

Effect of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ Composition on Crystallographic Texture in PZT Composites

Hiroki Muramatsu* and Toshio Kimura

School of Integrated Design Engineering, Graduate School of Science and Technology, Keio University

3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

Abstract

The factors determining the texture development in $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ matrix on platelike $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ grains was studied by examining the effect of matrix composition on the texture development. Platelike $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ particles (B6T17) were prepared by molten salt synthesis using NaCl-flux. Matrix $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT-x) particles ($x=0, 0.3, 0.5, 0.7,$ and 1) were prepared by a conventional method. The slurries containing PZT-x, B6T17, and excess PbO were tape-cast by a doctor blade technique. The green compacts were prepared by lamination of tape-cast sheets and sintered at various temperatures between 900° and 1250°C . The crystalline phases and microstructures were different depending on the PZT composition (x value). For the case of Ti-rich PZT ($x=0\sim 0.5$), texture development occurred with the most intense (111) peak and template grains maintained their platelike shape at sintered temperatures. However, for the case of Zr-rich PZT ($x=0\sim 0.3$), platelike templates disappeared and the specimens had a XRD pattern similar to that of untextured specimen. The template grains embedded in the Zr-rich matrix disappeared by reaction between template and matrix at sintering temperature. The presence and absence of templates result in the different course of texture development. In addition, the growth rate of PZT layer on the template grains is large in the specimens with Ti-rich PZT. Thus, the Zr concentration in PZT is an important factor for the development of crystallographic texture.

Keywords: Sintering, Tape casting, Grain growth, PZT, Epitaxial growth

Introduction

Several efforts have been made for the preparation of crystallographically textured, perovskite-type polycrystalline ceramics in order to improve their properties. The templated grain growth (TGG) method is a novel technique to prepare ceramics with crystallographic texture, and several bulk ceramics were fabricated by this method.¹ The templates used for the preparation of perovskite-type compounds have been limited to platelike BaTiO_3 and SrTiO_3 which give $\langle 100 \rangle$ -texture in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 . Recently, we found that platelike $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ (B6T17) grains gave $\langle 111 \rangle$ -texture in BaTiO_3 and $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$.^{2, 3} The texture in the matrix was developed by the template with the composition and crystal structure different from those of the matrix phase. Thus, we refer to this texturing technique as Hetero-Templated Grain Growth (H-TGG) method. In the PZT case, the addition of excess PbO was necessary to obtain textured ceramics. Excess PbO formed a liquid phase at sintering temperatures and promoted the dissolution of PZT matrix and the precipitation onto the template B6T17 grains.³ The structural similarity between $(00l)_{\text{B6T17}}$ and $(111)_{\text{PZT}}$ developed the $\langle 111 \rangle$ -texture in the PZT matrix. However, a large volume fraction of B6T17 templates (40 vol%) was necessary to prepare highly textured PZT. For example, when the specimen containing 20 vol% templates was sintered at 1200°C , the template grains disappeared and no texture developed.

In this paper, the texture formation was studied by examining the effect of matrix composition on the development of crystallographic texture. The reaction between matrix and template was investigated to find out the factor of the texture development in the PZT-B6T17 system.

Experimental Procedure

Platelike B6T17 were prepared by molten salt synthesis using NaCl-flux.⁴ Chemically pure BaTiO₃ and TiO₂ were mixed in the molar ratio 6:11 and the equal weight of NaCl was added. The mixed powder was heated at 1150°C for 1 h and washed with deionized water several times to remove the flux. Matrix Pb(Zr_xTi_{1-x})O₃ (PZT-x) powders were prepared by a conventional method (x=0, 0.3, 0.5, 0.7, and 1). PbO, ZrO₂, and TiO₂ were mixed in the stoichiometric composition and calcinated at 800°C for 5 h. The obtained PZT powders were ground with a ball mill for 24 h using 2mm^φ ZrO₂ balls. The average grain size of PZT was about 0.5 μm. The B6T17 powder was the mixture of small equiaxed and large platelike particles. Platelike B6T17 particles had an edge length between 20 and 50 μm and a thickness about 3 μm.

