

Effect of Chemical Interaction on Texture Development in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ using $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ and $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$ Hetero-Templates

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Abstract

The hetero-templated grain growth method was applied to the development of texture in materials with the Aurivillius structure. When the template volume fraction was 0.20, the hetero-templated grain growth process developed texture in $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ (SBT) matrix grains based on plate-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT) template grains [the specimen is denoted as SBT/BiT(0.20)] but did not develop texture in BiT matrix grains based on plate-like SBT template grains [BiT/SBT(0.20)]. The origin of the lack of texture development in BiT/SBT(0.20) was examined from two points of view, namely, solid-state spreading and chemical reaction. Solid-state spreading is the main mechanism for texture development in some materials with the Aurivillius structure. At first, it was assumed that solid-state spreading was not operative in BiT/SBT(0.20), leading to the lack of texture development, but the occurrence of solid-state spreading was confirmed in both specimens. Therefore, this assumption was ruled out as a possible mechanism. Next, the possibility of a chemical reaction between SBT and BiT was examined and the formation of $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$ ($\text{S}_{0.5}\text{BT}$) was confirmed. This means that the template grains changed from SBT to $\text{S}_{0.5}\text{BT}$ in BiT/SBT(0.20). Therefore, texture development in the specimens with BiT matrix grains and plate-like $\text{S}_{0.5}\text{BT}$ template grains (BiT/ $\text{S}_{0.5}\text{BT}$) was examined, and it was found that an increase in the template volume fraction resulted in the suppression of texture development. SrTiO_3 in the template $\text{S}_{0.5}\text{BT}$ grains dissolved in BiT matrix grains and suppressed the growth and morphological change of the matrix grains, resulting in the suppression of texture development. It is therefore concluded that the dissolution of a high concentration of SrTiO_3 in BiT matrix grains from template grains is the origin of the lack of texture development in BiT/SBT(0.20) and in BiT/ $\text{S}_{0.5}\text{BT}$ with a large amount of template grains.

Keywords: Texture development, microstructure development, templated grain growth, bismuth titanate, strontium bismuth titanate

I. Introduction

Ferroelectric materials with the Aurivillius structure, often called bismuth layer-structured ferroelectrics (BLSFs), are one of the candidates for lead-free piezoelectric ceramics for high-temperature use¹. Because the crystal structure of BLSFs is highly anisotropic, the control of texture is important². The templated grain growth (TGG) process is one of the most convenient preparation methods for textured BLSF ceramics³⁻⁷. In this method, a green compact is made from a mixture of large, anisometric template grains and small, equiaxed matrix grains. The template grains are aligned in the green compact by methods such as tape-casting and extrusion. Dense, highly textured ceramics are obtained by sintering the green compact. The chemical species of the template grains can be either the same as or different from that of the matrix grains. In the latter case, the template is called a hetero-template.

One of the authors has been studying the mechanism of texture development in BLSFs using homo- and hetero-templates to find out the key processing parameters to obtain highly textured materials⁸⁻¹¹. It was found

that the combination of the chemical species of the matrix and template grains influenced the texture development⁸. For example, plate-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT) template grains could develop texture in the $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ (SBT) matrix, but plate-like SBT template grains could not develop texture in the BiT matrix. At that time, the reason for the effect of the chemical species of matrix and template grains on texture development was not known. Recently, it was found that solid-state spreading is one of the main mechanisms of texture development in materials with the Aurivillius structure¹². Furthermore, we found that the reaction between BiT and $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$ ($\text{S}_{0.5}\text{BT}$) occurs and influences the texture development in the BiT matrix using $\text{S}_{0.5}\text{BT}$ template grains¹³. These findings led us to re-examine the effect of the chemical species of matrix and template grains on the texture development in the BiT-SBT system.

