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Preparation of crystallographically textured $Bi_{0.5}Na_{0.5}TiO_3$–$BaTiO_3$ ceramics by reactive-templated grain growth method

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Abstract

Crystallographically textured ferroelectric and piezoelectric ceramics are prepared by tape casting of slurries containing powder particles with shape anisotropy. This paper describes the overview of these methods and the application of reactive-templated grain growth (RTGG) method to $\langle 1\,0\,0 \rangle$-textured $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) and $96Bi_{0.5}Na_{0.5}TiO_3$–$6BaTiO_3$ (BNT-BT) ceramics.

Keywords: A. Grain growth; Texture; Grain orientation; Template; Ferroelectrics; Piezoelectrics

1. Introduction

The electrical properties of polycrystalline ceramics are determined not only by the composition and crystal structure of the phase(s) present but also by the microstructure. Therefore, the control of microstructure is very important to obtain ceramics with better performances [1]. An introduction of crystallographic texture into sintered ceramics is one of the techniques to control the microstructure. In a crystallographically textured ceramic, a specific crystal axis of individual grains is aligned in one direction, and high electrical properties are expected.

This paper describes the fabrication of ferroelectric and piezoelectric ceramics with crystallographically textured from powder particles with shape anisotropy. In the first half of this paper, we give an overview of the preparation methods, namely, the oriented consolidation of anisotropic particles (OCAP), templated grain growth (TGG), and reactive-templated grain growth (RTGG) methods, using data mainly obtained in our laboratory. The latter half of this paper deals with the application of RTGG method to $\langle 1\,0\,0 \rangle$-textured $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) and $94Bi_{0.5}Na_{0.5}TiO_3$–$6BaTiO_3$ (BNT-BT) ceramics.

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2. Preparation and characterization methods

The tape casting is one of the most convenient methods to align particles with shape anisotropy in green compacts [2]. The particles with shape anisotropy are prepared, for example, by molten salt synthesis [3]. The slurry for tape casting is prepared by a usual method, i.e., by mixing powder(s), solvent, binder, plasticizer, and other ingredients. When the slurry passes under the doctor blade, interaction between particles aligns the particles with their plate face parallel to a cast sheet for plate-like particles and with their long axis parallel to the casting direction for needle-like particles [4,5]. Because the particle shape is determined by the crystal structure, a certain crystal axis is aligned in a specific direction. The cast sheets are cut, laminated, and pressed to prepare a green compact with a desired shape. The green compact is heated at about 500 °C for binder burn-out, then at high temperatures for sintering. During sintering, the degree of orientation increases as a result of particle rearrangement and grain growth. Thus, highly textured ceramics are obtained.

This method is divided into three groups based on the formulation of starting mixture. One method uses only particles with shape anisotropy as the solid ingredient [2,6]. We will call this method “oriented consolidation of anisotropic particles (OCAP) method.” Recently, this method is modified to TGG [7] and RTGG methods [8]. The TGG method

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uses the mixture of particles with shape anisotropy and equiaxed particles with the same composition or the same crystal structure. The RTGG method uses the mixture of precursor particles with shape anisotropy and equiaxed particles that react with the precursor to form the object material.

The application of OCAP and TGG methods is limited to the material with low symmetry; the particles with shape anisotropy are hardly obtained for compounds with high symmetry, because the anisotropy in the growth direction during the preparation is necessary to form an anisotropic shape. The RTGG method enables the preparation of the textured ceramics, for which the formation of particles with an anisotropic shape is difficult such as compounds with the regular perovskite structure.

Important structural properties of textured ceramics are the degree of orientation as well as sintered density and grain size, which are determined by ordinary methods. The most convenient method to determine the degree of orientation is the Lotgering method [9]. This paper uses the degree of orientation measured by this method.

