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Preparation of ⟨1 1 1⟩-textured $BaTiO_3$ ceramics by templated grain growth method using novel template particles

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Abstract

Dense $BaTiO_3$ ceramics with ⟨1 1 1⟩-texture were prepared by the TGG process. Platelike $BaTiO_3$ particles with their ⟨1 1 1⟩ direction perpendicular to the plate face were prepared by the reaction of platelike $Ba_6Ti_{17}O_{40}$ particles with $BaCO_3$ particles in molten NaCl. A green compact was composed of the aligned, platelike $BaTiO_3$ template particles dispersed in the matrix of small, equiaxed $BaTiO_3$ particles. Sintering caused densification and also the growth of template particles at the expense of matrix particles, resulting in texture development. Densification prior to grain growth was found to be necessary to obtain highly textured ceramics, and the effect of pre-sintering conditions on texture development was examined.

Keywords: A. Sintering; B. Microstructure-final; $BaTiO_3$; Texture

1. Introduction

Most of widely used piezoelectric ceramics contain high concentration of lead in their compositions; for example, $Pb(Zr,Ti)O_3$ (PZT) contains more than 60 wt% lead. The toxicity of lead is a serious problem caused by the evaporation of lead oxide in the fabrication process and by leakage from discarded lead-containing devices. Therefore, the development of lead-free piezoelectric ceramics is an urgent need [1]. The piezoelectric performance of lead-free materials is inferior to that of lead-containing materials, and microstructural control as well as compositional design is required to enhance piezoelectric properties [2].

Texture control of polycrystals is an important approach to enhance piezoelectric properties without drastically changing the composition of the ceramics [3]. A reactive-templated grain growth (RTGG) method is one of the most convenient preparation methods of textured ceramics. However, the RTGG method includes *in situ* reaction in a green compact, and this reaction makes it difficult to obtain dense ceramics because of the expansion of the compact caused by the formation of product phase [4].

$BaTiO_3$ ceramics with ⟨1 1 1⟩-texture [5] have been prepared only by the RTGG method using platelike $Ba_6Ti_{17}O_{40}$ (B6T17) particles as reactive templates [6] but dense, highly textured ceramics are hardly obtained. This paper deals with the preparation of ⟨1 1 1⟩-textured $BaTiO_3$ ceramics by a simpler method; a templated grain growth (TGG) method [7].

2. Experimental procedure

Platelike $BaTiO_3$ particles were prepared by double molten salt synthesis (DMSS). First, $BaTiO_3$ (Sakai Chemical Industry Co. Ltd., Osaka, Japan) and TiO_2 (anatase) powder (Ishihara Sangyo Kaisha, Osaka, Japan) were mixed with a ball mill. The molar ratio was 6:9 (BaO rich) to compensate Ba-loss in molten salt [4]. The mixture was dry-mixed with NaCl in the weight ratio of 1:1 and heated at 800 °C for 1 h to melt NaCl and then at 1150 °C for 1 h to prepare platelike B6T17 particles. The product was washed with water many times to remove NaCl. Secondly, platelike $BaTiO_3$ particles were prepared from obtained B6T17 and $BaCO_3$ (the molar ratio of 1:11) by the same procedure as the first step.

The platelike $BaTiO_3$ particles and equiaxed $BaTiO_3$ particles with an average diameter of about 0.5 μm in the weight ratio of 2:8, 3:7, and 4:6 were mixed with solvent (toluene and ethanol in the volume ratio of 6:4), binder

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(polyvinyl butyral) and plasticizer (dibutyl phthalate) for 2 h using a planetary ball mill with Ø20 mm steel balls coated with plastic to prepare slurries. The slurries with the powder content [8] of 25 vol.% and the binder content [8] of 7.5 wt% were tape-cast by the doctor-blade process. Green compacts were prepared by laminating the tape-cast sheets at 50 MPa and heating at 500 °C for 2 h to burn out the organic materials. They were sintered in air at 1250–1400 °C for 2–10 h. Some specimens were pre-sintered at 1300 °C for 2–50 h before sintering. Crystalline phases were evaluated by X-ray diffraction (XRD) analysis using Cu Kα radiation, and the degree of orientation (F-value) was calculated by the Lotgering method [9]. The microstructure was observed with a scanning electron microscope (SEM).

