG) method using BLSF templates with the composition different from that of the matrix. The formation and growth of layers of matrix grains on the templates were main mechanism for the texture development. Another mechanism of texture development was the formation of the face-to-face contact between platelike template grains and matrix grains grown to be platelike.

1. Introduction

The control of crystallographic texture is an important technique to improve the properties of ceramics.[1] One of the most convenient methods to prepare textured ceramics is sintering of a green compact in which particles with shape anisotropy are aligned.[2] Because the particle shape is closely related to the crystal structure, the sintering of aligned particles results in the formation of textured ceramics. Sometimes, a mixture of equiaxed and anisotropic particles are used to enhance densification. This method is called the templated grain growth (TGG) method.[3, 4]

It is difficult to apply the TGG method to the compounds with the perovskite structure, because there are no appropriate template particles. If there are precursor particles, which have shape anisotropy and act as reactive-templates, the reactive-templated grain growth (RTGG) method is applicable.[5]

When the appropriate reactive-template particles are not available, the third method to prepare textured ceramics is to use the template particles with chemical composition different from the objective material. The example is platelike $Ba_6Ti_{17}O_3$ (B6T17) particles for texturing $BaTiO_3$ and $Pb(Zr_{0.5}Ti_{0.5})_3$ (PZT).[6, 7] In this case, B6T17 is hetero-template and we call this process as hetero-templated grain growth (H-TGG) method. The other example of the H-TGG process is reported for $Pb(Mg_{1/3}Nb_{2/3)}TiO_3$-$PbTiO_3$ using $BaTiO_3$ and $SrTiO_3$ hetero-templates.[8]

This paper deals with the texture formation in BLSF matrices using BLSF hetero-templates. Although BLSFs are easily textured by the TGG method using homo-templates,[4, 9, 10] the aim of the present work is to find out the mechanisms controlling the texture development by the H-TGG method. The BLSFs used in this experiment were $Bi_4Ti_3O_{12}$ (BiT), $SrBi_4Ti_4O_{15}$ (SBT), and $BaBi_4Ti_4O_{15}$ (BBT), and various combinations of the matrix and templates were examined.

2. Experimental Procedure

The matrix BiT, SBT, and BBT powders were prepared from the constituent oxides and carbonates (starting materials) by a conventional solid-state reaction. The calcined powders were ball-milled for 24 h, and had the average particle size of about 0.5 μm. The platelike template particles were prepared by molten salt synthesis[11] using the same weight of salt as the starting materials. The platelike particles with diameters between 10 and 50 μm were used.

The mixtures of matrix and template particles were mixed with solvent (60 vol% toluene – 40 vol% ethanol), binder (poly(vinyl butyral)), and plasticizer (di-*n*-butyl phthalate), and tape-cast to form sheets in which platelike template particles were aligned. The specimens are designated by the (matrix)/(template) notation. The amount of templates was 20 vol% for the BLSF/BLSF specimens.

The sheets were cut (10 mm x 10 mm) and laminated to form green compacts with a thickness of about 1 mm. The compacts were heated at 500°C for binder burn-out, and then sintered under various conditions.

The texture was evaluated by X-ray diffraction analysis at the major face of the compact, using the Lotgering F value,[12] and the microstructure was observed at the face perpendicular to the major face with a scanning electron microscope.

3. Results and Discussion

3.1 Texture development in SBT-matrix specimens

Figure 1 shows the X-ray diffraction patterns of the SBT/BiT specimen sintered at various temperatures for 2 or 10 h, together with the powder pattern of SBT reported in the literature.[13] The most intense peak in the specimen sintered at 1000°C for 2 h was (109) but the relative intensity of (00<u>18</u>) increased as the sintering temperature was increased, indicating that the <001>-texture developed in the specimen. The F value was indicated in the parenthesis in Fig. 1. The development of <001>-texture was also observed in the SBT/BBT specimen, and the F value was 0.97 and 1.0 for the specimens sintered at 1150°C for 2 and 10 h, respectively.

Figure 2 shows the microstructures of the SBT/BBT specimen sintered at 11150°C. The dark platelike grains were BBT, and SBT grains grew to be platelike. In the specimen sintered at 1150°C for 0 h (Fig. 2(a)), two kinds of SBT grains were present; one was small grains and another was large platelike grains. The latter grains grew forming layers on the template BBT grains and their c-axis was parallel to the c-axis of BBT grains, as deduced from the XRD patterns. Prolonged heating at 1150°C increased the volume of the SBT layers (Fig. 2(b)). Similar microstructure development was observed in the SBT/BiT specimen.

These results indicate that the platelike BBT templates give the <001>-texture in matrix SBT by forming the SBT layers on the BBT template grains. The similarity of crystal structure between BBT and SBT gives the <001>-texture in the SBT grains.

