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Effects of processing methods on texture development and densification in $SrBi_4Ti_4O_{15}$ ceramics

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This paper deals with the effects of preparation methods on the texture development and densification in textured $SrBi_4Ti_4O_{15}$ (SBT) ceramics. The specimens were prepared by the oriented consolidation of anisotropic particles (OCAP), templated grain growth (TGG) and reactive templated grain growth (RTGG) methods. The specimens with extensive texture were obtained by all methods except for TGG with small template and large matrix particles. The origin of extensive texture development was the growth of aligned platelike particles. A characteristic of microstructure was the formation of colonies, in which platelike grains contacted face-to-face. The size of colonies was dependent on the preparation method, and determined the size of pores between colonies, which had a large effect on the sintered density. The OCAP and RTGG methods gave the green compacts composed of only platelike particles and large colonies and pores formed during sintering. The TGG method gave the green compacts composed of platelike and equiaxed particles and prevented the formation of large colonies and pores during sintering. Thus, the dense, highly-textured SBT ceramics were obtained by the TGG method.

1. Introduction

Bismuth layer-structured ferroelectrics (BLSF), such as $Bi_4Ti_3O_{12}$, $SrBi_4Ti_4O_{15}$ and $CaBi_4Ti_4O_{15}$, are one of the candidates for lead-free piezoelectric ceramics [1]. However, the properties of these ceramics are much smaller than those of lead-containing compositions because of an anisotropic crystal structure. To overcome this shortcoming, textured ceramics have been prepared [2–6]. There are mainly two preparation methods of textured ceramics; the application of pressure during sintering [2, 3] and the formation of green compacts with aligned platelike and needlelike particles [4–7]. This paper is related to the latter method.

The tape casting is one of the most convenient methods to align the particles with shape anisotropy in green compacts [4–7]. At first, only particles with shape anisotropy were used to prepare slurries for tape casting [4, 7, 8]. We will call this method "oriented consolidation of anisotropic particles (OCAP) method". Recently, this method was modified to templated grain growth (TGG) [5, 9, 10] and reactive templated grain growth (RTGG) methods [11, 12]. The TGG method uses the mixture of particles with shape anisotropy and equiaxed particles with the same composition. The RTGG method uses the mixture of precursor particles with shape anisotropy and equiaxed particles with the composition to form the object material by the reaction with precursor. This method enables the preparation of the textured ceramics, for which the formation of particles with shape anisotropy is difficult such as compounds with the perovskite structure.

These three methods (OCAP, TGG, and RTGG) inherently have advantage and disadvantage. However, the characteristics of textured ceramics obtained by the different processing methods have not been compared for the same material. This paper deals with the texture development and densification in $SrBi_4Ti_4O_{15}$ (SBT) prepared by three methods. SBT is selected because platelike SBT and $Bi_4Ti_3O_{12}$ particles are expected to be easily prepared and the reaction shown by Equations 1 and 2 is available in the RTGG method [1, 6, 12, 13].

$$2Bi_2O_3 + SrCO_3 + 4TiO_2 = SrBi_4Ti_4O_{15} + CO_2 \quad (1)$$

$$Bi_4Ti_3O_{12} + SrCO_3 + TiO_2 = SrBi_4Ti_4O_{15} + CO_2 \quad (2)$$

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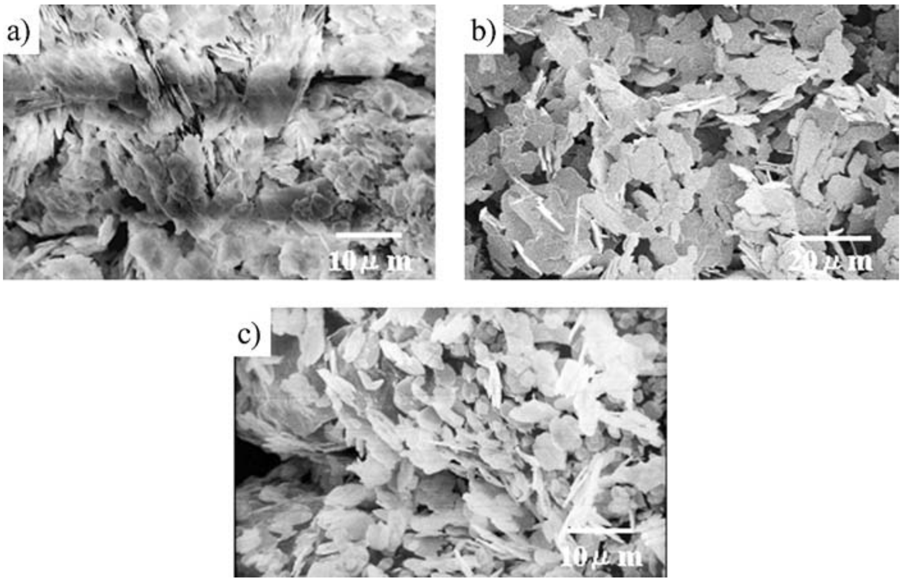

Figure 1 SEM photographs of platelike SBT particles prepared at (a) 900 and (b) 1100°C for 1 h and (c) platelike $Bi_4Ti_3O_{12}$.

