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Development of texture in $Bi_{0.5}Na_{0.5}TiO_3$ prepared by reactive-templated grain growth process

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Abstract

The effect of sodium concentration on texture development in $Bi_{0.5}Na_{0.5}TiO_3$ [BNT] bulk ceramics was examined. The ⟨1 0 0⟩-textured specimens were prepared by the reactive-template grain growth process using platelike $Bi_4Ti_3O_{12}$ particles. Texture did not extensively develop in stoichiometric and Na-deficient BNT, but excess Na promoted extensive texture development together with densification. The role of excess Na was discussed based on the formation of a liquid phase.

Keywords: Grain growth; Sintering; Platelets; Bismuth sodium titanate; Microstructure-final

1. Introduction

$Bi_{0.5}Na_{0.5}TiO_3$ [BNT] is one of the candidates for lead-free piezoelectric ceramics, but the piezoelectric properties of BNT are not good enough for practical applications to replace PZT (lead zirconate titanate)-based materials.[1] The properties of ceramics are determined not only by the chemical composition but also by microstructure, which includes texture. It is reported that textured ceramics have enhanced piezoelectric properties.[2–5]

Compounds with the perovskite structure have been textured by the reactive-templated grain growth (RTGG) process using anisometric particles as reactive templates.[2,6–8] A mixture of reactive templates and complementary compounds is tape cast to align the reactive template particles in a green compact and then calcined to form the target compound. The calcined compact is composed of matrix grains with random orientation and oriented grains transformed from the reactive templates, so that texture develops by the preferential growth of oriented grains at the expense of matrix grains during sintering.

The preparation of textured BNT has been examined by the RTGG process using platelike $Bi_4Ti_3O_{12}$ [BiT] particles as reactive templates, but dense, highly textured BNT has not been obtained.[6] It has been reported that the addition of Bi_2O_3 to BNT gives rise to dense, highly textured BNT and the origin is explained by the formation of a liquid phase.[9] It is expected that the addition of Na_2CO_3 also forms a liquid phase. In the present study, we examined the effects of the addition of Na_2CO_3 to BNT on the grain growth behavior and grain boundary structure, which influence the development of texture. We found that the addition of Na_2CO_3 gave rise to dense, highly textured BNT.

2. Experimental procedure

Bi_2O_3 (Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan, 99.99%), Na_2CO_3 (Wako Pure Chemical Industries, Ltd., Osaka, Japan, >99.5%), TiO_2 (Wako Pure Chemical Industries, Ltd., Osaka, Japan, 99.7%) were used as raw materials.

Platelike BiT particles with diameter between 5 and 20 μm and thickness between 0.5 and 0.7 μm were obtained by molten salt synthesis and used as reactive templates. BNT was prepared based on the following reaction:

$$\text{platelike BiT} + 2Na_2CO_3 + 5TiO_2 = 8BNT + 2CO_2 \qquad (1)$$

The amount of Na_2CO_3 was designed to give stoichiometric, 2 mol% Na-excess, and 2 mol% Na-deficient BNT (Table 1). The reactants in Eq. (1) were mixed with solvent (60 vol% toluene–40 vol% ethanol), binder (poly(vinyl butyral)), and plasticizer (di-*n*-butyl phthalate), and resultant slurries were tape cast by a doctor blade technique.[10] Green compacts were prepared by laminating the tape cast sheets, heated at 500 °C for 2 h to remove the organic ingredients and at 750 °C for 2 h for calcination to form BNT. The calcined compacts were isostatically

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Table 1
Composition of specimens

	Bi	Na	Ti
Na-deficient	0.5	0.49	1
Soichiometric	0.5	0.5	1
Na-excess	0.5	0.51	1

Table 2
Relative density and the degree of orientation of BNT sintered at 1000 °C for 2 h

	Relative density (%)	The degree of orientation
Na-deficient	57	0.51
Stoichiometric	61	0.53
Na-excess	92	0.86

pressed at 98 MPa and then sintered between 775 and 1200 °C for 2 h in a flowing oxygen atmosphere.

The crystalline phases and the degree of orientation were determined by X-ray diffraction (XRD) analysis using Cu Kα radiation. The degree of orientation was determined by the Lotgering method.[11] The microstructures of the compacts were observed with a scanning electron microscope (SEM) on fractured surfaces. The density of the sintered compacts was determined by the Archimedes method. The theoretical density of 5.997 g cm^{-3} of BNT was used to calculate the relative density.[12]

3. Results

3.1. Development of ⟨1 0 0⟩-texture

Fig. 1 shows the XRD patterns of the textured BNT specimens with different Na concentrations sintered at 1000 °C, as well as the pattern of non-textured, stoichiometric BNT. The intensity of (1 0 0) and (2 0 0) peaks of the textured specimens was higher than that of the non-textured one, indicating that ⟨1 0 0⟩-textured BNT was obtained. Table 2 shows the relative density and the degree of orientation of the sintered BNT specimens with different Na concentrations. Both the density and the degree of orientation increased with the increase of the Na concentration.