3.2 Texture development in BiT- and BBT-matrix specimens

It is not always true that all BLSF hetero-templates develop extensive texture ($F > 0.8$) in the BLSF matrix. The maximum F values of the BiT-matrix specimens were 0.65 and 0.06 for the BiT/BBT and BiT/SBT specimens, respectively, sintered at 1150°C. These values were 0.53 (at 1100°C) and 0.13 (at 1150°C) for the BBT/BiT and BBT/SBT specimens, respectively.

Fig. 3 shows the microstructures of BiT/BBT and BiT/SBT specimens sintered at 1150°C for 2 h. The layers of the matrix BiT grains grew on the template grains. The growth of this layer was more extensive in the BiT/BBT specimen than in the BiT/SBT specimen, resulting in a large difference in the F value (0.65 and 0.06). It is well known that pure BiT grains grow to be platelike, but the BiT matrix grains in the BiT/SBT specimen had an equiaxed shape. The addition of BBT and SBT to BiT influences the growth behavior of BiT grains, resulting in a decrease in the grain growth rate, and SBT had a large effect on the grain growth. A small growth rate of the matrix BiT grains in the BiT-matrix specimens is responsible for the small F value.

Figure 4 shows the microstructures of the BBT/SBT and BBT/BiT specimens sintered at

1150°C and 1100°C, respectively for 2 h. The BBT layers were formed on the template SBT grains in the BBT/SBT specimen, but the layers remained to be thin and the rest of the matrix grains grew without influence of the template grains during prolonged heating at 1150°C. A small F value about 0.1 was related to the limited growth of the matrix layers on the templates, for which the presence of a large number of pores was responsible because pores hindered the mobility of grain boundaries.

The F value in the BBT/BiT specimen was not so large (about 0.5), but was larger than that of the BBT/SBT specimen (about 0.1). The origin of the texture development was different from that found in the SBT- and BiT-matrix specimens. In the BBT/BiT specimen, the matrix layers on the template grains did not form, but the BBT matrix grains grew to be platelike, and the grains adjacent to template BiT grains aligned parallel to the template grains.

The same microstructure feature was observed in the textured BBT/$Ba_6Ti_{17}O_{40}$ and SBT/$Sr_3Ti_2O_7$ specimens.[14] In these specimens, the formation of matrix layers on the template grains is slow and the matrix grains grow to be platelike without influence by the template grains. The platelike grains just touching a template grain form face-to-face contact, because large surface areas are vanished by the formation of grain contact. Thus, the platelike matrix grains align parallel to the template grain. The formation of face-to-face contact proceeds to the interior of matrix, resulting in an increase in the F value up to about 0.5.

3.3 Texture development in BNKT/SBT specimen

From the experimental results mentioned above, it is found that the textured matrix with a large F value are obtained by the formation and growth of matrix layers on the template grains. This condition is not limited to BLSF, but it is possible to obtain textured ceramics with the perovskite structure, because the crystal structures of BLSF and perovskite are similar. This possibility was examined using the $Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}TiO_3$ (BNKT)/SBT specimen. In the experiment, the mixture of constituent oxides and carbonates for BNKT were mixed with the platelike SBT particles. The amount of template was 30 vol%. The <100>-textured ceramics with F = 0.59 and 0.70 were obtained by sintering at 1100^o and 1200^{o}C, respectively, for 2 h. Fig. 5 shows the microstructures. The formation of matrix layers on the templates is clearly observed in Fig. 5(a).

4. Conclusions

It is shown that the BLSF hetero-templates develop crystallographic texture in the BLSF matrix, but the development of extensive texture is limited to the SBT-matrix systems. In these specimens, the texture is developed by the formation and growth of matrix layers on the template grains. The growth of matrix layers is important to develop the extensive texture. The technique to use BLSF as hetero-templates is extended to the matrix with the perovskite structure, and it is found that SBT is a suitable template for <100>-textured BNKT.

Another mechanism of texture development has been found in the BBT/BiT specimen. The texture is developed by the formation of fact-to-face contact between platelike template grains and matrix grains grown to be platelike.