2. Experimental procedure

Chemically pure $SrCO_3$, Bi_2O_3, and TiO_2 were used as raw materials. Platelike SBT particles were prepared by heating the mixture of $SrCO_3$, Bi_2O_3, and TiO_2 (a molar ratio of 1:2:4) in the presence of KCl at 900 and 1100°C for 1 h. The products were washed with deionized water more than 10 times to remove KCl. Figs 1a and b show the photographs of obtained powders. Both particles had platelike morphology and the size was dependent on the heating temperature; the particles obtained at 900°C had the diameter between 5 and 10 μm and thickness between 0.2 and 0.3 μm, and those obtained at 1100°C had the diameter between 15 and 20 μm and thickness between 0.3 and 0.5 μm. X-ray diffraction analysis indicated that the powders were single phase SBT and the crystallographic c-axis lay perpendicular to the plate face. We call the small and large platelike SBT particles as SBT-pl[S] and SBT-pl[L], respectively. Platelike $Bi_4Ti_3O_{12}$ (BIT) used for the RTGG method was a commercial product prepared by Ohtsuka Chemical Co., Ltd. These particles had a similar size to SBT-pl(S) and the diameter was about 7 μm and a thickness was between 0.2 and 0.3 μm (Fig. 1c).

Equiaxed SBT particles were prepared by the conventional solid-state reaction at 950°C for 2 h, from the mixture of $SrCO_3$, Bi_2O_3, and TiO_2. The reaction product was ground by a ball mill for 24 h using 15 mm^{ϕ} ZrO_2 balls. The ground powder with an average particle size of about 1.0 μm was divided into two parts. One was used as-ground and another was further ground using 2 mm^{ϕ} ZrO_2 balls for 24 h. The average particle size of the latter powder was about 0.5 μm. We call the large and small SBT particles as SBT-eq[L] and SBT-eq[S], respectively.

Table I shows the powders used for the preparation of specimens. For the OCAP method, only SBT-pl[S] was used. For the TGG method, platelike and equiaxed SBT was used for the template and matrix particles, respectively, and the amount of template particles was 20 vol%. Two combinations of platelike and equiaxed particles were selected (Table I). For the RTGG method using Equation 1, the template was SBT-pl[S] and the matrix was the raw materials for SBT ($SrCO_3 + 2Bi_2O_3 + 4TiO_2$). We will call this method as SR. For another RTGG method using Equations 1 and 2 (we will call BR), the template was platelike BIT and matrix was the raw materials for SBT ($SrCO_3 + 2Bi_2O_3 + 4TiO_2$) plus ($SrCO_3 + TiO_2$). ($SrCO_3 + TiO_2$) was added to change BIT into SBT. In both methods (SR and BR), the amount of template particles after the SBT formation was designed to be 20 vol%. The reactions occurring in the SR and BR methods are shown in Equations 3 and 4, respectively.

$$0.2\mathrm{SBT} + 0.8(\mathrm{SrCO_3} + 2\mathrm{Bi_2O_3} + 4\mathrm{TiO_2}) = \mathrm{SBT} + 0.8\mathrm{CO_2} \quad (3)$$

$$0.2(\mathrm{BIT} + \mathrm{SrCO_3} + \mathrm{TiO_2}) + 0.8(\mathrm{SrCO_3} + 2\mathrm{Bi_2O_3} + 4\mathrm{TiO_2}) = \mathrm{SBT} + \mathrm{CO_2} \quad (4)$$

The slurries for tape-casting were prepared by mixing powders (Table I), solvent (60 vol% toluene −40% ethanol), binder (poly(vinyl butyral)) and plasticizer (di-*n*-butyl phthalate) using a ball mill for 2 h. The tape-cast sheets with a thickness of about 0.1 mm were cut, laminated and pressed at 80°C and 50 MPa for 3 min to form green compacts with a thickness of about 2 mm.