II. Experimental Procedure

Reagent-grade SrCO_3 (Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan), Bi_2O_3 (Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan), and TiO_2 (Ishihara Sangyo Kaisha Ltd., Osaka, Japan) were used as starting

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materials. Plate-like BiT, $S_{0.5}$ BT, and SBT powders for the template grains were prepared by means of molten salt synthesis¹⁴. Stoichiometric mixtures of the starting materials were mixed with KCl having the same weight as the mixtures of the starting materials and heated at 1100 °C for BiT and $S_{0.5}$ BT and at 1200 °C for SBT. The soaking time was 2 h. The products were washed with deionized water about ten times. The obtained powders were all single-phase materials, as confirmed by X-ray diffraction analysis (XRD). Figs. 1a, 1b, and 1c show the scanning electron micrographs of the obtained powders. The grains had a plate-like shape and the plate faces were perpendicular to the crystallographic $\langle 001 \rangle$ direction¹⁵. Diameters were between 4 and 15 μm for BiT, between 2 and 12 μm for $S_{0.5}$ BT, and between 2 and 10 μm for SBT. Thicknesses were approximately 0.2 μm for BiT, 0.4 μm for $S_{0.5}$ BT, and 1.0 μm for SBT.

Equiaxed BiT and SBT powders for the matrix grains were prepared with the conventional solid-state method. Stoichiometric mixtures of starting materials were calcined at 750 °C for BiT and at 950 °C for SBT. The soaking time was 1 h for BiT and 2 h for SBT. The calcined powders were ball-milled for 2 h using ZrO_2 balls with a diameter of 15 mm, and then ball-milled for an additional 24 h using ZrO_2 balls with a diameter of 2 mm. The obtained powders were single-phase BiT and SBT, as confirmed by XRD. Figs. 1d and 1e show the scanning electron micrographs of the obtained powders. The majority of the grains were equiaxed in shape, but some plate-like grains with aspect ratios between 2 and 3 were present. Most of the grains were between 0.2 and 0.8 μm in size for BiT and between 0.2 and 1.0 μm for SBT.

Green compacts were prepared by means of tape-casting¹⁶. Slurries for tape-casting were prepared by mixing the matrix and template powders, a solvent (60 vol% toluene, 40 vol% ethanol), a binder (poly (vinyl butyral)), and a plasticizer (di-n-butyl phthalate) and by ball-milling for 2 h. The slurries were tape-cast to form sheets in which

the template grains were aligned with their plate faces parallel to the sheet surface. The sheets were cut into smaller sheets 30 \times 30 mm. The small sheets were laminated and pressed in a die at 80 °C and 50 MPa for 3 min to form compacts with thicknesses of approximately 2 mm. The compacts were further cut into small pieces (10 \times 10 mm) and used for the sintering experiment. The small pieces were heated at 500 °C for 2 h to burn out the binder and then sintered at various temperatures for 2 h in air (the heating rate was 100 °C/h).

The crystalline phases and the degree of orientation were evaluated by means of XRD (D8 ADVANCE, Bruker AXS, Karlsruhe, Germany) using $\text{CuK}\alpha$ radiation on the major surface (which is the same as the sheet surface) of the sintered specimens. The degree of orientation was evaluated with the Lotgering F value using the diffraction lines between $2\theta = 20^\circ$ and 60° ; $F = 1$ and 0 indicate that the compacts are perfectly textured and randomly oriented, respectively¹⁷. The microstructure of fractured and thermally etched sections perpendicular to the major surface was observed with a field-emission scanning electron microscope (Model S-4700, Hitachi, Tokyo, Japan). For some specimens, the surfaces were polished and thermally etched. The density was measured with the Archimedes method using water as the immersion medium, and the relative density was calculated from the theoretical densities of BiT, $S_{0.5}$ BT, and SBT, assuming that no chemical reaction had occurred. The theoretical densities of BiT, $S_{0.5}$ BT, and SBT were 8.045, 7.680, and 7.448 g/cm^3 , respectively^{18–20}.

The specimens are denoted using the format “matrix species/template species”. The volume fraction of the template grains is indicated in parentheses behind the specimen’s name. For example, BiT/SBT(0.10) indicates that the matrix and template are BiT and SBT, respectively, and the volume fraction of SBT is 0.10. The list of prepared specimens and their overall composition based on the binary BiT-SrTiO₃ system is shown in Table 1.

Table 1: Chemical species of matrix and template grains and composition (template volume fraction and overall composition in the binary BiT-ST system).

