



# Preparation of Bulk $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ with Crystallographic Texture by Templated Grain Growth Method

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**Abstract.** Polycrystalline  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) ceramics with (111)-texture were prepared by the templated grain growth (TGG) method using the platelike  $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$  (B6T17) particles as templates. Textured PZT was obtained by sintering of green compacts containing matrix PZT, aligned B6T17, and excess PbO. Excess PbO formed a liquid phase and promoted the dissolution of PZT grains and the precipitation on B6T17 grains. A similarity of the arrangement of ions on (001) of B6T17 and (111) of PZT gave (111)-texture to matrix PZT.

**Keywords:** crystallographic texture, templated grain growth, lead zirconate titanate, texture engineering

## Introduction

Several efforts have been made for the preparation of crystallographically textured perovskite-type ceramics in order to improve the properties of polycrystalline materials. 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 were limited to  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  single crystals. The reactive templated grain growth (RTGG) method is an advanced method derived from the TGG method [2]. In this method, the template particles are used as a precursor and an objective material is formed by *in-situ* reaction of templates with the other ingredients, and several perovskite-type compounds have been crystallographically textured [2, 3]. In the TGG and RTGG processes, the chemical composition of template particles has been limited.

We found that platelike  $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$  (B6T17) particles gave (111)-texture in  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT). This indicates the availability of templates with chemical composition different from the matrix. This paper deals with the mechanism of texture development in PZT using B6T17 templates.

## Experimental Procedure

Matrix PZT particles ( $\text{Zr}/\text{Ti} = 0.5/0.5$ ) were prepared by a conventional solid-state reaction method. Chemically pure PbO,  $\text{ZrO}_2$  and  $\text{TiO}_2$  powders were ball-milled for 24 h, heated at  $800^\circ\text{C}$  for 5 h, and ground with a ball mill for 24 h using  $2\text{ mm}^\phi$   $\text{ZrO}_2$  balls. The platelike B6T17 particles were prepared by molten salt synthesis [3].  $\text{BaTiO}_3$  and  $\text{TiO}_2$  were mixed in the molar ratio 6:11 and the equal weight of NaCl was added. The mixed powder was heated at  $1150^\circ\text{C}$  for 1 h and washed with deionized water several times to remove NaCl. Figure 1 shows the SEM photographs of PZT and B6T17 particles. The average particle size of PZT was about  $0.5\ \mu\text{m}$ . The B6T17 was the mixture of small equiaxed and large platelike particles. Platelike B6T17 particles had an edge length between 20 and  $50\ \mu\text{m}$  and a thickness about  $3\ \mu\text{m}$ .

The powder mixture containing 40 vol% of template B6T17 powder and 60 vol% matrix PZT powder were mixed with solvent (60% toluene–40% ethanol), binder (poly(vinyl butyral)) and plasticizer (di-*n*-butyl phthalate) to prepare slurry for tape-casting. Excess PbO between 1 and 5 wt% of PZT was added in some specimens. The slurries were tape-cast by a doctor blade technique. The tape-cast sheets were cut,

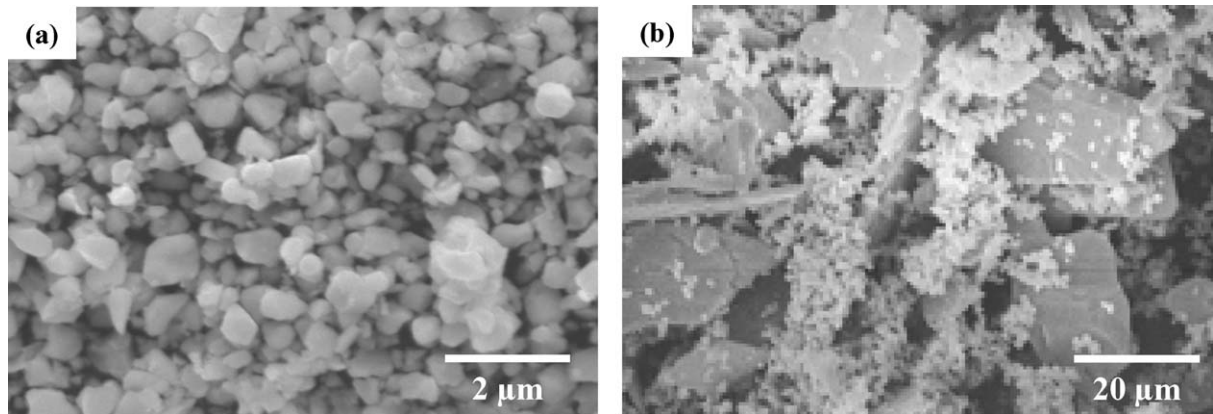


Fig. 1. SEM images of (a)  $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$  and (b)  $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ .

laminated and pressed at  $80^\circ\text{C}$  and 50 MPa for 3 min to form green compacts with a thickness of about 2 mm. The green compact was heated at  $500^\circ\text{C}$  to remove the organic ingredients. The specimens were isostatically pressed at 98 MPa for 3 min and sintered at various temperatures between  $1100^\circ$  and  $1250^\circ\text{C}$  for a desired soaking time. The sintering atmosphere was controlled by the double crucible method using  $\text{PbO} + \text{PbZrO}_3$ .

The crystalline phase and texture development were evaluated by X-ray diffraction (XRD) analysis using  $\text{CuK}\alpha$  radiation on the major surface of the compacts (Fig. 2). The degree of orientation was estimated by the Lotgering factor,  $F$ ; the intensity of the diffraction lines of PZT between  $2\theta = 20^\circ$  and  $60^\circ$  was used for the calculation [4]. The microstructures were observed at a side face (Fig. 2) with a scanning electron microscope (SEM). An electron probe microanalyzer (EPMA) was

used to examine the distribution of components in the specimens.

## Results and Discussion

Figure 3 shows the XRD patterns of the compacts sintered at  $1200^\circ\text{C}$  for 5 h. The XRD pattern of the specimen without excess  $\text{PbO}$  was similar to that of untextured PZT, whereas the specimen with 1 wt% excess  $\text{PbO}$  had higher (111)-peak intensity than untextured PZT. It indicated that excess  $\text{PbO}$  promoted the development of (111)-texture in PZT. Thus, the crystallographic texture was introduced by the plate-like  $\text{Ba}_6\text{Tl}_7$  particles under the existence of excess  $\text{PbO}$ . The amount of excess  $\text{PbO}$  had a small effect on the  $F$  value, and the specimen containing 1 wt% excess  $\text{PbO}$  was examined in the following experiments.

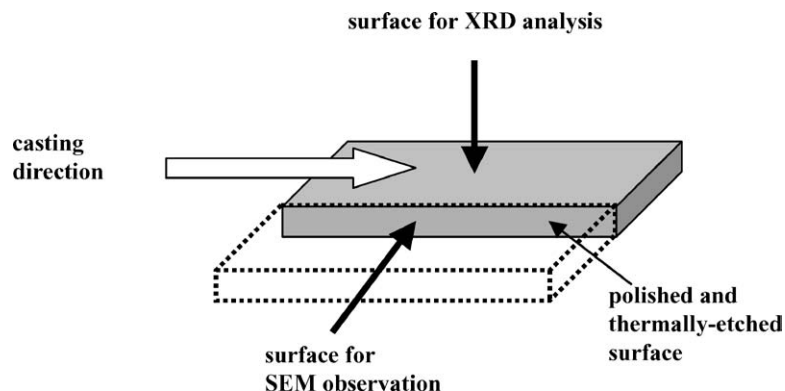


Fig. 2. Configuration of specimen and surfaces for XRD and SEM.

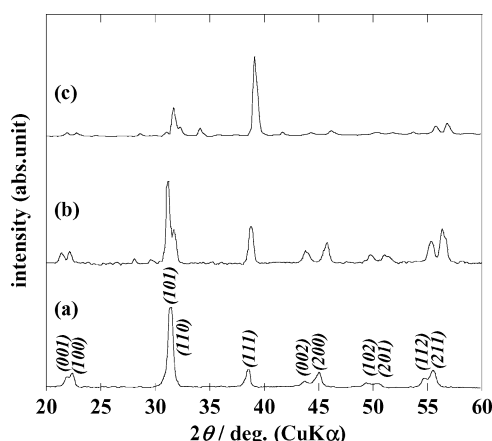


Fig. 3. XRD patterns of (a) untextured PZT, (b) specimen without excess PbO, and (c) specimen with 1 wt% excess PbO. Peaks other than those of PZT belong to B6T17.