TABLE I Powder mixtures for the preparation of specimens

Preparation method		Template particles	Matrix particles
OCAP		SBT-pl(S)	
TGG	TGG(b)	SBT-pl(L)	SBT-eq(S)
	TGG(s)	SBT-pl(S)	SBT-eq(L)
RTGG	SR	SBT-pl(S)	$SrCO_3 + Bi_2O_3 + TiO_2$
	BR	BIT	$SrCO_3 + Bi_2O_3 + TiO_2$

The compacts were further cut into small pieces (10 × 10 mm).

The green compacts were heated in an oxygen atmosphere to 700°C and kept for 2 h to burn-out organic ingredients and then subjected to cold isostatic pressing (CIP) at 98 MPa for 2 min to increase green density. The compacts were then sintered at various temperatures between 1000 and 1200°C for various durations.

The crystalline phases and the texture development were evaluated by X-ray diffraction (XRD) analysis using Cu K_α radiation on the major surface of the specimens. The Lotgering's F value was used to evaluate the texture [14]; the intensities of the diffraction lines between $2\theta = 20^\circ$ and 60° were used for the calculation. The microstructure was observed at a fractured, side face with a scanning electron microscope (SEM). The density was measured by the Archimedes method. The theoretical density of 7.448 g/cm^3 was used to calculate the relative density [15].

3. Results and discussion

3.1. Texture development and densification

Fig. 2 shows the F value of the various specimens sintered at temperatures between 1000 and 1200°C for 2 h and at 1200°C for 10 h. The OCAP and SR specimens had the F value of about unity at 1000°C and above, whereas the F value of the TGG(b) and BR specimens was small at 1000°C and increased as the sintering temperature and time were increased. Actually, no texture was formed in the TGG(s) specimens. All specimens except for TGG(s) had the F value of more than 0.9 by sintering at 1200°C for 10 h. The effects of processing method on the F value will be discussed after examining the microstructures.

Fig. 3 shows the density of sintered specimens shown in Fig. 2. The density of all specimens except for TGG(b) and TGG(s) was small even at 1200°C (less than 80% of theoretical). The density of the TGG(b) and TGG(s) specimens was small at 1000°C but increased as the sintering temperature increased and reached more than 90% at 1200°C. The effects of processing method on the density will be discussed after examining the microstructures.

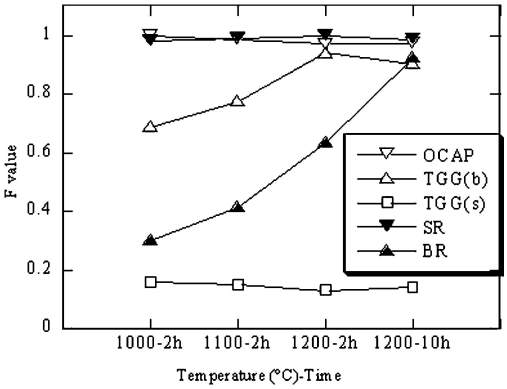

Figure 2 Effect of sintering conditions on the F value of the specimens made by various methods.

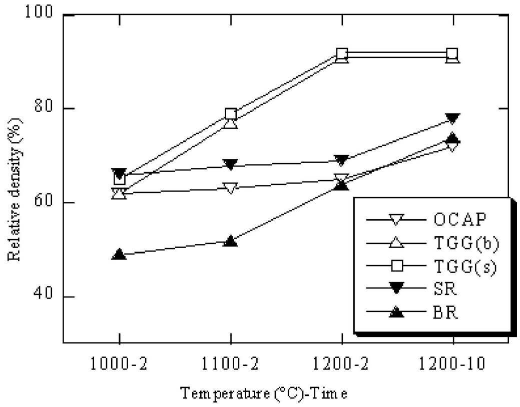

Figure 3 Effect of sintering conditions on the density of the specimens made by various methods.

3.2. Microstructure development

3.2.1. OCAP method

Fig. 4 shows the microstructures of the calcined and sintered OCAP specimens. Good alignment of platelike particles was observed in the calcined compact (Fig. 4a). The diameter and thickness of individual platelike particles increased by sintering (above 1000°C). Furthermore, the face-to-face contact between platelike particles developed above 1000°C, forming particle groups with no pores within them. The size of particle groups increased as the sintering temperature and time were increased, especially at 1200°C. We will call these particle groups as "colonies" [16]. Another microstructural characteristic was the presence of large pores between colonies.