3. Characteristics of ceramics obtained by OCAP method

Ceramics with a fairly large degree of orientation have been prepared by the OCAP method, but the problem was the sintered density [6]. Fig. 1 shows the sintered density of the $Bi_4Ti_3O_{12}$ compacts prepared by the OCAP method. Two salt systems, NaCl–KCl and Li_2SO_4–Na_2SO_4, were used in the preparation of plate-like $Bi_4Ti_3O_{12}$ particles. The sintered density was small for the compact of plate-like particles prepared using chloride salt, although it had a larger degree of orientation than the compact of plate-like particles prepared using sulfate salt.

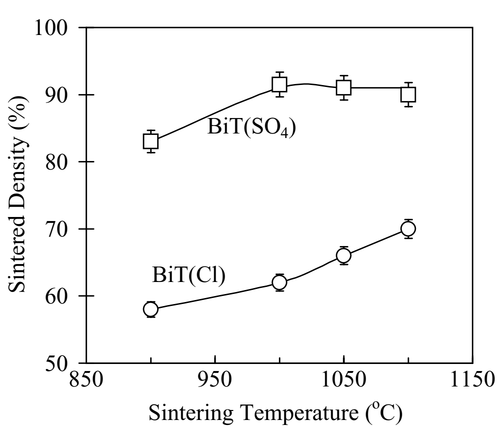

Fig. 1. Sintered density of textured $Bi_4Ti_3O_{12}$ (BiT) compacts prepared by OCAP method using plate-like BiT powders prepared by molten salt synthesis using NaCl–KCl and Li_2SO_4–K_2SO_4. BiT(Cl) and BiT(SO_4) indicate the compacts of plate-like BiT made using chloride and sulfate salt, respectively.

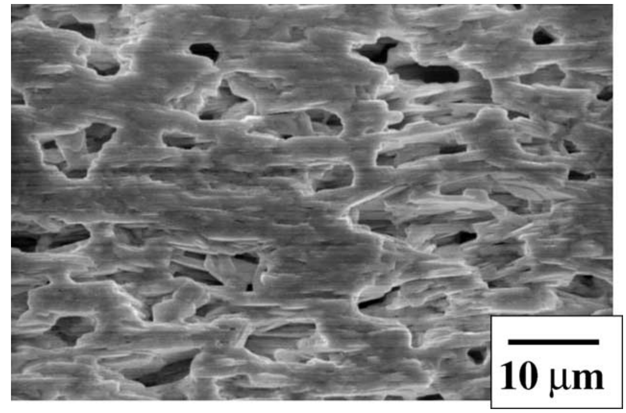

Fig. 2. Microstructure of $SrBi_4Ti_4O_{15}$ ceramics prepared by OCAP method at 1200 °C for 2 h.

Fig. 2 shows the microstructure of sintered $SrBi_4Ti_4O_{15}$ compact from plate-like particles prepared using KCl salt. The relative density of this compact was 65% and contained a large number of pores. Plate-like $Bi_4Ti_3O_{12}$ particles prepared using chloride salt (Fig. 1, BiT(Cl)) gave the same microstructure. The pores were formed by the rearrangement of plate-like particles to develop face-to-face contact and were difficult to be eliminated because of their large sizes.

The methods to increase the sintered density of compact containing plate-like particles are (1) to use plate-like particles with a small extent of particle rearrangement, and (2) to add small equiaxed particles to the plate-like particles (TGG method). Fig. 1 includes the sintered density of $Bi_4Ti_3O_{12}$ compact of plate-like particles prepared using sulfate salt. These particles had a small tendency for particle rearrangement. Thus, dense, highly-textured $Bi_4Ti_3O_{12}$ ceramics was obtained [6].

4. Characteristics of ceramics obtained by TGG method

The TGG method uses the mixture of plate-like (or needle-like) and equiaxed particles as starting materials. The equiaxed particles fill the space between plate-like particles and suppress the particle rearrangement by avoiding the formation of face-to-face contact between plate-like particles. Fig. 3 shows the microstructure of sintered $SrBi_4Ti_4O_{15}$ compact prepared by the TGG method (template content = 20 vol.%). The large pores shown in Fig. 2 were not formed and a high sintered density (91% of theoretical) was attained.