Specimen name	Matrix	Template	Template volume fraction	Overall composition x in (1-x)BiT-xST
SBT/BiT(0.20)	SBT	BiT	0.20	0.433
BiT/SBT(0.20)	BiT	SBT	0.20	0.144
BiT/ $S_{0.5}$ BT(0.00)	BiT	$S_{0.5}$ BT	0.00	0.000
BiT/ $S_{0.5}$ BT(0.05)	BiT	$S_{0.5}$ BT	0.05	0.022
BiT/ $S_{0.5}$ BT(0.075)	BiT	$S_{0.5}$ BT	0.075	0.033
BiT/ $S_{0.5}$ BT(0.10)	BiT	$S_{0.5}$ BT	0.10	0.043
BiT/ $S_{0.5}$ BT(0.20)	BiT	$S_{0.5}$ BT	0.20	0.091

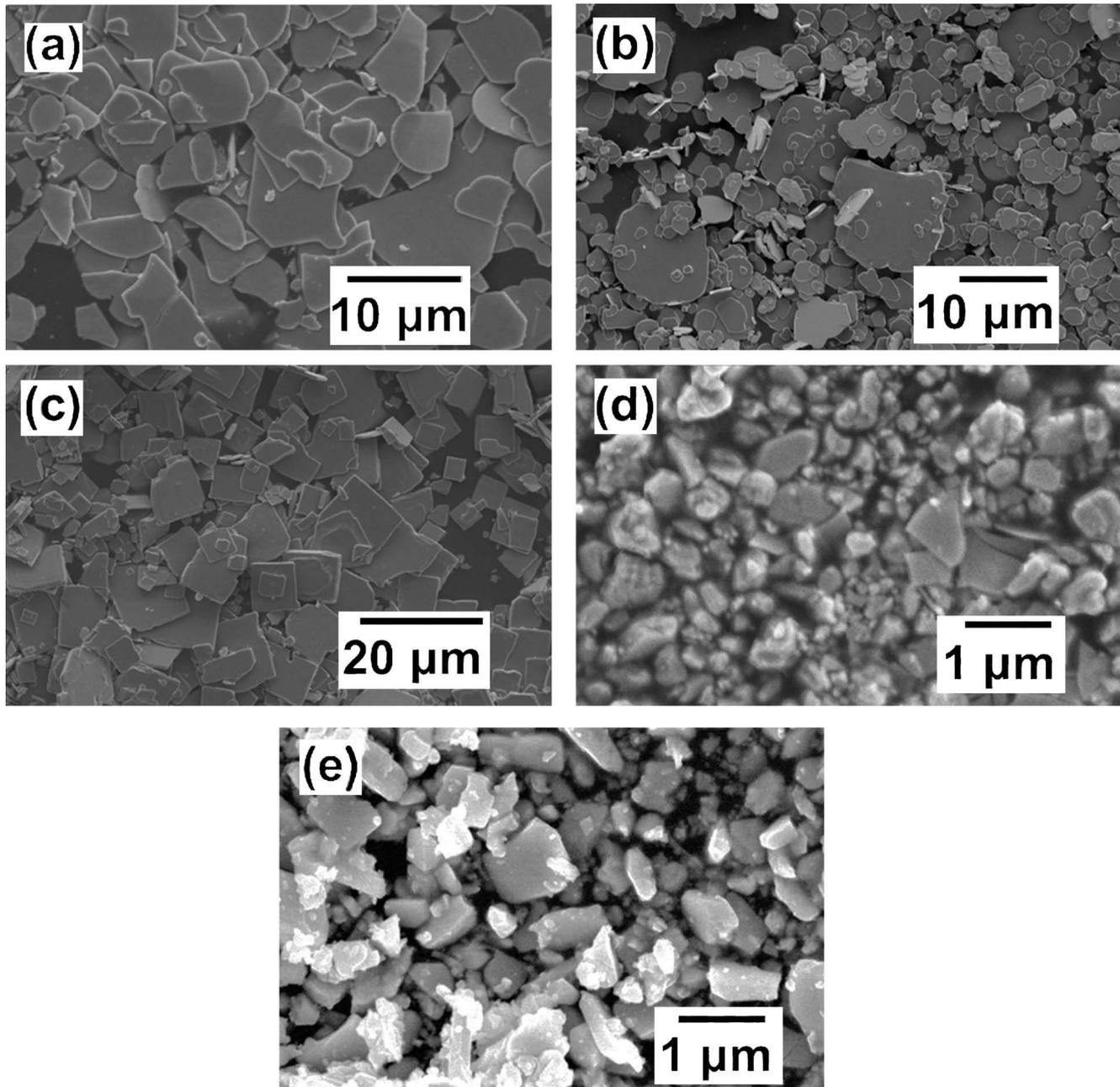


Fig. 1 Scanning electron micrographs of (a) BiT, (b) $\text{S}_{0.5}\text{BT}$, and (c) SBT powders prepared by molten salt synthesis and (d) BiT and (e) SBT powders prepared by solid-state reaction.