The OCAP method makes the green compact with well-aligned SBT particles (Fig. 4a), which is the origin of a large F value in the sintered compacts (Fig. 2). The characteristics of the microstructure development are the formation of colonies and large pores between them, which are responsible for the low density (Fig. 3). The formation of face-to-face contact is caused by particle rearrangement, which is caused mainly by the rotation of platelike particles [17]. In this case, the rearrangement does not contribute to the densification of overall compact [18]. Pores in the green compact are accumulated adjacent to the colonies as shown in Fig. 4c. An increase in the size of colonies results in the formation of closed pores as shown in Fig. 4d. These pores grow by pore coalesce associated with the growth of colonies. The densification by the reduction of pore volume is slow because of large pore sizes. The particle rearrangement and pore coalescence are responsible for the slow densification between 1000 and 1200°C and at 1200°C, respectively.

3.2.2. TGG method

Fig. 5 shows the microstructures of the calcined and sintered TGG(b) specimens. The calcined compact was composed of aligned platelike particles and small equiaxed particles. Growth of platelike and matrix grains was evident in the specimens sintered at 1000°C and above. The platelike grains thickened and the matrix grains grew to be platelike. The specimen sintered

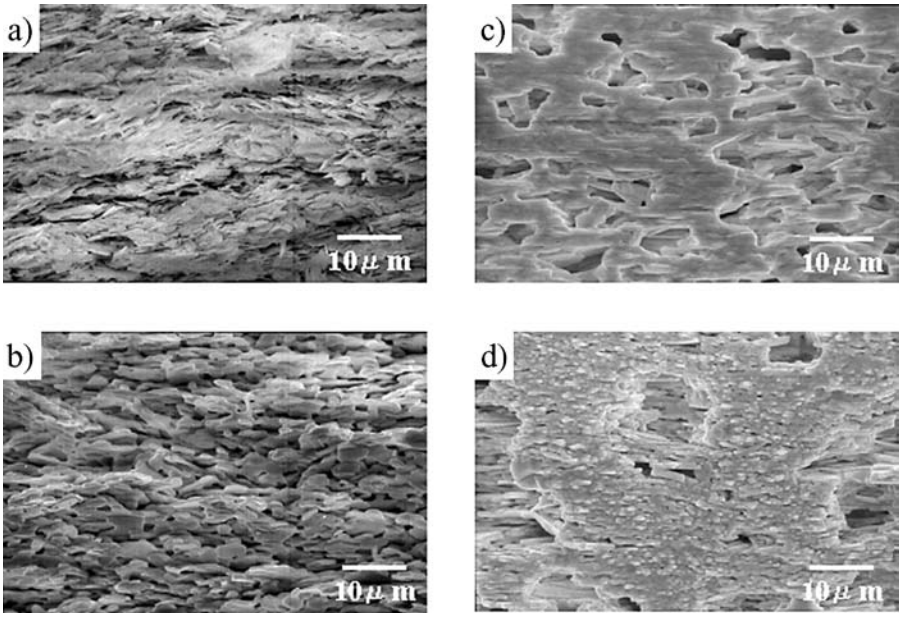

Figure 4 Microstructures of OCAP specimens heated at (a) 700, (b) 1000, and (c) 1200°C for 2 h and (d) at 1200°C for 10 h.

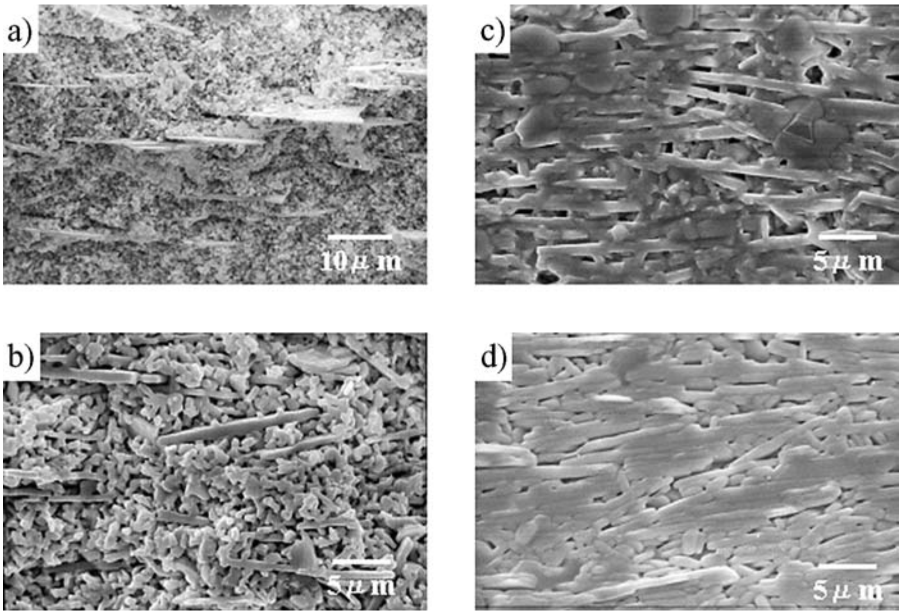

Figure 5 Microstructures of TGG(b) specimens heated at (a) 700, (b) 1000 and (c) 1200°C for 2 h and (d) at 1200°C for 10 h.