The addition of equiaxed particles into the green compact reduces the volume fraction of aligned particles. Fig. 4 shows the degree of orientation in the $SrBi_4Ti_4O_{15}$ compact prepared by the OCAP and TGG method. The OCAP compact had a large degree of orientation even at low sintering temperatures. The degree of orientation of the TGG compact was small at low sintering temperatures because of the

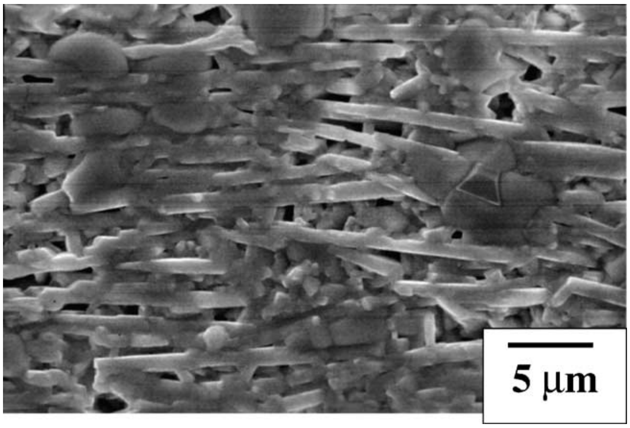

Fig. 3. Microstructure of $SrBi_4Ti_4O_{15}$ ceramics prepared by TGG method at 1200 °C for 2 h.

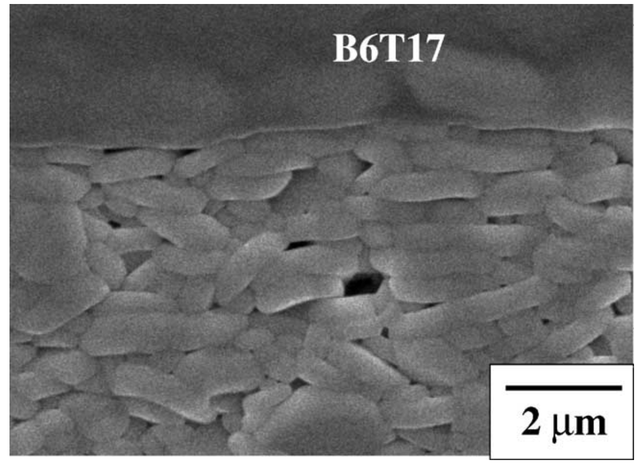

Fig. 5. Microstructure of $BaTi_4Ti_4O_{15}$–$Ba_6Ti_{17}O_{40}$ composite sintered at 1100 °C for 10 h.

presence of equiaxed, randomly oriented particles, but increased as the sintering temperature increased. The origin of the texture development was partly attributed to the growth of template grains at the expense of small equiaxed grains.

We found another origin in the texture development in the bismuth layer-structured ferroelectrics (BSLF) such as $Bi_4Ti_3O_{12}$ and $BaBi_4Ti_4O_{15}$. Plate-like $Ba_6Ti_{17}O_{40}$ particles gave the ⟨1 0 0⟩-texture in $BaBi_4Ti_4O_{15}$. Fig. 5 shows the microstructure of $BaBi_4Ti_4O_{15}$ specimen containing plate-like $Ba_6Ti_{17}O_{40}$ particles; a large grain at the top of the photograph is a plate-like $Ba_6Ti_{17}O_{40}$ particle and small grains are matrix $BaBi_4Ti_4O_{15}$ grains originally equiaxed. The matrix grains grew to be plate-like, but no growth of $Ba_6Ti_{17}O_{40}$ grains was observed. The origins of texture development are the growth of matrix $BaBi_4Ti_4O_{15}$ grains to be plate-like, the formation of face-to-face contact between $Ba_6Ti_{17}O_{40}$ and $BaBi_4Ti_4O_{15}$ grains and between $BaBi_4Ti_4O_{15}$ grains, and the steric hindrance of plate-like grains to the growth of matrix grains. Therefore, the growth of matrix grains as well as that of template grains is important to prepare highly textured ceramics by the TGG method.