III. Results and Discussion

(1) Texture development in SBT/BiT and BiT/SBT specimens

SBT/BiT(0.20) was sintered at 1000 °C, 1100 °C, and 1200 °C for 2 h and at 1200 °C for 10 h; BiT/SBT(0.20) was sintered at 1000 °C, 1100 °C, and 1150 °C for 2 h and at 1150 °C for 10 h. The reason why BiT/SBT(0.20) was not sintered at 1200 °C was that a liquid phase formed in this specimen at 1200 °C. The difference in the overall composition (Table 1) is responsible for the difference in the formation temperature of a liquid phase. Fig. 2 shows the XRD patterns of SBT/BiT(0.20) sintered at 1000 °C for 2 h and at 1200 °C for 10 h and BiT/SBT(0.20) sintered at 1000 °C for 2 h and at 1150 °C for 10 h. The develop-

ment of texture can be judged from the relative intensity of the diffraction line at $2\theta \approx 40^\circ$, marked by asterisks. In the SBT/BiT(0.20) case, the relative intensity increased as the sintering temperature increased to 1200 °C (from Fig. 2a to Fig. 2b), whereas the relative intensity decreased for BiT/SBT(0.20) at 1150 °C (from Fig. 2c to Fig. 2d). This indicated that the texture developed in SBT/BiT(0.20) but did not develop in BiT/SBT(0.20). Fig. 3 shows the effect of sintering temperature on the degree of orientation. The degree of orientation of SBT/BiT(0.20) sintered for 2 h increased from 0.37 at 1000 °C to 0.60 at 1200 °C, and the degree of orientation reached 0.87 on sintering at 1200 °C for 10 h. In BiT/SBT(0.20), on the other hand, the degree of orientation decreased from 0.32 at 1100 °C to 0.05 at 1150 °C, and prolonged heating for 10 h at 1150 °C did not

increase the degree of orientation; the F value was 0.06. The reason for these behaviors was examined based on the microstructures of the specimens sintered in various conditions (Figs. 4 and 5).

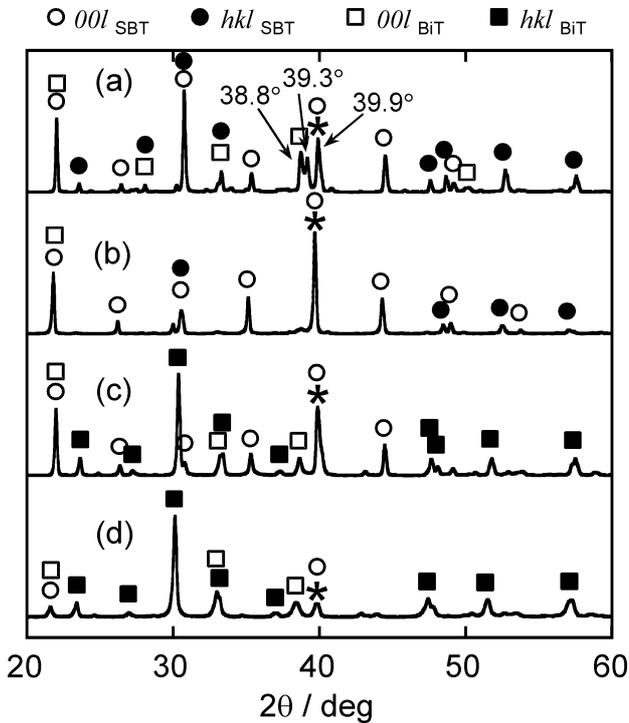


Fig. 2 X-ray diffraction patterns of SBT/BiT(0.20) sintered (a) at 1000 °C for 2 h and (b) at 1200 °C for 10 h and BiT/SBT(0.20) sintered (c) at 1000 °C for 2 h and (d) at 1150 °C for 10 h.