Figure 4 shows the effects of sintering temperature and soaking time on the texture development and density of the specimen with 1 wt% excess PbO. The F value gradually increased with an increase in soaking time and reached to about 0.5 by sintering for 10 h at 1200°C. The sintering temperature also gave a large effect and the F value reached about 0.6 by sintering at 1250°C for 5 h.

Figure 5 shows the microstructures of the specimens sintered at 1100°, 1200°, and 1250°C for 5 h. At 1100°C, a few matrix grains attached to the template grains. As the sintering temperature was increased to 1200°C, the amount of matrix grains attached to the templates increased and the growth of PZT layer was observed. Further increase in the sintering temperature drastically changed the microstructure; the microstructure at 1250°C was different from that at 1100° and 1200°C. The presence of template B6T17 grains was confirmed in the specimens sintered up to 1200°C, but B6T17 grains disappeared at 1250°C. The EPMA image of the specimen sintered at 1250°C showed the uniform distribution of Ba ions, indicating the reaction between template and matrix grains or melting of template grains.

The microstructures of specimens at 1100° and 1200°C indicate that the crystallographic texture is given by the formation of PZT layers attached to the template grains. Excess PbO plays an important role in the formation of PZT layers, because no such layers were observed in the specimen without excess PbO. The melting point of PbO is 888°C and excess PbO

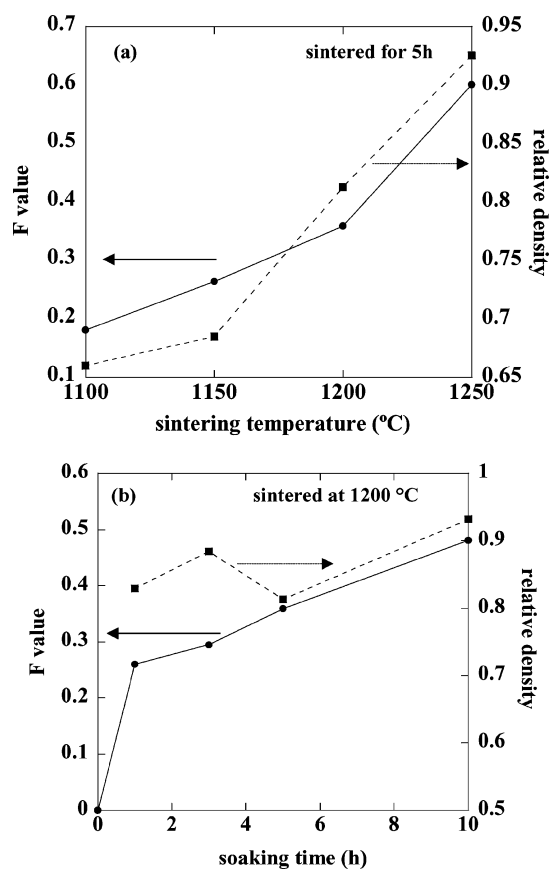


Fig. 4. The effect of (a) sintering temperature and (b) soaking time on texture development and density.

forms a liquid phase at sintering temperatures. The PZT layers attached to the template grains are formed by the dissolution of matrix PZT grains into a liquid phase and the precipitation onto the template grains. In the preparation of textured-BaTiO<sub>3</sub>, abnormal grain growth induced by B6T17 plays an important role in the development of (111)-texture [5], whereas in the present case of PZT, the solution-precipitation is an important mechanism. The growth of PZT layer determined the extent of texture development. In the present experiment, the growth is rather slow, and a fairly large amount of template (40 vol%) is necessary to obtain ceramics with extensive texture.

Figure 6 shows the arrangement of ions on the (001)-plane of B6T17 [6] and (111)-plane of PZT. The oxygen and lead or barium ions form close packing on (111)<sub>PZT</sub> and nearly close packing on (001)<sub>B6T17</sub>, and PZT and B6T17 are characterized by the cubic and hexagonal close packing of oxygen and lead or barium ions. The