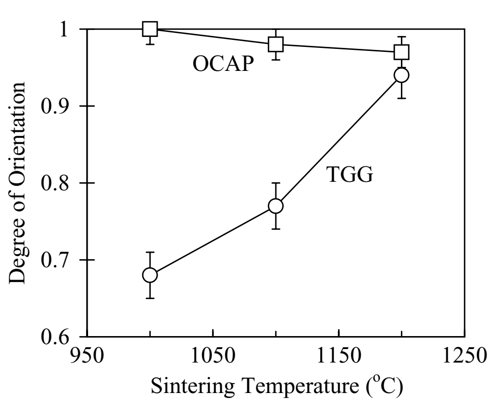

Fig. 4. Degree of orientation of the $SrBi_4Ti_4O_{15}$ ceramics made by OCAP and TGG methods, sintered at various temperature for 2 h.

The typical microstructure of textured BLSF ceramics is one shown in Fig. 3 (SBT), and the grain size is fairly uniform, although two kinds of particles with quite different sizes are present in a green compact. The growth rate of small grains is larger than that of large grains, resulting in uniform microstructure. In some compounds, however, compacts with duplex microstructure are obtained. Fig. 6 shows a typical microstructure. Fig. 7 shows the shapes of $BaBi_4Ti_4O_{15}$ (BBT) and $SrBi_4Ti_4O_{15}$ (SBT) used in the preparation of specimens shown in Figs. 6 and 3, respectively. Both particles have the plate-like shape, but the shape of plate face is rectangular and irregular for BBT and SBT, respectively, indicating that BBT and SBT have surface structure with atomically smooth and rough, respectively. In BBT, a large driving force for grain growth is necessary because of the smooth structure [10]. In this case, the driving force is the difference in grain size and only large grains have enough driving force for grain growth. Thus, the non-uniform microstructure develops as shown in Fig. 6.

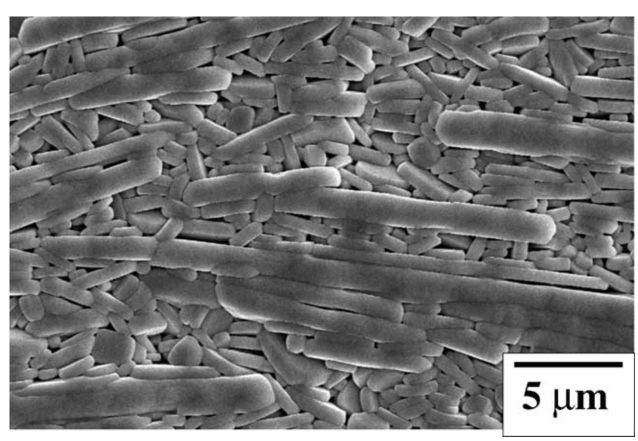

Fig. 6. Microstructure of $BaBi_4Ti_4O_{15}$ ceramics made by TGG method, sintered at 1130 °C for 5 h.