3. Results and discussion

Fig. 1 shows the micrographs of particles obtained by the first and second steps of DMSS. These particles had a platelike shape, indicating that the platelike shape was preserved during the reaction in the second step. The crystalline phase of the particles shown in Fig. 1a was B6T17 as judged from the XRD pattern (not shown here). Fig. 2 shows the XRD pattern of the particles shown in Fig. 1b. Only diffraction lines belonging to $BaTiO_3$ were observed, indicating that the $BaTiO_3$ formation reaction was completed in the second step. The most intense peak of (1 1 1), instead of (1 1 0) for the ordinary powder diffraction pattern (Fig. 2 b), indicates that the ⟨1 1 1⟩ direction lies perpendicular to the plate face, because platelike particles cause preferred orientation in a sample holder for XRD. These results indicate that platelike $BaTiO_3$ particles with their ⟨1 1 1⟩ direction perpendicular to the plate face are successfully prepared by DMSS. Some losses of the aspect ratio were observed in the formation of $BaTiO_3$ due to breaking into small grains and growing along the thickness direction. However, their platelike shape was enough to use as template particles for the TGG method.

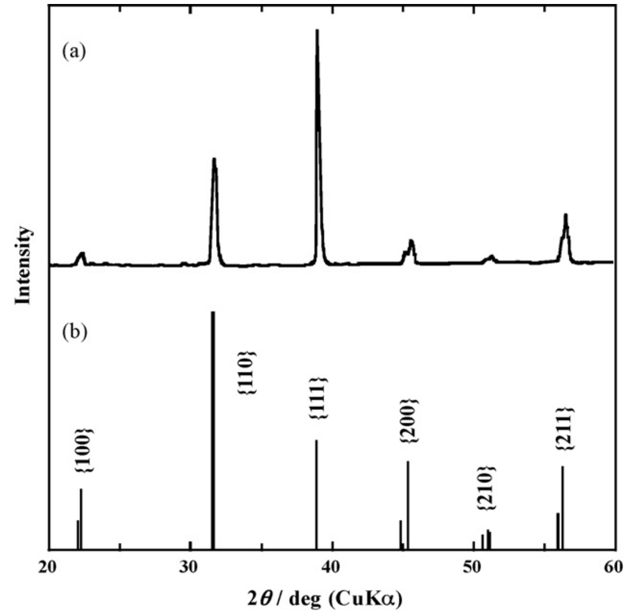

Fig. 2. XRD pattern of (a) prepared $BaTiO_3$ particles and (b) $BaTiO_3$ reported by JCPDS (5-0626). The diffraction lines are indexed based on the cubic system (not on the tetragonal system) to avoid complexity.