at 1200°C for 10 h was composed of two regions; one was the colony-like region containing several aligned platelike grains and another was the region containing small grains with the small aspect ratios. Large pores were not present in the microstructure.

The green compact (Fig. 5a) of the TGG(b) specimen is composed of platelike and small equiaxed particles. The *F* value of the TGG(b) specimen sintered at 1000°C for 2 h was 0.65 and increased as the sintering temperature was increased (Fig. 2), for which the growth of aligned platelike grains at the expense of small matrix particles is responsible (Figs 5b and c). The small equiaxed particles prevent the formation of face-to-face contact between platelike grains and the colonies do not form extensively until the final stage. Therefore, large pores between large colonies (Fig. 4d) do not form and the density of the compact reaches more than 90% of the theoretical at 1200°C. A wedge-like shape of pores between platelike grains with slightly misalignment (Fig. 5d) is stable as compared to pores with a spherical shape because of low surfaced energy and is responsible for the low densification rate at 1200°C.

Fig. 6 shows the calcined and sintered TGG(s) specimens. The platelike particles were aligned in the calcined compact, but extensive grain alignment was not observed in the sintered compact, resulting in a small F value (Fig. 2). The specimen sintered at 1200°C for 10 h was composed of platelike grains smaller than those in TGG(b).

The growth of template grains at the expense of matrix grains is most important for the texture development by the TGG method and the driving force of grain growth is the difference in the grain size. In the TGG(b) specimen, the difference between sizes of

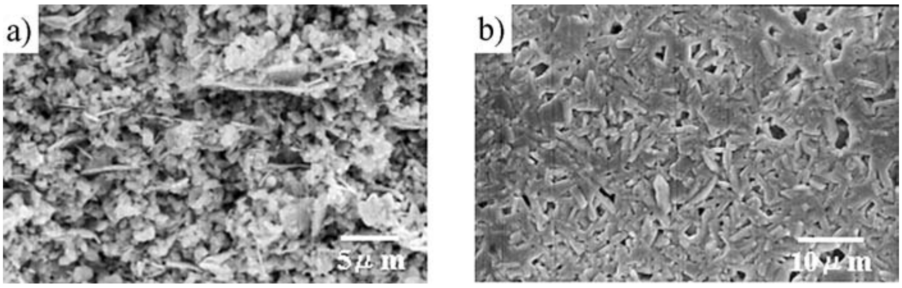

Figure 6 Microstructures of TGG(s) specimens heated (a) at 700°C for 2 h and (b) at 1200°C for 10 h.