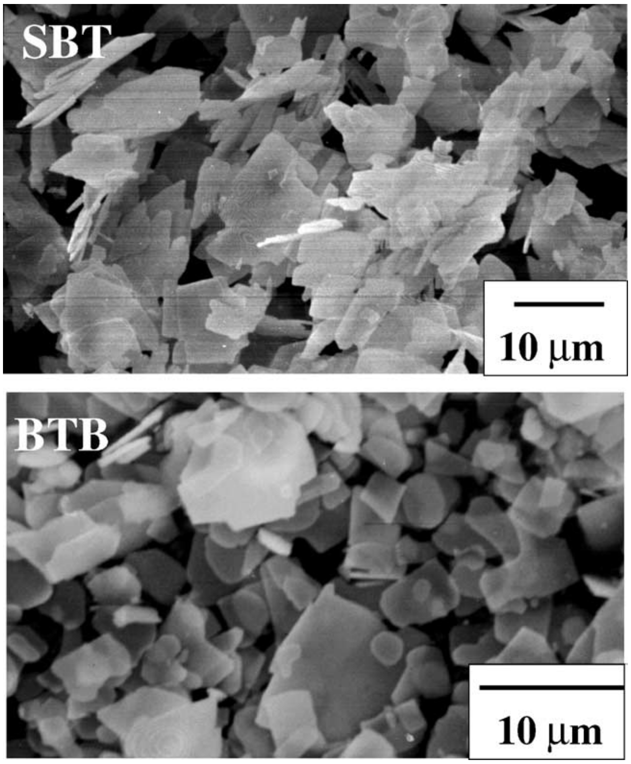

Fig. 7. Shape of plate-like $SrBi_4Ti_4O_{15}$ (SBT) and $BaBi_4Ti_4O_{15}$ (BBT) particles prepared by molten salt synthesis.

5. Characteristics of ceramics obtained by RTGG method

The OCAP and TGG methods are applicable only to the compounds with low symmetry. The RTGG method enables us to prepare textured ceramics for the compounds with high symmetry, such as regular perovskite structure. Here, the preparation method is described with using $Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}TiO_3$ (BNKT) as an example [11]. Plate-like $Bi_4Ti_3O_{12}$ (BiT) particles are used as template. The mixture of BiT, Na_2CO_3, K_2CO_3, TiO_2, and Bi_2O_3 is used as starting materials and the green compact contains aligned plate-like BiT dispersed in the other ingredients. Oriented (template) and randomly-oriented BNKT grains are formed after calcination, and the degree of orientation is increased during sintering by the growth of template BNKT grains at the expense of randomly-oriented grains. Thus, dense, highly textured BNKT ceramics are obtained [1].

Important points to obtain dense, highly textured ceramics are as follows.

(1) The design of reaction route. The precursor, which has an anisotropic shape and contains element(s) of the final composition, must be properly selected. In the case of BNKT, BiT is the suitable precursor because Na and K diffuse into BiT lattice to form template BNKT grains. When $Na_2Ti_3O_7$ and $K_2Ti_2O_{15}$ are used as precursors, the reaction with Bi_2O_3 does not form proper template grains [12]. Another example is found in the formation of textured BNKT-PZT solid solutions [13]. The diffusion of Zr in the BNKT lattice is slow compared to that of the other elements, and the elements constituting BNKT diffuse into PZT grain and template BNKT grains disappear in the PZT rich compositions. Therefore, the design for chemistry and reaction route is very important.

(2) Dispersion of powder particles in the slurry. The powder particles must be dispersed well in the slurry; otherwise, the particles with an anisotropic shape do not align by the doctor blade process. The slurry for tape casting inevitably contains several compounds, and unlike particles tend to form agglomerates in the slurry (heterocoagulation). Fig. 8 shows the microstructure of green compact containing plate-like $Ba_6Ti_{17}O_{40}$ and equiaxed $BaCO_3$ particles after binder burn-out [14]. When the plate-like particles are well dispersed, their side-faces are observed on the fracture surface of the specimen as shown in Fig. 8b. Fig. 8a shows the microstructure of the specimen with no dispersant; agglomerates containing $Ba_6Ti_{17}O_{40}$ and $BaCO_3$ are formed, and plate-like $Ba_6Ti_{17}O_{40}$ particles are not aligned properly.