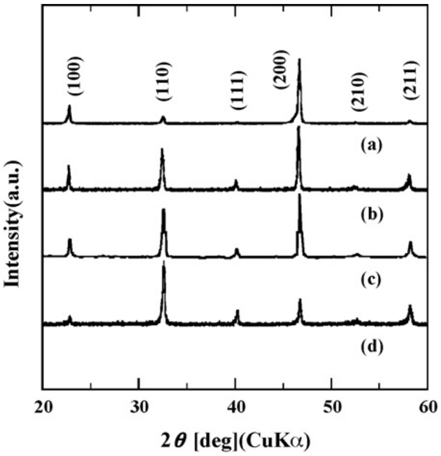

Fig. 1. XRD patterns of (a) Na-excess, (b) stoichiometric, (c) Na-deficient, and (d) non-textured BNT, sintered at 1000 °C for 2 h.

Fig. 2 shows the microstructure of the textured BNT specimens with the different Na concentrations, sintered at 1000 °C. The microstructures of the stoichiometric and Na-deficient specimens were composed of small, irregularly shaped grains, whereas grain growth was promoted in the Na-excess sample, the grain boundaries being nearly straight and parallel to the direction of tape casting. Hereafter, this kind of grain boundary is called "flat" grain boundary.

The density and the degree of orientation of stoichiometric BNT increased by heating at higher temperatures and for longer soaking periods, but the maximum values reached for relative density and degree of orientation were 80% and 0.79, respectively, by sintering at 1200 °C for 2 h, remaining still smaller than those of the Na-excess specimen sintered at 1000 °C for 2 h. These results indicate that densification and texture development are dependent on the Na excess.

3.2. Microstructure development in BNT with excess Na

Because the grain shape is important for texture development in BNT, the effects of sintering temperature on the microstructure as well as texture and density were examined. Fig. 3 shows the degree of orientation and the relative density as a function of the sintering temperature. The degree of orientation increased between 800 and 1100 °C, whereas the relative density jumped between 900 and 1000 °C.

Fig. 4 shows the microstructures. Grain growth started even at 775 °C and grains with well-developed crystal faces were formed (Fig. 4(a) and (b)). Hereafter, this kind of grain is called "faceted" grain, in contrast to flat grain boundaries. Between 800 and 900 °C, oriented template grains grew preferentially at

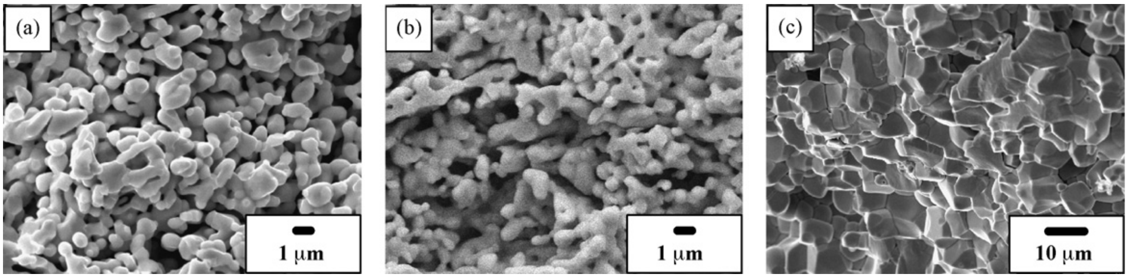

Fig. 2. Microstructures of (a) Na-deficient, (b) stoichiometric, and (c) Na-excess BNT, sintered at 1000 °C for 2 h.

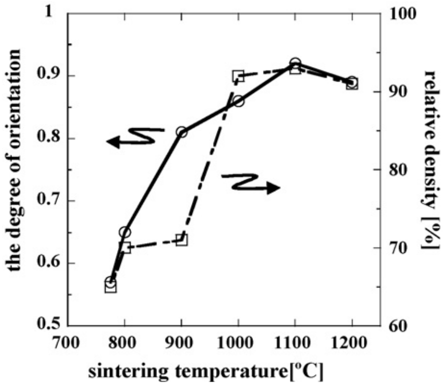

Fig. 3. Effects of sintering temperature on the degree of orientation and on the relative density of specimens with excess Na, heated for 2 h.

the expense of matrix grains with random orientation, and the grains with flat boundaries were formed (Figs. 4(c) and 2(c)). Microstructure development between 775 and 1000 °C indicates that the flat boundaries are composed of (1 0 0) faces, which are parallel to the outer face of the compact. Thus, these grains contribute the evolution of texture. Increases in the number and size of grains with flat boundaries are directly related to an increase in the degree of orientation.