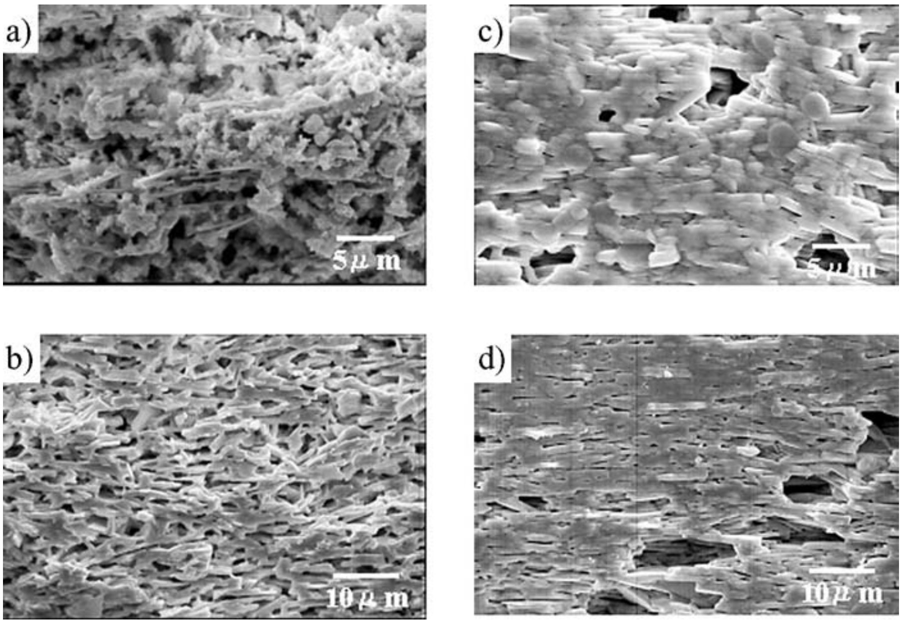

Figure 7 Microstructures of SR specimens heated at (a) 700, (b) 1000, and (c) 1200°C for 2 h and (d) at 1200°C for 10 h.

platelike and matrix grains is large, resulting in the preferential growth of platelike grain (Figs 5b and c), which is responsible for an increase in the F value. In the TGG(s) specimen, on the other hand, the size difference is not large enough to promote the preferential growth of platelike grains and matrix grains have a chance to grow. As SBT grains tend to grow to be platelike [1], the microstructure at 1200°C is composed of platelike grains with mostly random orientation (Fig. 6b). The mechanism of the formation of face-to-face contact does not operate in the course of microstructure development and therefore, there are no large pores between colonies and the density reaches more than 90% at 1200°C.

3.2.3. RTGG method

Fig. 7 shows the microstructures of the calcined and sintered SR specimens. Because the SBT formation reaction was completed between 900 and 950°C as confirmed by XRD, the matrix particles in the calcined specimen (Fig. 7a) was the mixture of starting materials ($SrCO_3$, Bi_2O_3 and TiO_2) and intermediate compounds [1]. The specimen sintered at 1000°C was composed of aligned platelike SBT grains and these grains grew at high temperatures. The microstructure development above 1100°C was similar to that of the OCAP specimen; the colonies developed extensively at 1200°C and large pores formed between colonies.

The SR specimen has a similar F value and density to those of the OCAP specimen (Figs 2 and 3). The origin of the similarity is attributed to the microstructure at 1000°C. There are two possibilities for the formation of this microstructure; the SBT formation reaction in the matrix occurs on the surface of the platelike SBT particles and newly formed SBT contributes to the growth of preexisting platelike SBT particles, or newly formed SBT particles have a platelike shape and the preexisting platelike particles restrict the growth direction of newly formed, platelike particles to form parallel arrangement. The specimen containing platelike $BaBi_4Ti_4O_{15}$ particles as template particles instead of platelike SBT was prepared to determine which mechanism had operated. Fig. 8 shows the microstructure of the specimen containing platelike $BaBi_4Ti_4O_{15}$ and raw materials for SBT as template and matrix particles, respectively, sintered at 1000°C for 2 h. If the latter mechanism were operative in this specimen, the microstructure similar to Fig. 7b would be obtained but the result was not the case; the specimen shown in Fig. 8 is composed of platelike particles and small equiaxed particles. The former is $BaBi_4Ti_4O_{15}$ and the latter is newly formed SBT. This evidence indicates that the platelike particles in Fig. 7b are formed by the addition of newly formed SBT to the preexisting template platelike particles.

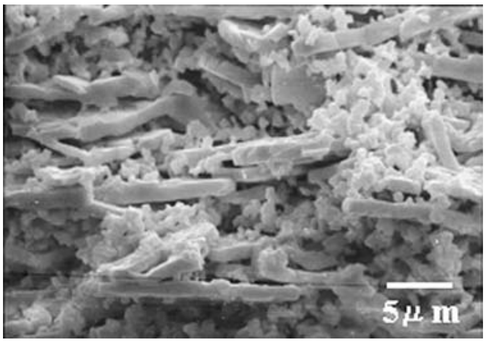

Figure 8 Microstructure of specimen containing platelike $BaBi_4Ti_4O_{15}$ and raw materials for SBT, sintered at 1000°C for 2 h.

There are only platelike particles after the completion of the SBT formation reaction as shown in Fig. 7b and the particle alignment is determined by the templated platelike particles, resulting in a large F value at 1000°C. The microstructure development above 1100°C is similar to that of the OCAP specimen and the characteristics are the formation of large colonies and large pores between them, which are responsible for the low sintered density (Fig. 3). The difference between the SR and TGG(b) specimens is the lack of matrix particles in the SR specimen after the SBT formation; the raw materials for SBT do not form small equiaxed SBT particles, which prevent the formation of face-to-face contact, resulting in the formation of large pores between colonies.