In this experiment, the 40 vol% template composition was selected since the highest degree of orientation was obtained under this condition. The powder mixtures containing 40 vol% template B6T17 powder, 60 vol% matrix PZT-x powder, and 1 wt% excess PbO as sintering aid were mixed with solvent (60% toluene - 40% ethanol), binder (poly(vinyl butyral)) and plasticizer (di-*n*-butyl phthalate) to prepare slurries for tape-casting. The slurries were tape-cast by a doctor blade technique. The green compacts were prepared by lamination of tape-cast sheets and heated at 500°C to remove the organic ingredients. The specimens were isostatically pressed at 98 MPa for 3 min and sintered at various temperatures between 900° and 1200°C for 5 h. The sintering atmosphere was controlled by a double crucible method using PbO + PbZrO₃.

The crystalline phase and texture development were evaluated by X-ray diffraction (XRD) analysis using CuKα radiation on the major surface of the compacts. The degree of orientation was estimated by the Lotgering factor, *F*; the intensity of the diffraction lines of PZT between 2θ = 20° and 60° was used for the calculation.⁵ The microstructures were observed at a side face with a scanning electron microscope (SEM). An electron probe microanalyzer (EPMA) was used to examine the distribution of elements in the specimens.

Results and Discussion

Figure 1 shows the XRD patterns of the compacts sintered at 1200°C for 5h. The diffraction pattern of randomly oriented Pb(Zr_{0.52}Ti_{0.48})O₃ is shown at the bottom of Fig.3.⁶ The specimens with Ti-rich matrix (x=0~0.5) had higher (111)-peak intensity than untextured PZT. On the other hand, the specimens with Zr-rich matrix (x=0.7~1) had a similar diffraction pattern to untextured PZT. The peak at 28 ~ 29° belonged to monoclinic-ZrO₂. **Figure 2** shows the *F* value of specimens sintered at various temperatures. The *F* value gradually increased with an increase in the sintering temperature except for the PZ specimen, and PZT-05 had the highest *F* value at 1200°C.

Figure 3 shows the microstructures of the specimens sintered at 1200°C for 5 h. For Ti-rich PZT (Fig.5 (b) and (c)), the template grains maintained their platelike shape and matrix PZT grains grew on the template grains as shown in the inlet of Fig.5 (c). For PT, PZT-07, and PZ (Fig.5 (a), (d), and (e)), on the other hand, platelike grains disappeared. The texture development is closely related to the microstructure development. The presence of template grains is the major factor determining the *F* value, and the reaction occurred during sintering is determined primarily by the phase relation. Because the phase relation in the system PbO-BaO-TiO₂-ZrO₂ at high temperatures (for example, at 1200°C) is not available in the literature, we will deduce the phase relation from the phase diagram for the PbO-TiO₂-ZrO₂ system⁷, in which part of Pb is replaced by Ba.

The composition of the PT specimen lies on the PbTiO₃-TiO₂ join in the PbO-TiO₂-ZrO₂ system, and the eutectic temperature is about 1240°C.⁷ The substitution of Ba for Pb might lower the eutectic temperature below 1200°C. Thus, the PT specimen is composed of (Pb, Ba)TiO₃ and a liquid phase at 1200°C, and the platelike B6T17 grains disappeared.

The compositions of all specimens except for the PT specimen locate in the PZT+ZrO₂ field in the PbO-TiO₂-ZrO₂ system.⁷ If the reaction proceeds completely, the template B6T17 grains disappeared. This is the case for the PZT-07 and PZ specimens. Figure 4 shows the EPMA images of the PZT-05 specimen sintered at 1200°C for 5 h. The distributions of Ba and Ti indicate the presence of platelike template grains, but the distribution of Zr suggests the segregation of ZrO₂, which agrees with the presence of ZrO₂ diffraction line (Fig. 3). These results indicate that the reaction to the PZT and ZrO₂ mixture is just started in the PZT-05 specimen sintered at 1200°C for 5 h. As a matter of fact, the platelike template grains disappeared in the PZT-05 specimen sintered at 1250°C for 5 h. Large F values in the PZT-03 and -05 specimens are originated from the lower reaction rate than in the PZT-07 and PZ specimens.

