Fabrication of $\langle 111 \rangle$ Oriented BaTiO_3 Bulk Ceramic by Reactive Templated Grain Growth Method

Tsutomu SUGAWARA, Yoko NOMURA, Toshio KIMURA and Toshihiko TANI*

School of Integrated Design Engineering, Graduate School of Science and Technology, Keio University,
3-14-1, Hiyoshi, Kohoku-ku, Yokohama-shi 223-8522

*Toyota Central Research and Development Laboratories, Inc., 41-1, Yokomichi, Nagakute, Aichi-gun, Aichi 480-1192

反応性テンプレート粒成長法による $\langle 111 \rangle$ 配向性 BaTiO_3 バルクセラミックスの製造

菅原 努・野村陽子・木村敏夫・谷 俊彦*

慶應義塾大学大学院理工学研究科, 223-8522 横浜市港北区日吉 3-14-1

*(株)豊田中央研究所, 480-1192 愛知県愛知郡長久手町横道 41-1

A polycrystalline BaTiO_3 bulk ceramic with a preferred $\langle 111 \rangle$ orientation was fabricated by the reactive templated grain growth method. A green compact was made by tape-casting of slurry containing plate-like $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ template particles and BaCO_3 powder. Single phase BaTiO_3 was obtained by calcining the green compact at 1000°C . The calcined compacts were sintered between 1250 and 1400°C . The degree of orientation increased with an increase in the sintering temperature. Growth of $\langle 111 \rangle$ -oriented BaTiO_3 grains originated from the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ particles is responsible for the increase in the degree of orientation.

[Received June 29, 2001; Accepted August 9, 2001]

Key-words: Barium titanate, Grain orientation, Reactive templated grain growth

1. Introduction

Grain orientation is an important technique to improve performance of ferroelectric ceramics.^{1)–5)} There have been two fabrication methods to prepare grain-oriented ferroelectric ceramics; one aligns grains by applying pressure during sintering^{1),2),6)} and another prepares green compacts with aligned particles.^{5)–11)} In the latter method, plate- or needle-like powder particles are aligned in a green compact by tape-casting, extrusion, and slip-casting. In these methods, grain growth during sintering⁶⁾ and particle growth during Ostwald ripening in molten salt¹²⁾ are necessary to be anisotropic. Therefore, these methods are only applicable to materials with low symmetry, such as those belonging to the bismuth layer-structured ferroelectrics and tungsten-bronze-type niobates.

Many compounds with good dielectric and piezoelectric properties have a crystal structure with high symmetry, such as regular perovskite. To obtain grain-oriented ceramics for these compounds, the reactive templated grain growth (abbreviated as RTGG) method³⁾ has been employed, in which ceramics are made by *in situ* reaction and successive sintering using starting material powders with a plate- or needle-shape. Thus, grain-oriented $\text{Bi}_{0.5}(\text{Na}_{0.85}\text{K}_{0.15})_{0.5}\text{TiO}_3$ with the perovskite structure was fabricated, and significant improvement of the piezoelectric properties due to grain orientation was reported.³⁾ Because this method requires a starting material with an anisotropic shape and the topotactic or epitaxial relation between the starting material and product,¹³⁾ the application of this method has been restricted to a few compounds, and the selection of starting material is important to apply this method to other compounds.

The primary purpose of this note is to investigate the feasibility of fabricating BaTiO_3 with a significant $\langle 111 \rangle$ orientation. The $\langle 111 \rangle$ -oriented BaTiO_3 ceramics would exhibit a hysteresis-free strain vs. electric field curve as shown in a single crystal.¹⁴⁾ $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ (abbreviated as B6T17) was selected for the starting material from two points of view. The powder with an anisotropic shape is expected to be obtained from the crystal structure,¹⁵⁾ and the $\langle 111 \rangle$

grain-orientation is expected from the topotactic relation between crystal axes of B6T17 and BaTiO_3 , i.e., $(001)_{\text{B6T17}} // (111)_{\text{BaTiO}_3}$ and $[010]_{\text{B6T17}} // [110]_{\text{BaTiO}_3}$.^{16),17)} The crystal structure of B6T17 is monoclinic with $a = 0.9887$ nm, $b = 1.7096$ nm, $c = 1.8918$ nm, and $\beta = 98.72^\circ$.¹⁵⁾

2. Experimental

Plate-like B6T17 was prepared from BaTiO_3 and TiO_2 in the presence of NaCl. BaTiO_3 and TiO_2 , with the average particle sizes of 0.5 and $0.6 \mu\text{m}$ respectively, were mixed in a $6 : 11$ molar ratio with a ball mill for 24 h using ethanol as a medium. The dried mixture was mixed with an equal weight of NaCl in an electrically-driven agate mortar and pestle for 30 min, and then heated at 1150°C for 1 h. NaCl was removed from the reaction product by washing with distilled water more than 10 times.