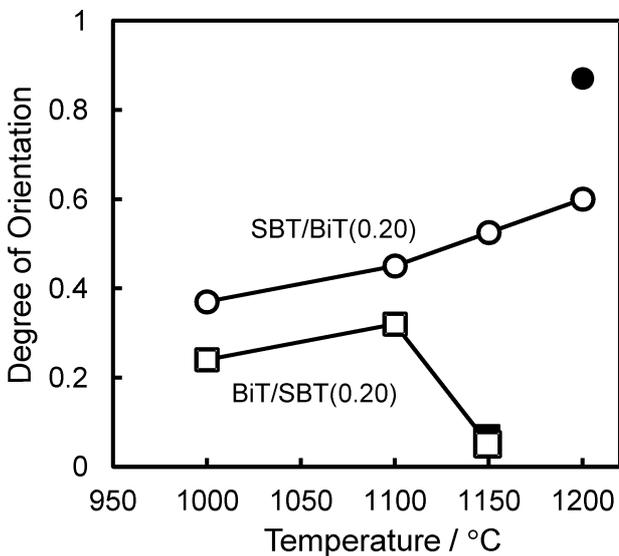


Fig. 3 The effect of sintering temperature on the degree of orientation of SBT/BiT(0.20) and BiT/SBT(0.20) sintered for 2 h (open marks) and 10 h (closed marks).

The microstructure development in SBT/BiT(0/20) is explained using Figs. 2, 3, and 4. All diffraction lines in SBT/BiT(0.20) sintered at 1000 °C for 2 h (Fig. 2a) were assigned to SBT and BiT except for the line at $2\tau = 39.3^\circ$. Many diffraction lines of SBT and BiT overlapped each other, and the lines characteristic of SBT and BiT were 0014 of BiT at $2\theta = 38.8^\circ$ and 0018 of SBT at $2\theta = 39.9^\circ$. The most intense line was located at 30.7° and was assigned to 119 of SBT, which is the most intense line of the powder

diffraction pattern of SBT¹⁸. The 00l lines of SBT and BiT had relatively high intensity. For example, the diffraction line at 22.0° with the relative intensity of 0.70 was 0010 of SBT and 008 of BiT and that at 39.9° with the relative intensity of 0.52 was 0018 of SBT. The relative intensity reported for the powder diffraction pattern is 0.13 and 0.04 for 0010 and 0018 of SBT, respectively²⁰. The intensity of the 0010 and 0018 lines, which are higher than the reported values, indicated that SBT/BiT(0.20) sintered at 1000 °C had a <001> texture with a degree of orientation of 0.37 (Fig. 3). The microstructure of this specimen was composed of both large and small grains (Fig. 4a). The large, plate-like grains were BiT and were aligned with their plate faces parallel to the surface of the specimen. The small grains were SBT, which were not exactly equiaxed but had some plate-like characteristics. Some of these grains were oriented with their plate faces parallel to the surface of the specimen, resulting in the development of some texture.