The PZT-03 and -05 specimens had a larger F value than the PZT-07 and PZ specimens sintered at 1100°C (Fig. 4), although the platelike template grains were present in these specimens. The texture develops by the dissolution of PZT matrix grains in a liquid phase and the precipitation on the template grains. The rate of dissolution and precipitation is dependent on the composition, and the solubility plays an important role as often observed in liquid phase sintering. The solubility of TiO₂ is larger than that of ZrO₂ in a PbO-rich liquid⁷, and therefore the growth rate of PZT layer on the template grains is large in the specimens with Ti-rich PZT.

These results indicate that it is important to promote the solution-precipitation process before the template grains disappeared by reaction between template and matrix at sintering temperatures. Therefore, it is necessary to find out a suitable sintering aid for lowering the sintering temperature and accelerating the rate of solution-precipitation to obtain highly textured PZT specimen.

Conclusion

The effect of matrix composition on the texture development in the PZT matrix was studied by changing the Zr/Ti ratio. In the case of Ti-rich PZT (x=0~0.5), the template grains remained up to high temperatures and gave <111>-texture to the matrix, and in the case of Zr-rich PZT (x=0.7~1), platelike templates disappeared at 1200°C and no extensive texture development occurred. The texture development was determined by two factors; the presence of template grains and the rate of solution-precipitation. These factors are dependent on temperature. Thus, it is important to lower the sintering temperature for the preparation of highly textured PZT.

References

- 1 Sabolsky, E.M., Trolier-McKinstry, S., & Messing, G.L., Dielectric and Piezoelectric Properties of <001> fiber-textured 0.675 Pb(Mg_{1/3}Nb_{2/3})O₃- 0.325 PbTiO₃ ceramics. *J. Appl. Phys.*, 2003, **93**, 4072-4080.
- 2 Kimura, T., Miura Y., & Muramatsu, H., Mechanism of Texture Formation in Ferroelectric Ceramics made by Templated Grain Growth Method. *In Extended Abstract of 11th US-Japan Seminar on Dielectric and Piezoelectric Ceramics*, 2003, pp. 347-350.
- 3 Muramatsu, H., & Kimura, T., Preparation of Bulk Pb(Zr,Ti)O₃ with Crystallographic Texture by Templated Grain Growth Method. *J. Electroceramics* in press.
- 4 Sugawara T., Nomura Y., Kimura T., & Tani, T., Fabrication of <111> Oriented BaTiO₃ Bulk Ceramics by Reactive Templated Grain Growth Method. *J. Ceram. Soc. Jpn.*, 2001, **109**, 897-900.
- 5 Lotgering, F. K., Topotactical Reaction with Ferrimagnetic Oxide Having Hexagonal Crystal Structure. *J. Inorg. Nucl. Chem.*, 1959, **9**, 113-123.
- 6 Powder Diffraction File No. 50-346, International Centre for Diffraction Data, Pennsylvania

2001.

7 Phase Diagrams for Electronic Ceramics I: Dielectric Ti, Nb and Ta oxide systems., ed. Roth, S. R., The American Ceramic Society, New York, 2003