Two preparation methods of slurry for tape-casting were employed. In the first method, B6T17 and BaCO_3 in a $1 : 11$ molar ratio were mixed with a solvent ($60 \text{ vol}\%$ toluene– $40 \text{ vol}\%$ ethanol) in a centrifugal ball mill for 3 h, and then poly(vinyl butyral) (binder) and di-*n*-butyl phthalate (plasticizer) were added and mixed for 2 h. In the second method, B6T17 was mixed with the solvent containing a small amount of poly(vinyl butyral) in the centrifugal ball mill for 2 h. Then, BaCO_3 was added and mixed for 1.5 h. Finally, remaining poly(vinyl butyral) and di-*n*-butyl phthalate were added and mixed for 2 h.

The slurries were tape-cast onto a plastic film. Green sheets were cut, stacked, and pressed at 80°C and 110 MPa for 3 min. The thickness of the compacts was about 2 mm. The compacts were further cut into small pieces ($10 \text{ mm} \times 10 \text{ mm}$).

The binder and plasticizer were burned out at 600°C for 2 h (heating rate was $50^\circ\text{C}/\text{h}$). Then, the compacts were calcined at 1000°C for 2 h (heating rate was $100^\circ\text{C}/\text{h}$). The formation of BaTiO_3 was completed at this stage, as judged by X-ray diffraction analysis. The calcined compacts were cooled to room temperature and pressed isostatically (CIP) at 100 MPa to increase green density, because the reaction between B6T17 and BaCO_3 caused expansion of the com-

pacts. The CIP-ed compacts were sintered between 1250 and 1400°C for 2 h (the heating rate was 100°C/h).

The phases present and the degree of orientation were determined by X-ray diffraction (XRD) analysis using $\text{Cu K}\alpha$ radiation on the major surface of compacts (parallel to the casting direction). The sintered compacts were polished before XRD measurement to examine the grain orientation in the bulk. The degree of orientation, F , was calculated by the following equations (Lotgering method¹⁸),

$$F = \frac{P - P_0}{1 - P_0} \quad (1)$$

$$P = \frac{I_{\{111\}}}{\sum I_{\{hkl\}}} \quad \text{and} \quad P_0 = \frac{I_{0\{111\}}}{\sum I_{0\{hkl\}}} \quad (2)$$

where I and I_0 are the peak heights for the sintered compact and randomly oriented BaTiO_3 , respectively, and $\{111\}$ and $\{hkl\}$ stand for the Miller indices. The diffraction lines between $2\theta = 20$ and 60° were used to calculate $\sum I_{\{hkl\}}$ and $\sum I_{0\{hkl\}}$. The microstructure was observed on fracture surfaces perpendicular to the major surface of sintered compacts with a scanning electron microscope (SEM). The density of sintered compacts was determined by the Archimedes method.

3. Results and discussion

Figure 1 shows the SEM photograph of the B6T17 powder. The powder was mainly composed of plate-like particles with the length of plate face between 10 and 20 μm and a thickness of about 3 μm . Figure 2 shows the XRD pattern

Fig. 1. SEM photograph of B6T17 powder.

Fig. 2. XRD pattern of B6T17 powder. The sample was prepared by tape-casting.

of the B6T17 powder. To examine the crystallographic direction, the sample for XRD measurement was prepared by tape-casting. All XRD peaks were assigned to those of B6T17 (JCPDS No. 35-817). While the most intense peak of B6T17 with random orientation is (331) at $2\theta = 31.3^\circ$, the XRD pattern in Fig. 2 had the intense (006) and (008) peaks at $2\theta = 28.6^\circ$ and 38.5° , respectively, indicating that the $\langle 001 \rangle$ direction of B6T17 lies perpendicular to the plate face, because the plate face of the particles aligned parallel to the major face of the sheet.

Figure 3 shows the XRD pattern of the RTGG-processed compact sintered at 1400°C for 2 h as well as BaTiO_3 powder. The RTGG-processed compact was made from the slurry prepared by the first preparation method. The most intense peak was $\{111\}$ of BaTiO_3 for the RTGG-processed compact, while it was $\{110\}$ for the BaTiO_3 powder. The degree of orientation of the RTGG-processed compact was 0.25, which was smaller than expected.