The rapid densification between 900 and 1000 °C was caused by the disappearance of large pores. The pores in the 900 °C specimen hardly shrank because their sizes were larger than grain sizes (Fig. 4(c)). Grain growth between 900 and 1000 °C reversed the situation (Fig. 2(c)); the pore sizes were smaller than grain sizes, resulting in the jump in the relative density.[13]

4. Discussion

Figs. 1 and 2 show that excess Na promotes texture development and densification. Excess Na forms the grains with flat grain boundaries, whereas the grains formed in the stoichiometric and Na-deficient samples show an irregular shape. The origin of the difference in the grain shape might be attributed to the formation of a liquid phase in the Na-excess specimen. Although the composition of the liquid phase is not specified, a mixture of $NaCO_3$ and Na_2O is one of the candidates for the liquid phase (the eutectic temperature in the Na_2CO_3–Na_2O system is 695 °C).[14] The liquid phase reduces the relative magnitude of (1 0 0) grain boundary energy with respect to other boundary energies, resulting in the formation of faceted grains (Fig. 4(a) and (b)). These faceted grains grow at the expense of matrix grains. The microstructure of the 900 °C sample is composed of the grains grown from the faceted grains and the sample shows a large degree of orientation. The growing grains impinge each other, forming flat boundaries between them (Figs. 4(c) and 2(c)).

The faceted grains act as templates and grow at the expense of small matrix grains, resulting in the development of texture. It is proposed that the growth of $Bi_{0.5}(Na_{0.5}K_{0.5})_{0.5}TiO_3$ template grains is caused by spreading of matrix grains over the surfaces of template grains by surface diffusion. The development of flat (1 0 0) boundaries promotes the spreading.[15] This mechanism might operate in the Na-excess specimen. A liquid phase promotes texture development by forming a large area of (1 0 0) boundaries.

The flat grain boundaries disappeared at 1200 °C. This might be caused by the evaporation of the liquid phase. The grain boundary energy of (1 0 0) is relatively low in the presence of the liquid phase, but this condition is lost after the evaporation of the liquid phase. Thus, the microstructure usually observed in non-textured ceramics has resulted. Because the change in the grain boundary structure does not change the orientation of grains, the 1200 °C sample has a large degree of orientation because the texture mostly developed before all of the liquid phase evaporated.

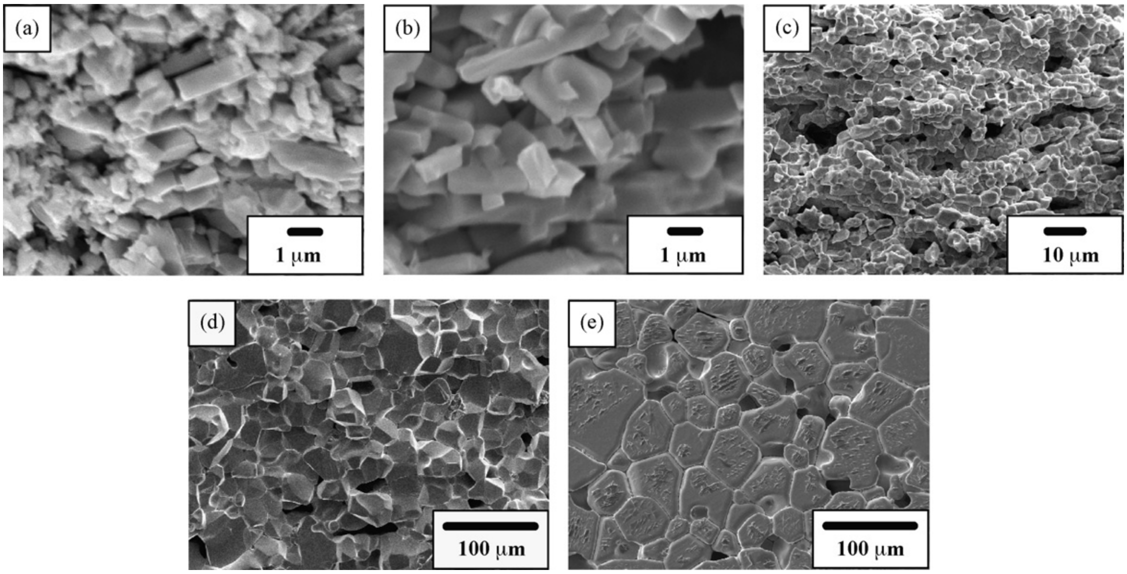

Fig. 4. Microstructures of Na-excess specimen sintered at (a) 775 °C, (b) 800 °C, (c) 900 °C, (d) 1100 °C, and (e) 1200 °C for 2 h. (Microstructure at 1000 °C has shown in Fig. 2(c).)

5. Conclusions

Texture development of BNT prepared by the RTGG process was dependent on the Na concentration. While extensive texture did not develop in the stoichiometric and Na-deficient specimens, the addition of excess Na promoted texture development and densification. The role of excess Na is to form a liquid phase. The liquid phase reduces the relative magnitude of (1 0 0) grain boundary energy with respect to other boundary energies, resulting in the formation of the faceted grains and flat grain boundaries. The development of flat (1 0 0) boundaries promotes preferential growth of template grains, resulting in the development of texture.

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