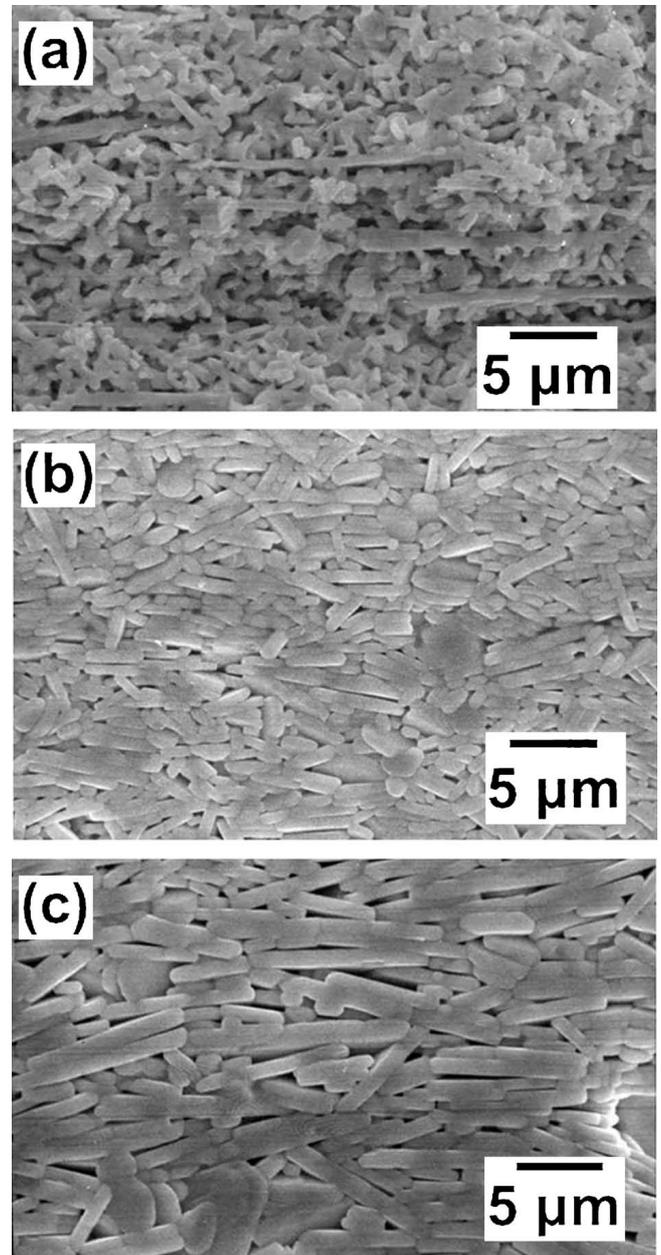


Fig. 4 4 Microstructures of SBT/BiT(0.20) sintered (a) at 1000 °C for 2 h, (b) at 1200 °C for 2 h, and (c) at 1200 °C for 10 h.

Sintering of SBT/BiT(0.20) at 1200 °C increased the size of the matrix grains. The grains in the specimen sintered for 2 h had plate-like characteristics with high aspect ratios (Fig. 4b). The number of grains oriented with their plate faces parallel to the surface of the specimen increased as compared to the specimen sintered at 1000 °C and the degree of orientation reached 0.60 (Fig. 3). Extensive grain growth was evident in the specimen sintered at 1200 °C for 10 h (Fig. 4c). The number of grains whose plate size was larger than 10 μm increased, indicating that the matrix grains grew to sizes comparable to those of the template grains. All diffraction lines of SBT/BiT(0.20) sintered at 1200 °C for 10 h were assigned to belong to SBT because the intensity of 0014 of BiT at $2\theta = 38.8^\circ$ was almost null (Fig. 2b). The pattern had intense $00l$ lines and weak hkl lines other than $00l$, indicating the development of extensive $\langle 001 \rangle$ texture. The degree of orientation was 0.87 (Fig. 3).