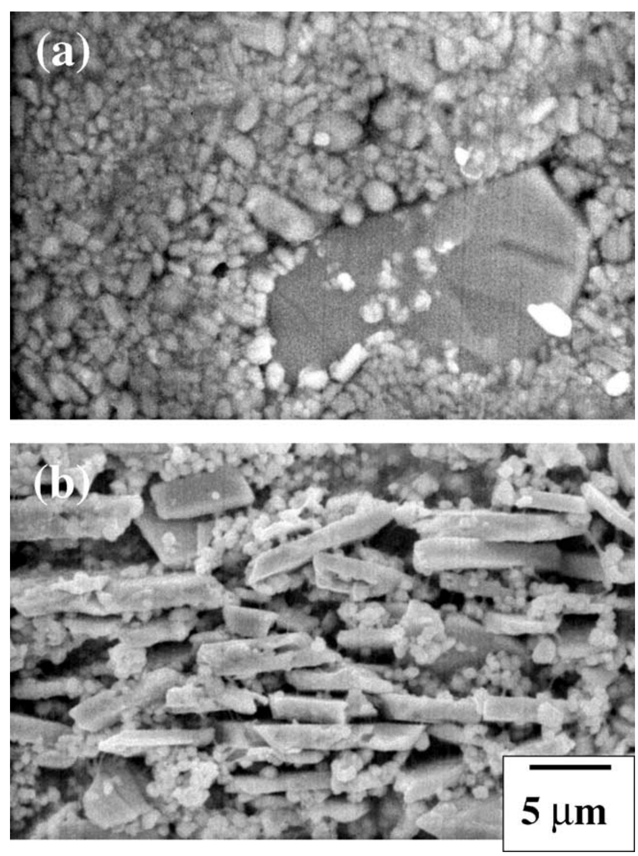

Fig. 8. Microstructures of green compact containing $Ba_6Ti_{17}O_{40}$ and $BaCO_3$ after binder burn-out. The observed face is perpendicular to the top surface. Alignment of plate-like $Ba_6Ti_{17}O_{40}$ particles is clearly observed in the compact (b) with dispersant. The compact (a) was prepared without dispersant.

(3) Control of relative growth rates of template and matrix grains. In the RTGG process, like in the TGG process, the growth of template grains at the expense of matrix grains is important to obtain highly textured ceramics. As the driving force of grain growth is the difference in the grain size, the growth behavior of matrix and template grains is important. The details will be described in the preparation of textured BNT ceramics.

6. Texture development in BNT ceramics I

BNT ceramics were prepared by the RTGG method for ⟨1 0 0⟩-texture, using plate-like BiT and other ingredients as starting materials [11]. The amount of plate-like BiT was designed so that 20% of titanium and 53.3% of bismuth in final BNT were supplied from plate-like BiT. The green compact was sintered at various temperatures for 2 h. The degree of orientation was 0.36 and 0.24 for the compacts sintered at 1100 and 1200 °C, respectively. These values were quite small as compared with BNKT, which had the degree of orientation of 0.63 and 0.79 for the specimens sintered at 1100 and 1200 °C, respectively.