Fig. 9 shows the microstructures of the calcined and sintered BR specimens. The SBT formation reaction was completed at 950°C in this compact and therefore, the compact calcined at 700°C was composed of platelike BIT and the mixture of starting materials and intermediate compounds [1]. The specimen sintered at 1000°C for 2 h was composed of SBT. In this case, the equiaxed grains existed between platelike grains (Fig. 9b), whereas almost all grains were platelike in the SR specimen at 1000°C (Fig. 7b). Grains grew at high temperatures but the aspect ratio of grains was small. The colonies developed in the specimen sintered at 1200°C for 10 h, but the sizes of colonies and pores between colonies were smaller than those of the SR specimen.

Two kinds of SBT formation reaction (Equations 1 and 2) occurs in the BR specimen. In the SR specimen, reaction 1 contributes to the growth of platelike template particles. In the BR specimen, however, reactions 1 and 2 occur at almost the same time and reaction 1 does not contribute to the formation of platelike SBT particles, although platelike SBT particles form by reaction 2. If SrO and TiO_2 diffuse into BIT in reaction 2, aligned, platelike SBT particles are expected to form (reaction 2-a). If the SBT formation reaction occurs out of platelike BIT particles, the equiaxed SBT with no orientation relation to BIT forms (reaction 2-b). The microstructure at 1000°C (Fig. 9b) indicates the particles are almost equiaxed and a small number of platelike particles is present. This observation agrees with a small F value (Fig. 2). Both reaction 2-a and -b might be occurred. The platelike grains have larger size than the matrix grains at 1000°C and the former grains grow preferentially at high temperatures, as evidenced by an increase in the F value (Fig. 2) and alignment of platelike grains (Fig. 8d). Extensive colony formation is not observed up to 1200°C for 2 h and large pores between large colonies do not present in the BR specimen, resulting in an increase in the sintered density with an increase in the sintering temperature and soaking time (Fig. 3).

The lower density of the BR specimen than that of the SR specimen was caused by the lower density at 1000°C (Fig. 3). The RTGG method has an inherent disadvantage; the compound formation reaction in a compact sometimes reduces the green density of the compact before sintering. The RTGG method uses CIP after calcination to increase green density to overcome this disadvantage. However, the CIP conditions were

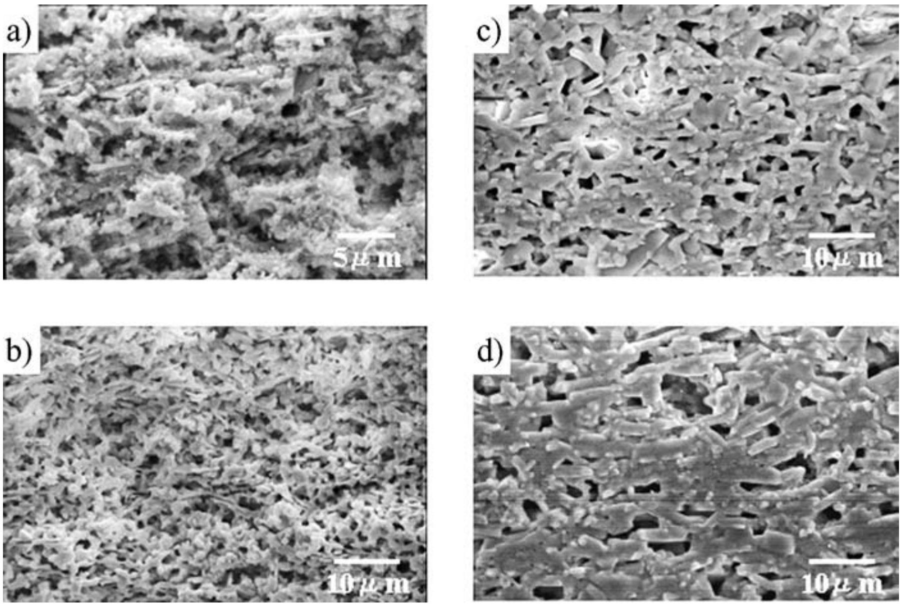

Figure 9 Microstructures of BR specimens heated at (a) 700, (b) 1000, and (c) 1200°C for 2 h and (d) at 1200°C for 10 h.