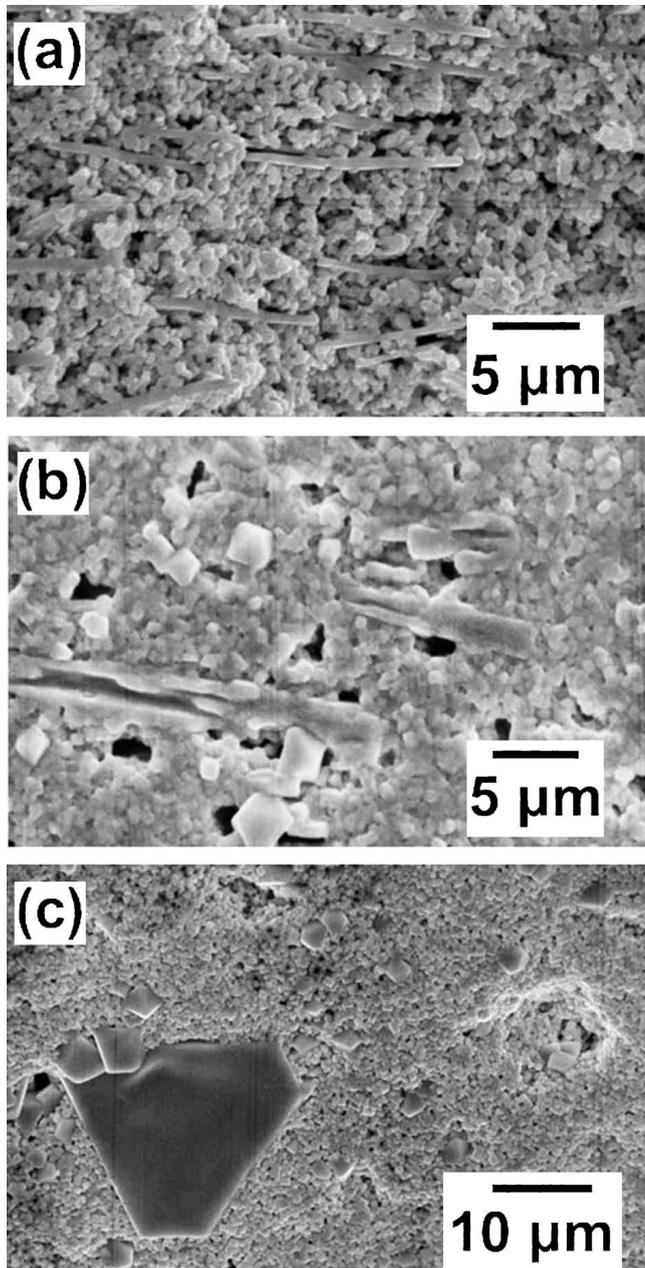


Fig. 5 Microstructures of BiT/SBT(0.20) sintered (a) at 1000 °C for 2 h, (b) at 1150 °C for 2 h, and (c) at 1150 °C for 10 h.

The microstructure development in BiT/SBT(0.20) is explained using Figs. 2, 3, and 5. BiT/SBT(0.20) sintered at 1000 °C for 2 h was composed of large, plate-like grains and small, equiaxed grains (Fig. 5a). The diffraction pattern shown in Fig. 2c indicated that the most intense line was located at $2\theta = 30.3^\circ$, which was assigned to 117 of BiT. The next intense lines were located at $2\theta = 21.7^\circ$ and 39.9° , 0010 and 0018 of SBT, respectively. These facts indicated that BiT/SBT(0.20) sintered at 1000 °C for 2 h was composed of aligned, plate-like SBT grains and randomly oriented, equiaxed BiT grains.

Sintering at 1150 °C caused densification (a decrease in the pore volume), but significant grain growth was not observed. Characteristic changes were the formation of groups of plate-like grains and the growth of abnormal grains on sintering for 2 and 10 h, respectively. Furthermore, the matrix grains were small and nearly equiaxed in shape, as compared to SBT/BiT(0.20). The most intense diffraction line in BiT/SBT(0.20) sintered at 1150 °C for 10 h was 117 of BiT, and the relative intensity of 0010 and 0018 of SBT decreased from that in BiT/SBT(0.20) sintered at 1000 °C (Figs. 2c and 2d). The degrees of orientation of BiT/SBT(0.20) sintered at 1150 °C for 2 and 10 h were 0.05 and 0.06, respectively (Fig. 3). These results indicated that the texture did not develop in BiT/SBT(0.20). In the following sections, we focus on the reason for the lack of texture development in BiT/SBT(0.20).

(2) Examination of solid-state spreading

In some materials with the Aurivillius and perovskite structures, the texture development is caused not by the growth of template grains at the expense of matrix grains but by the shape change of matrix grains in the presence of template grains^{12, 21, 22}. When a compact composed of template and matrix grains is heated, the third grain, tentatively called a “terrace”, develops between the template and matrix grains. The terrace has the same crystallographic orientation as the template grain. The terrace is formed by solid-state spreading, the driving force for which is the reduction in the total surface energy²³. In the present case, the surface of the template grain disappears and the surface of terraces, the composition of which is the same as the matrix grains, forms; a grain boundary between the template grain and the terrace is also formed. Therefore, the magnitude of the driving force is dependent on the combination of the chemical species of template and matrix grains. It is possible that solid-state spreading is operative in SBT/BiT(0.20), resulting in the texture formation, whereas it is not operative in BiT/SBT(0.20).