References

1. Igarashi, H., Matsunaga, K., Taniai, T. & Okazaki, K., Dielectric and piezoelectric properties of grain-oriented $PbBi_2Nb_2O_9$ ceramics. *Am. Ceram. Soc. Bull.*, 1978, **57**, 815-817.
2. Holmes, M., Newnham, R. E. & Cross, L. E., Grain-oriented ferroelectric ceramics. . *Am. Ceram. Soc. Bull.*, 1979, **58**, 872.
3. Horn, J. A., Zhang, S. C., Selvaraj, U., Messing, G. L. & Trolier-McKinstry, S., Templated grain growth of textured bismuth titanate. . *J. Am. Ceram. Soc.*, 1999, **82**, 921-926.
4. Duran, C., Trolier-McKinstry, S. & Messing, G. L., Fabrication and electrical properties of textured $Sr_{0.53}Ba_{0.47}Nb_2O_6$ ceramics by templated grain growth. . *J. Am. Ceram. Soc.*, 2000, **83**, 2203-2213.
5. Tani, T., Crystalline-oriented piezoelectric bulk ceramics with a perovskite-type structure, *J. Korean Phys. Soc.*, 1998, **32**, S1217-S1220.
6. Kimura, T., Miura, Y. & Muramatsu. H., Mechanisms of texture formation in ferroelectric ceramics made by templated grain growth method. In *Extended Abstract of 11th US-Japan Seminar on Dielectrics and Ferroelectrics Ceramics*, 2003, pp. 347-350.
7. Muramatsu, H. & Kimura, T., Preparation of bulk $Pb(Zr,Ti)O_3$ with crystallographic texture by templated grain growth method. *J. Electroceramics*, in press.
8. Trolier-McKinstry, S., Sabolsky, E., Kwon, S. Duran, C., Yoshimura, T., Park, J. –H., Zhang, Z. & Messing, G. L., Oriented films and ceramics of ralaxor ferroelectric – $PbTiO_3$ solid solutions. Piezoelectric Materials in Devices, ed. N. Setter. EPFL Swiss Federal Institute of Technology, Lausanne, 2002, pp. 497-518.
9. Chazono, H., Kimura, T. & Yamaguchi, T., Fabrication of grain-oriented $Bi_4Ti_3O_{12}$ ceramics by normal sintering, I. Tapecasting and sintering. *Yogyo Kyokai Shi*, 1985, **93**, 485-490.

10. Ogawa, H., Kimrua, M., Ando, A. & Sakabe, Y., Temperature dependence of piezoelectric properties of grain-oriented $CaBi_4Ti_4O_{15}$ ceramics. *Jpn. J. Appl. Phys.*, 2001, **40**[Part I] 5715-18.

11. Kimura, T. & Yamaguchi, T. Morphology control of electronic ceramic powders by molten salt synthesis. *Adv. Ceram.*, 1987, **21**, 169-177.

12. Lotgering, F. K., Topotactical reactions with ferromagnetic oxides having hexagonal crystal structures – I. *J. Inorg. Nucl. Chem.*, 1959, **9**, 113-123.

13. Powder Diffraction File No. 43-973. International Centre for Diffraction Data, Pennsylvania, 1990.

14. Sakuma, Y. & Kimura, T., Mechanisms of texture development in bismuth layer-structured ferroelectrics prepared by templated grain growth. *J. Electroceramics*, in press.

Legends to illustrations

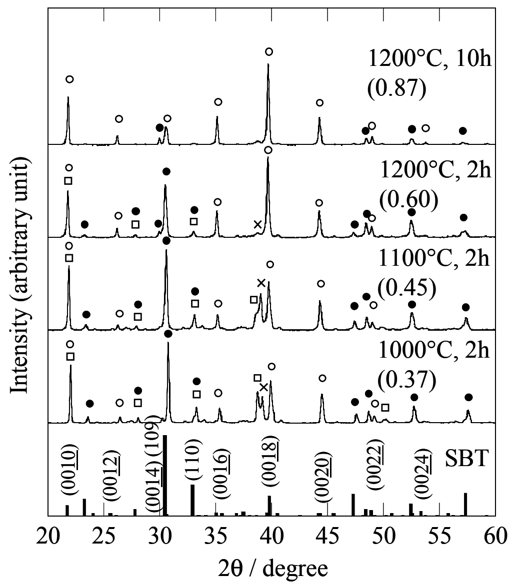
Fig. 1. Diffraction patterns of SBT/BiT specimen sintered under various conditions. Open and filled circles indicate the diffraction lines for (00l) and other than (001), respectively, of SBT, and squares and crosses indicate the diffraction lines of BiT and unknown phase, respectively. The F value is indicated in the parenthesis. Lines at the bottom of the figure indicate the powder diffraction pattern of SBT reported in the literature.

Fig. 2. Microstructures of SBT/BBT specimen sintered at 1150^{o}C for (b) 0 and (b) 2 h.

Fig. 3. Microstructures of (a) BiT/BBT and (b) BiT/SBT specimens sintered at 1150^{o}C for 2 h.

Fig. 4. Microstructures of (a) BBT/SBT and (b) BBT/BiT specimens sintered at 1150^{o} and 1100^{o}C, respectively, for 2.

Fig. 5. Microstructures of BNKT/SBT specimen sintered at (a) 1100^{o} and (b) 1200^{o}C for 2 h.