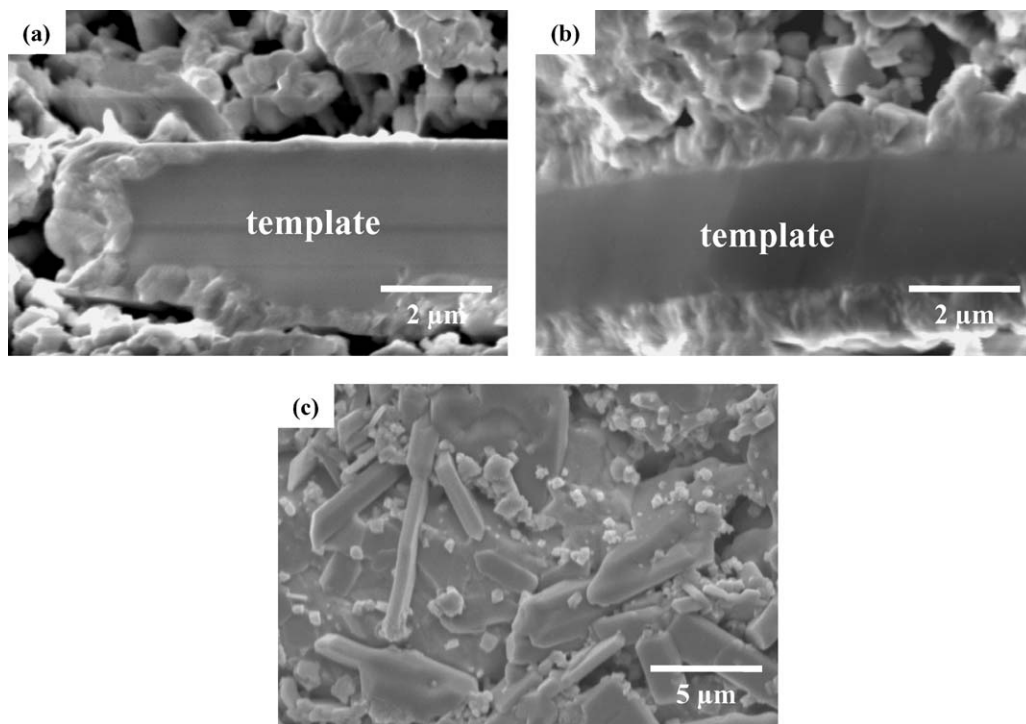


Fig. 5. Microstructures of specimens sintered at (a) 1100°, (b) 1200°, and (c) 1250°C for 5 h.

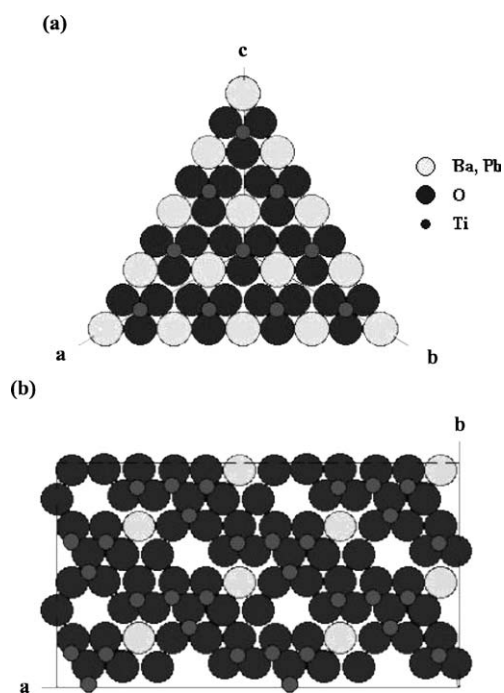


Fig. 6. Arrangement of ions on (a) (111)-plane of PZT and (b) (001)-plane of B6T17.

similarity of the arrangement of ions on  $(001)_{B6T17}$  and  $(111)_{PZT}$  gives the  $\langle 111 \rangle$ -texture to the PZT layers attached to template B6T17 grains.

Figure 5 indicates that the different mechanism of texture development operates at 1250°C. The reason for getting a large F value at 1250°C is not clear at present. Probably, a liquid phase forms by the reaction between PZT and B6T17. The PZT layers with the  $\langle 111 \rangle$ -texture form before the formation of liquid phase, and this PZT layers grow at the expense of matrix PZT grains with random orientation, resulting in a large F value at 1250°C.

### Conclusions

PZT bulk ceramics with the  $\langle 111 \rangle$ -texture were obtained by the TGG method using platelike B6T17 particles as templates and excess PbO. Excess PbO formed a liquid phase and promoted the dissolution of PZT into the liquid phase and the precipitation onto the template B6T17 grains. The structural similarity between  $(001)_{B6T17}$  and  $(111)_{PZT}$  developed the  $\langle 111 \rangle$ -texture in the PZT grains attached to the template B6T17 grains. Thus, PZT with the  $\langle 111 \rangle$ -texture was obtained.

**References**

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