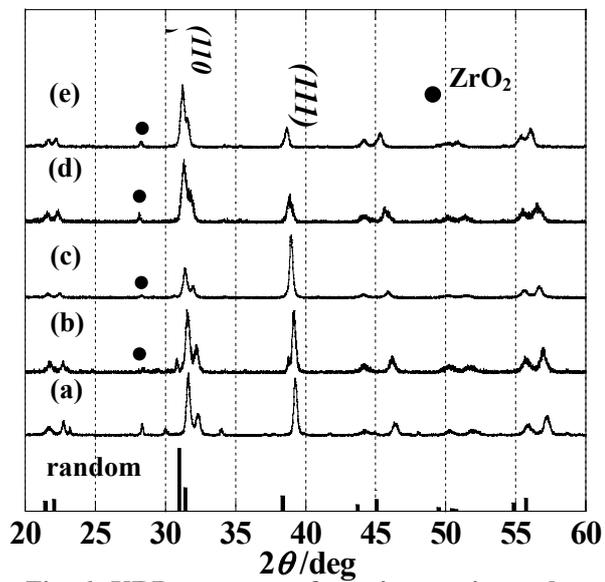
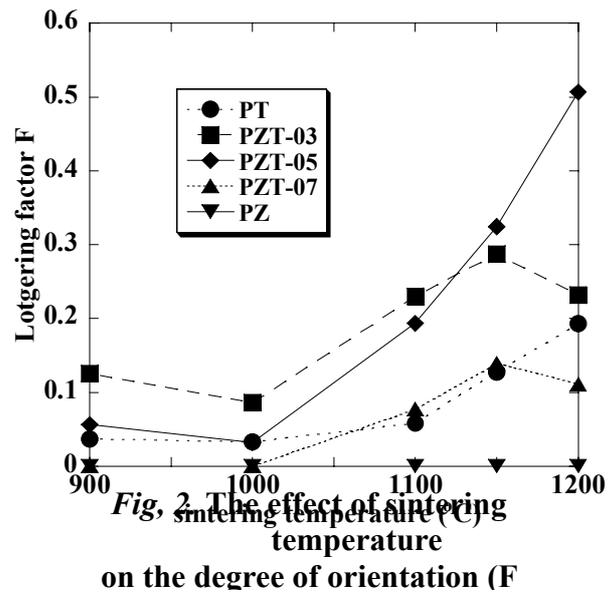


Fig. 1. XRD patterns of specimens sintered at 1200°C for 5h (a) PT (PZT-0), (b) PZT-03, (c) PZT-05, (d) PZT-07, and (e) PZ (PZT-1) The lines at the bottom figure indicates the powder pattern for $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$.