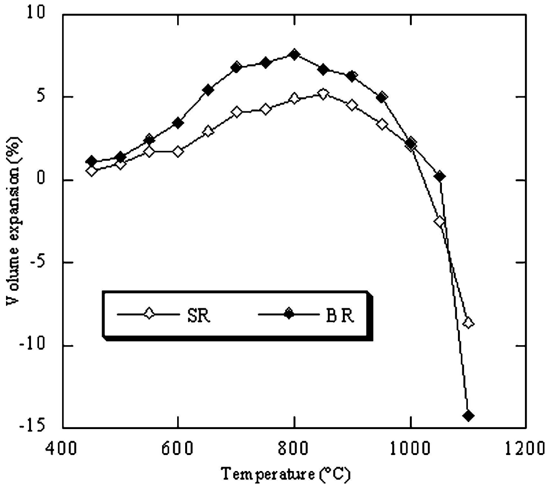

Figure 10 Volume expansion of SR and BR specimens heated at the constant rate of 200°C/h.

not suitable for the BR specimen as judged from the low density at 1000°C (Fig. 3).

The two origins are possible for the low density of the green compacts made by the RTGG method; in the present case, the SBT formation reaction causes a decrease in solid volume and the expansion of compact. The formation of SBT by reactions 3 and 4 causes the reduction of solid volume by 12.7 and 14.7%, respectively, which increases the pore volume in the compact. The second origin is the expansion of compact. Fig. 10 shows the volume change in the SR and BR specimens. The compact expands rapidly between 500 and 700°C and slowly between 700 and 850°C. The BR specimen has a larger degree of expansion than the SR specimen. These two origins and the ineffective CIP procedure are responsible for the low density of the BR specimen.

4. Conclusions

The textured SBT bulk ceramics were prepared by the OCAP, TGG and RTGG methods and the effects of processing methods on the texture development and densification were examined. All methods gave the specimens with extensive texture, except for the specimen prepared by the TGG method using small platelike SBT and relatively large matrix SBT particles. The sintered density was strongly dependent on the preparation method. The TGG method gave the specimen with the highest density. The platelike grains had a tendency to form colonies, in which platelike grains contacted face-to-face. The formation of large pores between colonies was responsible for the low sintered density in the specimens prepared by the OCAP and RTGG methods. These findings draw the conclusion that the TGG method using large platelike and small matrix powders is the best method to obtain dense, highly-textured SBT ceramics.

References

1. M. D. MAEDER, D. DAMJANOVIC, C. VOISARD and N. SETTER, *J. Mater. Res.* **17** (2002) 1376.
2. H. IGARASHI, K. MATSUNAGA, T. TANIAI and K. OKAZAKI, *Am. Ceram. Soc. Bull.* **57** (1978) 815.
3. T. TAKENAKA and K. SAKATA, *Jpn. J. Appl. Phys.* **19** (1980) 31.
4. S. SWARTZ, W. A. SCHULZE and J. V. BIGGERS, *Ferroelectrics* **38** (1981) 765.
5. J. A. HORN, S. C. ZHANG, U. SELVARAJ, G. L. MESSING and S. TROLIER -MCKINSTRY, *J. Am. Ceram. Soc.* **82** (1999) 921.
6. H. OGAWA, M. KIMURA, A. ANDO and Y. SAKABE, *Jpn. J. Appl. Phys.* **40**(Part I) (2001) 5715.
7. M. GRANAHAN, M. HOLMES, W. A. SHULZE and R. E. NEWNHAM, *J. Am. Ceram. Soc.* **64** (1981) C-68.
8. H. WATANABE, T. KIMURA and T. YAMAGUCHI, *ibid.* **72** (1989) 289.
9. K. HIRAO, M. OHASHI, M. E. BRITO and S. KANZAKI, *ibid.* **78** (1995) 1687.
10. M. M. SEABAUGH, I. H. KERSCHT and G. L. MESSING, *ibid.* **80** (1997) 1181.
11. T. TANI, *J. Korean Phys. Soc.* **32** (1998) S1217.
12. T. TAKEUCHI, T. TANI and Y. SAITO, *Jpn. J. Appl. Phys.* **38**(Part I) (1999) 5553.
13. T. KIMURA and T. YAMAGUCHI, *Ceram. Int.* **9** (1983) 13.
14. F. K. LOTGERING, *J. Inorg. Nucl. Chem.* **9** (1959) 113.
15. JCPDS File No. 43-973.
16. H. WATANABE, T. KIMURA and T. YAMAGUCHI, *J. Am. Ceram. Soc.* **74** (1991) 139.
17. G. PETZOW and H. E. EXNER, *Z. Metallkde.* **67** (1976) 611.
18. Y. INOUE, T. KIMURA and T. YAMAGUCHI, *Am. Ceram. Soc. Bull.* **62** (1983) 704.

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