Figure 4 shows an example of microstructure on a fracture surface perpendicular to the major face of the compact after binder burn-out. The plate-like B6T17 particles were

Fig. 3. XRD patterns of. (a) RTGG-processed sample and (b) BaTiO_3 powder. The RTGG-processed sample was made from the slurry prepared by the first preparation method, and was sintered at 1400°C for 2 h.

Fig. 4. Microstructure of fracture surface perpendicular to the major face of cast compact after binder burn-out at 600°C for 2 h. The compact was made from the slurry prepared by the first preparation method. The casting direction is indicated by the arrow.

hardly observed, and if observed, the orientation was rather random. The large particle in Fig. 4 was B6T17 and plate face was observed. The side face of a plate-like particle should be observed in the fracture surface perpendicular to the major face of the compact, if the B6T17 particles were aligned by tape-casting.

The observation of the microstructure of green compact indicates that the small degree of orientation shown in Fig. 3 is caused by the mis-alignment of B6T17 particles in the cast sheet. Probably, agglomerates of B6T17 and BaCO_3 were formed in the slurry and disturbed the alignment of B6T17 particles. The fact that B6T17 particles were hardly observed on the fracture surface perpendicular to the casting direction indicates that B6T17 particles are covered with BaCO_3 particles to form agglomerates with an isotropic shape.

To improve the dispersion of powder particles in the slurry, the second method of slurry preparation was employed, since a small amount of poly(vinyl butyral) acts as a dispersant.¹⁹⁾ Figure 5 shows the microstructure of a fracture surface perpendicular to the major face of the compact made from the slurry prepared by the second method. To show the particle alignment clearly, the compact after binder burn-out was fractured and immersed in a HNO_3 solution to remove a part of BaCO_3 . Figure 5 indicates that tape-casting of the slurry resulted in the alignment of B6T17 particles with their plate face parallel to the casting direction.

Figure 6 shows the XRD patterns of the compacts sintered at various temperatures for 2 h, measured at the major face parallel to the casting direction. The most intense peak of the sintered compacts was {111}, indicating that $\langle 111 \rangle$ of many grains lies perpendicular to the casting direction. This preferred orientation is expected from the orientation relation between B6T17 and BaTiO_3 .^{15),16)} The result shown in Fig. 6 indicates that the topotactic relation between B6T17 and BaTiO_3 is retained during the formation of BaTiO_3 .

The degree of orientation was dependent on the sintering temperature as shown in Fig. 6; an increase in the sintering temperature increased the degree of orientation.

Figure 7 shows the microstructures of fracture surfaces perpendicular to the major face of the compacts. The sample sintered at 1250°C was composed of plate-like and equiaxed grains. The formation of plate-like grains gives the preferred $\langle 111 \rangle$ orientation, whereas the orientation of equiaxed grains is random, as judged from Fig. 6(a). The diffusion of Ba into plate-like B6T17 resulted in the formation of plate-like BaTiO_3 grains.²⁰⁾ The origin of equiaxed grains is not certain. One possible origin is the presence of equiaxed particles in the B6T17 powder (Fig. 1). Another possible origin is the fragmentation of plate-like BaTiO_3 grain into small grains during the BaTiO_3 formation, because the plate-like BaTiO_3 grain is polycrystal. Plate-like character was maintained up to 1300°C, while grain growth was evident at and above 1300°C. At 1350 and 1400°C, plate-like character was lost and grains had an irregular shape, although the $\langle 111 \rangle$ direction of most grains lay perpendicular to the major face of the compact (Fig. 6). Growth of $\langle 111 \rangle$ -oriented grains at the expense of mis-oriented grains is responsible for the increase in the degree of orientation.²¹⁾

Large pores existed in the sample sintered at 1250°C, and these pores accumulated between the grains with plate-like character at 1300°C. These pores were hardly eliminated by sintering at higher temperatures, as shown in Fig. 7. The density of the samples sintered at 1250, 1300, 1350 and 1400°C was 43, 62, 81 and 81% of theoretical, respectively. The measurement of electrical properties, especially piezoelectric property, was difficult because of the low density. The attempts to increase the sintered density are under way.

Fig. 5. Microstructure of fracture surface perpendicular to the major face of cast compact after binder burn-out at 600°C for 2 h. The compact was made from the slurry prepared by the second preparation method. The compact was treated in a HNO_3 solution to remove a part of BaCO_3 and clearly observe the alignment of B6T17 particles. The casting direction is indicated by the arrow.

Fig. 6. XRD patterns of compacts sintered at various temperatures for 2 h. The compacts were made from the slurry prepared by the second preparation method. The F values indicate the degree of orientation.