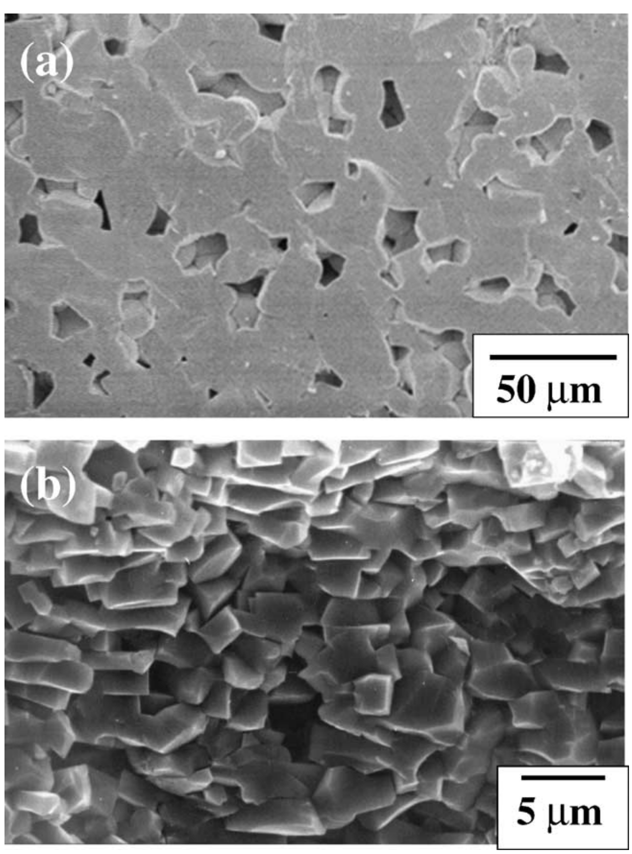

Fig. 9. Microstructures of textured (a) BNT and (b) BNKT specimens sintered at 1200 °C for 2 h.

Fig. 9 shows the microstructure of BNT and BNKT specimens sintered at 1200 °C for 2 h. The grain size was small for BNKT. In these specimens, the large, plate-like BN(K)T particles and small equiaxed particles (template and matrix grains, respectively) formed in the compacts calcined at 700 °C. In the BNKT specimen, small grain growth rate during sintering kept the size difference between template and matrix grains, resulting in the growth of template grains at the expense of matrix grains and the texture formation. In the BNT specimen, on the other hand, the size of matrix grain reach almost the same as that of template grains due to a large grain growth rate, and the condition of preferential growth of template grains was lost.

7. Texture development in BNT ceramics II

In the previous experiment, the amount of plate-like BiT particles was designed so that 20% of titanium and 53.3% of bismuth in final BNT were supplied from plate-like BiT (we call this specimen BNT(20)). If the BNT formation reaction from BiT is caused by the diffusion of Na and Bi into and out of BiT lattice, respectively, the volume fraction of template grains is 20% after the calcination stage. It is possible that an insufficient volume fraction of template grains prohibits their preferential growth. Therefore, the amount of plate-like BiT was increased in the initial formulation; 37.5% of titanium and 100% of bismuth were supplied from plate-like BiT (we call this specimen BNT(37.5)).

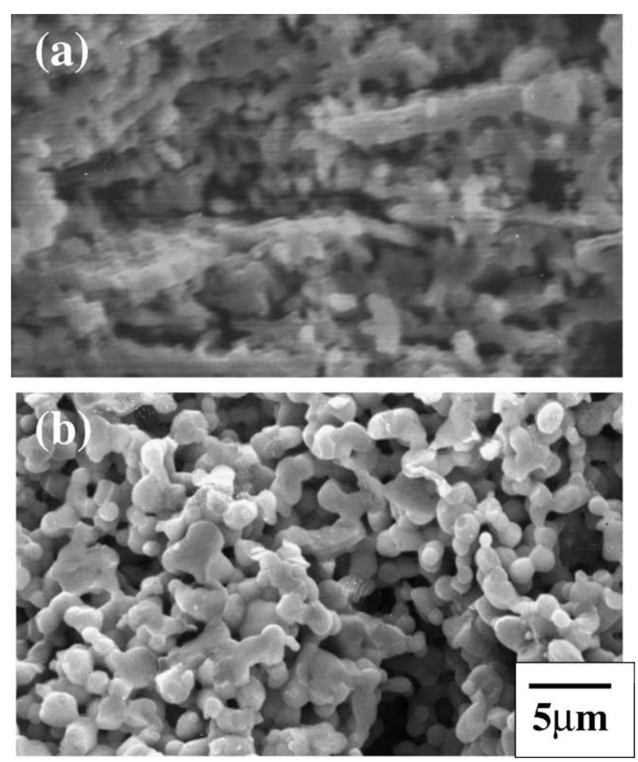

Fig. 10. Microstructures of the (a) BNT(37.5) and (b) BNT(20) specimens heated at 1000 °C for 2 h.