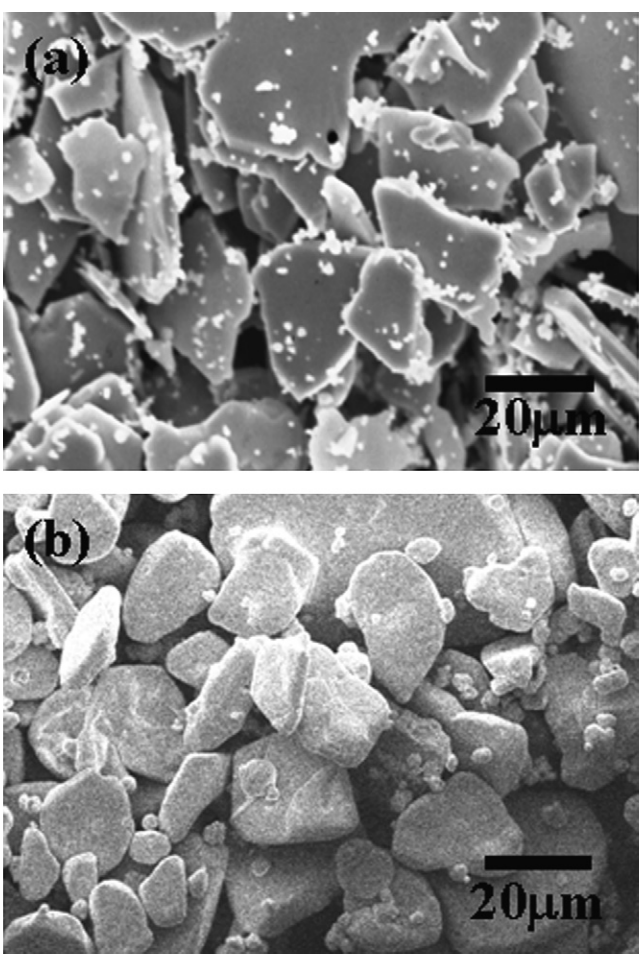

Fig. 1. SEM images of (a) $Ba_6Ti_{17}O_{40}$ and (b) $BaTiO_3$ particles.

Platelike B6T17 particles have their ⟨0 0 1⟩ direction perpendicular to the plate face [6]. The reaction between $BaCO_3$ and TiO_2 to form $BaTiO_3$ is caused by the unidirectional diffusion of BaO into TiO_2 [10,11]. In the present case, BaO diffuses into B6T17 to form $BaTiO_3$. Thus, the platelike shape of B6T17 was preserved. There is a topotactic relation between B6T17 and $BaTiO_3$; $(0\,0\,1)_{B6T17}//(1\,1\,1)_{BaTiO_3}$ [12]. Therefore, platelike $BaTiO_3$ particles with their ⟨1 1 1⟩ direction perpendicular to the plate face was obtained. It means that the plate faces of $BaTiO_3$ are (1 1 1). Fig. 1 indicates that the plate face of B6T17 is smooth and that of $BaTiO_3$ is rough. The surface energy of (0 0 1) of B6T17 is the lowest but that of (1 1 1) of $BaTiO_3$ is higher than that of (1 0 0), resulting in rough surfaces.

Fig. 3 shows the relative density and F-value as a function of sintering temperature. The F-value gradually increased between 1250 and 1300 °C in comparison with a sharp increase in the relative density. Microstructure observation revealed that grain growth hardly occurred in this stage. The F-value increased above 1300 °C and reached 0.36 at 1400 °C. The relative density increased up to 1350 °C (95% of theoretical) and then slightly decreased at 1400 °C.

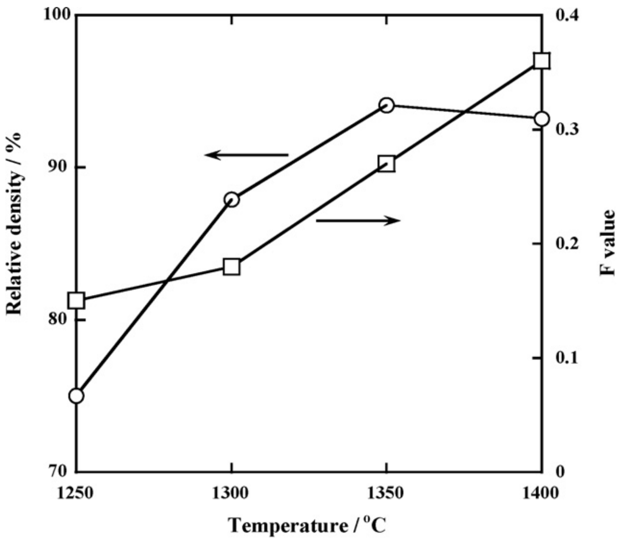

Fig. 3. Effects of sintering temperature on relative density and F-value of specimens sintered for 2 h.

In the present case, texture develops by the growth of template grains at the expense of small matrix grains. Therefore, grain growth is necessary to increase the F-value. Grain boundary migration is hindered by pores and an increase in the F-value is limited in a porous compact (between 1250 and 1300 °C). Therefore, the promotion of grain growth by increasing the density was examined to increase the F-value; the specimens were pre-sintered at 1300 °C.