4. Conclusions

A polycrystalline BaTiO_3 bulk ceramic with a preferred $\langle 111 \rangle$ orientation was fabricated by the reactive templated grain growth method, using plate-like B6T17 particles with the $\langle 001 \rangle$ direction perpendicular to the plate face. Alignment of B6T17 particles was achieved by tape-casting of a slurry containing B6T17 and BaCO_3 powders. The dispersion of powder particles in the slurry was important to align the plate-like B6T17 particles. Plate-like BaTiO_3 grains with the $\langle 111 \rangle$ direction perpendicular to the casting direction were formed during the reaction between B6T17 and BaCO_3 . Thus, the compact was composed of plate-like BaTiO_3 grains and equiaxed BaTiO_3 grains with random orientation. Growth of $\langle 111 \rangle$ -oriented grains at the expense of randomly-oriented grains increased the degree of orientation.

References

- 1) Igarashi, H., Matsunaga, K., Taniai, T. and Okazaki, K., *Am. Ceram. Soc. Bull.*, 57, 815–17 (1978).

Fig. 7. Microstructures of fracture surfaces perpendicular to the major face of compacts sintered at (a) 1250°, (b) 1300°, (c) 1350°C and (d) 1400°C for 2 h. The compacts were made from the slurry prepared by the second preparation method. The casting direction is indicated by the arrows.

- 2) Takenaka, T. and Sakata, K., *Jpn. J. Appl. Phys.*, **19**, 31–39 (1980).
- 3) Tani, T., *J. Korean Phys. Soc.*, **32**, S1217–20 (1998).
- 4) Hong, S.-H., Trolrier-McKinstry, S. and Messing, G. L., *J. Am. Ceram. Soc.*, **83**, 113–18 (2000).
- 5) Duran, C., Trolrier-McKinstry, S. and Messing, G. L., *J. Am. Ceram. Soc.*, **83**, 2203–13 (2000).
- 6) Kimura, T., Yoshimoto, T., Iida, N., Fujita, Y. and Yamaguchi, T., *J. Am. Ceram. Soc.*, **72**, 85–89 (1989).
- 7) Lin, S.-H., Swartz, S. L., Shulze, W. A. and Biggers, J. V., *J. Am. Ceram. Soc.*, **66**, 881–84 (1983).
- 8) Watanabe, H., Kimura, T. and Yamaguchi, T., *J. Am. Ceram. Soc.*, **74**, 139–47 (1991).
- 9) Brahmaroutu, B., Messing, G. L., Trolrier-McKinstry, S. and Selvaraj, U., Proceedings of the Tenth International Symposium on Applications of Ferroelectrics, East Brunswick, NJ, August 18–21, Ed. by Kulwicki, B. M., Amin, A. and Safari, A. (1996) pp. 883–86.
- 10) Horn, J. A., Zhang, S. C., Selvaraj, U., Messing, G. L. and Trolrier-McKinstry, S., *J. Am. Ceram. Soc.*, **82**, 921–26 (1999).
- 11) Takeuchi, T., Tani, T. and Saito, Y., *Jpn. J. Appl. Phys. Part I*, **38**, 5553–56 (1999).
- 12) Kimura, T. and Yamaguchi, T., *Ceram. Int.*, **9**, 13–17 (1983).
- 13) Seno, Y. and Tani, T., *Ferroelectrics*, **224**, 793–800 (1999).
- 14) Wada, S., Suzuki, S., Noma, T., Suzuki, T., Osada, M., Kaki-hana, M., Park, S.-E., Cross, L. E. and Shrout, T. R., *Jpn. J. Appl. Phys. Part I*, **38**, 5505–11 (1999).
- 15) Hofmeister, W., Tillmanns, E. and Baur, W. H., *Acta Cryst., Sect. C*, **40**, 1510–12 (1984).
- 16) Krasevec, V., Drofenik, M. and Kolar, D., *J. Am. Ceram. Soc.*, **70**, C193–95 (1987).
- 17) Senz, S., Graff, A., Blum, W., Hesse, D. and Abicht, H.-P., *J. Am. Ceram. Soc.*, **81**, 1317–21 (1998).
- 18) Lotgering, F. K., *J. Inorg. Nucl. Chem.*, **9**, 113–23 (1959).
- 19) Watanabe, H., Kimura, T. and Yamaguchi, T., *J. Am. Ceram. Soc.*, **72**, 289–93 (1989).
- 20) Suyama, Y. and Kato, A., *Bull. Chem. Soc. Jpn.*, **50**, 1361–66 (1977).
- 21) Seabaugh, M. M., Messing, G. L. and Vaudin, M. D., *J. Am. Ceram. Soc.*, **83**, 3109–16 (2000).