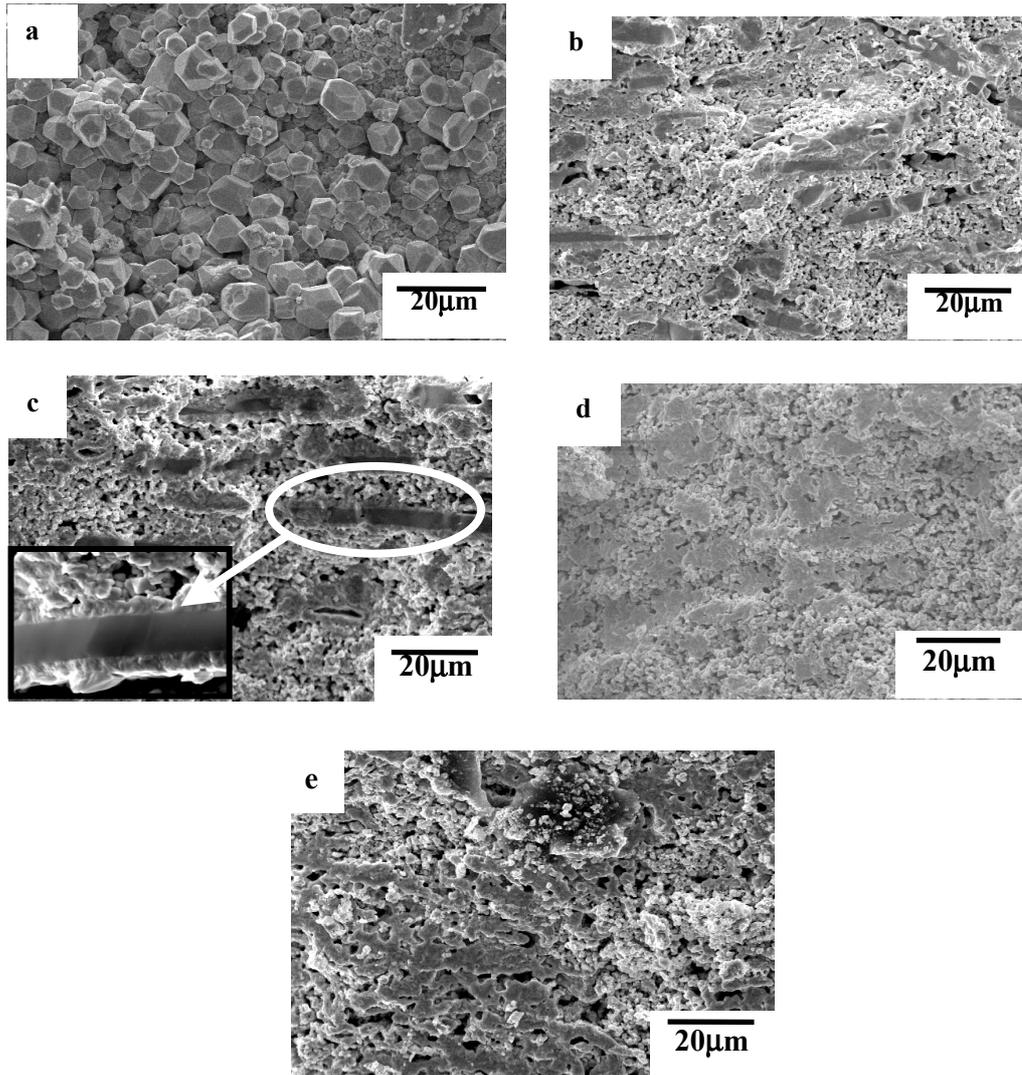


Fig. 3. Microstructures of specimens sintered at 1200°C for 5h (a) PT, (b) PZT-03, (c) PZT-05, (d) PZT-07, and (e) PZ.

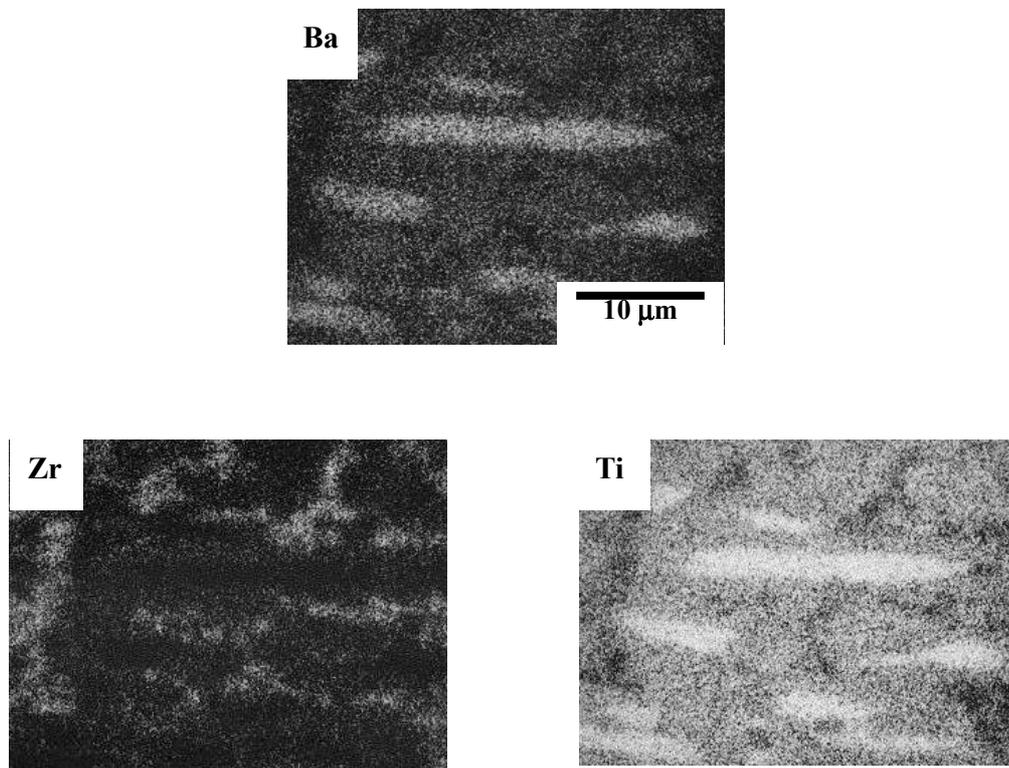


Fig. 4. EPMA images of PZT-05 specimen sintered at 1200°C for 5h.