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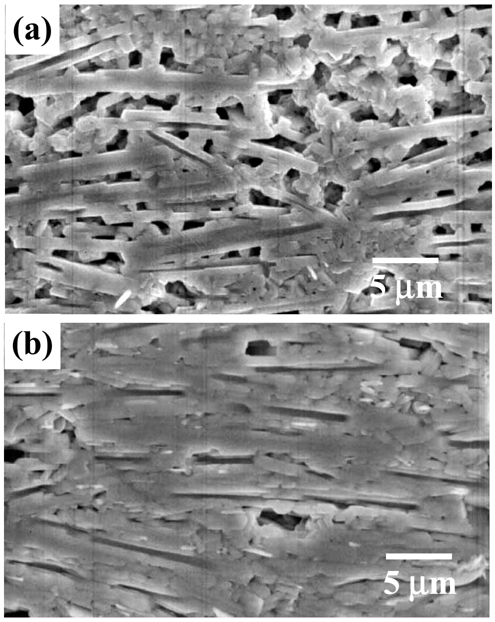

Fig. 2. Microstructures of SI (b) 0 and (b) 2 h.

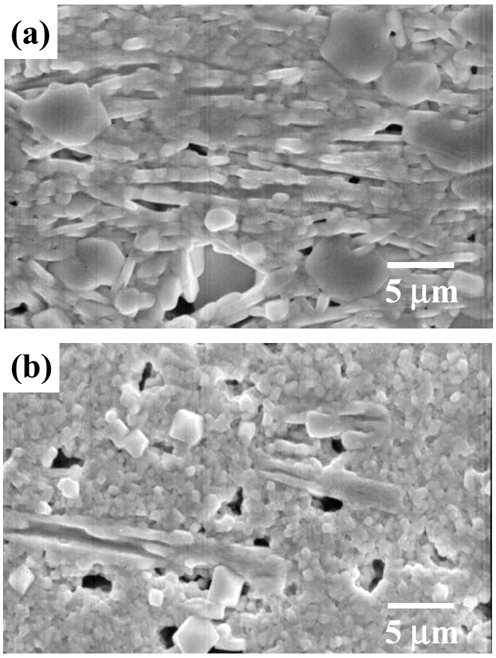

Fig. 3. Microstructures of (a ntered at 1150^{o}C for 2 h.

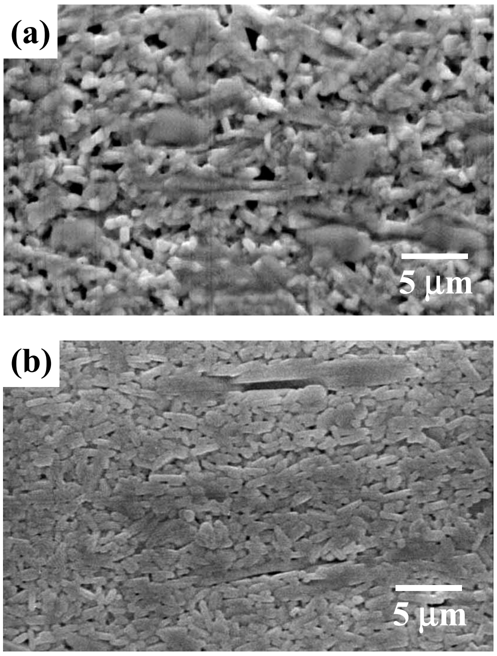

Fig. 4. Microstructures of (a) BBT/SBT and (b) BBT/BiT specimens sintered at 1150° and 1100°C, respectively, for 2.

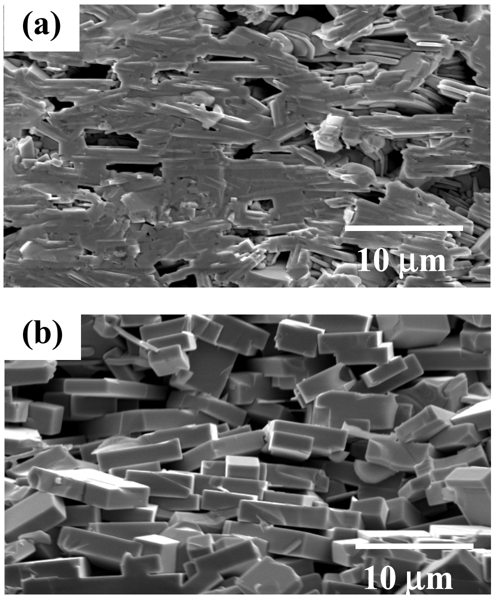

Fig. 5. Microstructures of BNKT/SBT specimen sintered at (a) 1100^o and (b) 1200^{o}C for 2 h.