Fig. 4 shows the relative density and F-value of specimens pre-sintered at 1300 °C and sintered at 1400 °C for 2 h, as a function of pre-sintering time. The sintering temperature of 1400 °C was selected because sintering at this temperature gave the largest F-value, although the maximum density was obtained at 1350 °C (Fig. 3). The F-value increased with increasing pre-sintering time, indicating that the pre-sintering procedure promoted grain growth at 1400 °C by increasing density before grain growth. The specimen pre-sintered at

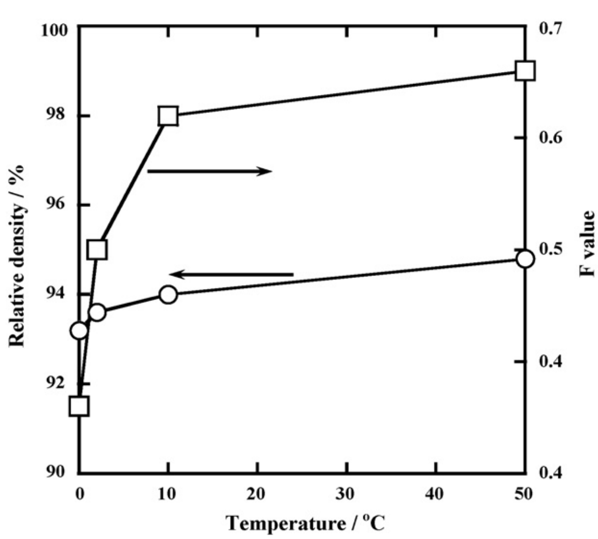

Fig. 4. Effects of pre-sintering time at 1300 °C on relative density and F-value of specimens sintered at 1400 °C for 2 h.

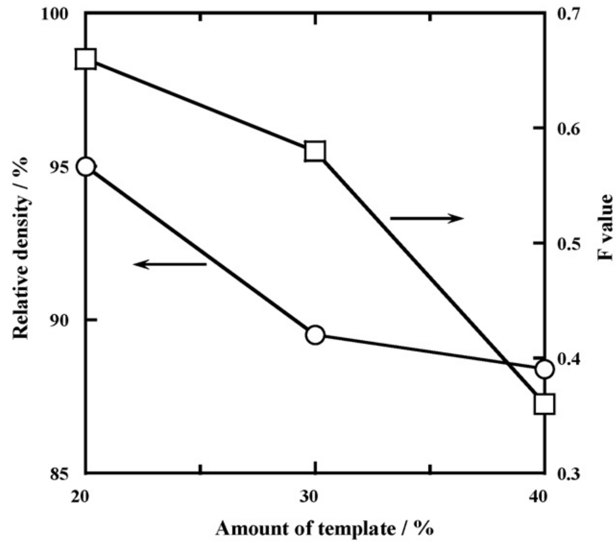

Fig. 5. Effects of the amount of template particles on relative density and F-value of specimens pre-sintered at 1300 °C for 50 h and sintered at 1400 °C for 2 h.

1300 °C for 50 h and sintered at 1400 °C for 2 h had the F-value of 0.66 and the relative density of 95%. These values are higher than those reported for the specimen prepared by the RTGG process [6].

Fig. 5 shows the relative density and F-value of specimens pre-sintered at 1300 °C for 50 h and sintered at 1400 °C for 2 h as a function of the amount of template particles. The relative density and F-value decreased with an increase in the amount of template particles. The origin of low F-values of the specimens containing 30 and 40% of template particles is the hindrance of densification by large platelike particles [13].

4. Conclusion

Dense $BaTiO_3$ ceramics with ⟨1 1 1⟩-texture were prepared by the combination of particle preparation by DMSS and texture development by TGG. Platelike $BaTiO_3$ particles with the ⟨1 1 1⟩ direction perpendicular to the plate face were obtained by the reaction of platelike B6T17 particles with $BaCO_3$ in molten NaCl. The textured ceramics were obtained by the growth of platelike $BaTiO_3$ grains at the expense of equiaxed matrix $BaTiO_3$ grains. Promotion of grain growth was necessary to obtain highly textured ceramics, and pre-sintering at 1300 °C for a long period to increase density had the positive effect.

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