Table 1
Piezoelectric properties of textured and non-textured specimens sintered at 1200 °C for 10 h

	BNT			BNT-BT		
	Non-textured	Textured	Ratio	Non-textured	Textured	Ratio
Relative density (%)	94.0	93.9		98.8	92.5	
k_p	0.070	0.184	2.6	0.121	0.232	1.9
$-d_{31}$ (pm/V)	7.5	18.6	2.5	19.7	31.4	1.6
g_{31} ($\times 10^{-3}$, V m/N)	2.0	6.2	3.1	2.4	6.9	2.9

The textured BNT ceramics was obtained by increasing the amount of template grains; the degree of orientation was 0.7 in BNT(37.5) sintered at 1200 °C for 2 h, as compared to 0.24 in BNT(20) prepared under the same conditions. Fig. 10 shows the microstructures of two specimens sintered at 1000 °C for 2 h. At this temperature, the BNT formation reaction was completed. The grains with plate-like characteristics were observed in the BNT(37.5) specimen, but such grains were lost in the BNT(20) specimen. Furthermore, the grain size of BNT(20) was larger than that of the matrix grains of the BNT(37.5) specimen.

The growth rate of individual grain is expressed as

$$\frac{dR}{dt} = 2M_b\gamma_{gb}\left(\frac{1}{R^*} - \frac{1}{R}\right) \tag{1}$$

where R is grain size (radius), t is time, M_b and γ_{gb} are grain boundary mobility and energy, respectively, and R^* is the critical grain size. Therefore, any grain with $R > R^*$ has a chance to grow. In the BNT(20) specimen, R^* is mainly determined by the matrix grains because of a small volume fraction of template grains, and some matrix grains have R larger than R^* and have a chance to grow. In the BNT(37.5), on the other hand, both matrix and template grains determine the R^* value, and template grains have $R > R^*$ and matrix trains have $R < R^*$, resulting in the preferential growth of template grains and the texture development.

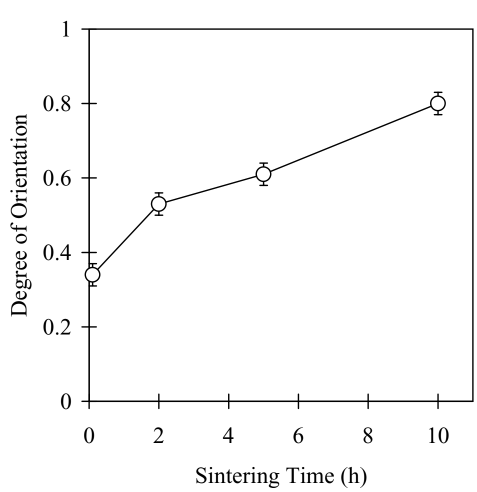

Fig. 11. The effect of soaking time on the degree of orientation for the BNT-BT specimen sintered at 1200 °C.

8. Texture development in BNT-BT ceramics

Large piezoelectric properties are expected for the 0.94BNT-0.06BT, because this composition lies on the morphotropic phase boundary. The textured BNT-BT ceramic was prepared by the RTGG process using a large amount of plate-like BiT. Fig. 11 shows the effect of soaking time on the degree of orientation; the ceramics with a large degree of orientation were obtained by sintering at 1200 °C for 10 h.

Table 1 shows the piezoelectric properties of textured BNT and BNT-BT specimens sintered at 1200 °C for 10 h together with those of non-textured specimens prepared by a conventional method. The textured specimen had larger piezoelectric coefficients than the non-textured specimen with the same composition.

9. Conclusions

Ferroelectric and piezoelectric ceramics are prepared by tape-casting of powder particles with shape anisotropy. The method is divided into three groups based on the formulation in the slurry. The OCAP and TGG method is applicable to the compounds, for which particles with shape anisotropy can be obtained. For the compounds with high symmetry such as perovskite, one of the methods is RTGG. The highly textured BNKT ceramics are obtained by using template grains originated by the reaction of plate-like BiT particles and other ingredients. In the BNT case, a large volume fraction of templated grains is necessary to make the condition of preferential growth for template grains. Thus, highly textured BNT and BNT-BT ceramics were prepared and these ceramics had larger piezoelectric properties than non-textured ceramics.

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