The formation of terraces can be confirmed by the careful observation of matrix grains just on the surfaces of template grains in the initial stage of sintering. In the present case, the specimens sintered at 950 °C for 2 h were examined and the microstructures are shown in Fig. 6. The formation of terraces between the matrix and template grains was evident in SBT/BiT(0.20). The terraces have a square-shaped, thin film-like structure. The edges of each terrace had the same orientation, indicating that the orientation is identical to and determined by the crystallographic orientation of the template grain. The formation of terraces

was less evident in BiT/SBT(0.20), but careful observation could confirm the presence of the terraces, shown by the arrow in Fig. 6b. The cross-section of BiT/SBT(0.20), shown in Fig. 6c, indicates the formation of layers covering the surface of the template grain. These layers are similar to a thin $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ layer formed on a SrTiO_3 single crystal by solid-state spreading²². These facts indicate that the terraces form in both SBT/BiT(0.20) and BiT/SBT(0.20). Therefore, the possibility that the terraces do not form in BiT/SBT(0.20) is ruled out as an explanation for the lack of texture development in BiT/SBT(0.20).

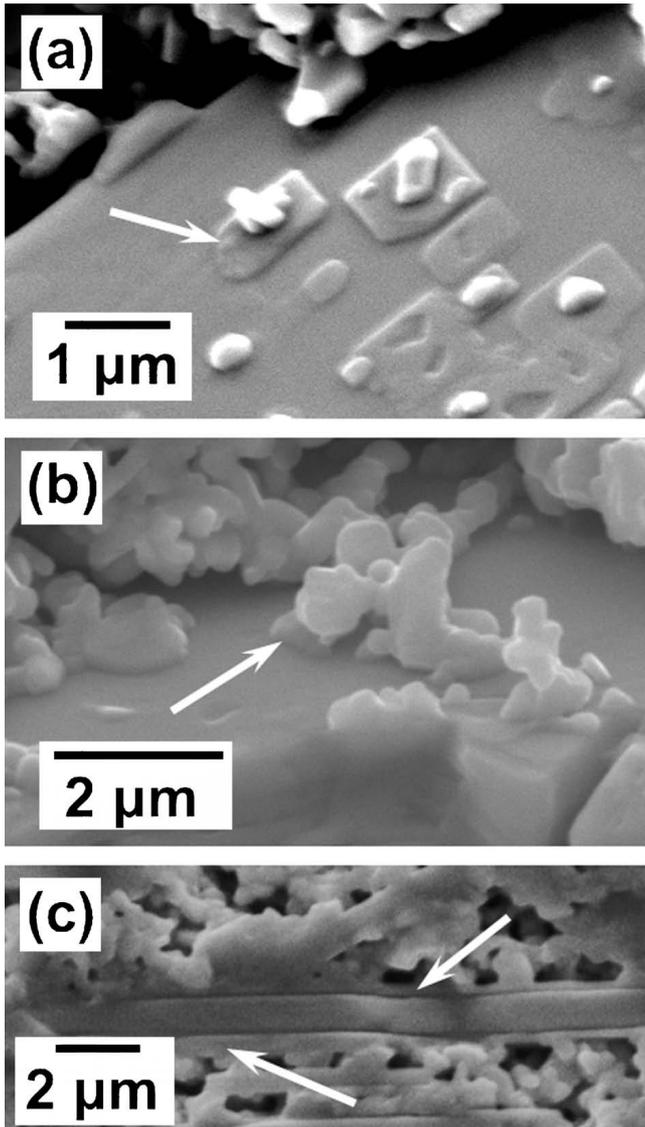


Fig. 6 Microstructures of (a) SBT/BiT(0.20) and (b) and (c) BiT/SBT sintered at 950 °C for 2 h. (a) and (b) are the microstructures on the fracture surfaces and (c) is the microstructure on the polished and etched section. Arrows indicate terraces.

(3) Chemical reaction

In BiT/SBT(0.20), the intensity of diffraction line at $2\theta = 39.9^\circ$, which is characteristic to SBT, decreased on heating at 1150 °C, as shown in Figs. 2c and 2d. This suggests that SBT disappeared by the chemical reaction between BiT and SBT, resulting in the formation of $\text{S}_{0.5}\text{BT}$ ²⁴. The diffraction lines of BiT, $\text{Sr}_{0.5}\text{BT}$, and SBT overlap each other, but the formation of $\text{S}_{0.5}\text{BT}$ can be confirmed by the

diffraction pattern below $2\theta = 20^\circ$ ²⁵. The composition of materials with the Aurivillius structure can be expressed as $(\text{Bi}_2\text{O}_2)(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})$. In this study, m is 3 for BiT, 3.5 for $\text{S}_{0.5}\text{BT}$, and 4 for SBT. Fig. 7 shows the diffraction pattern of BiT/SBT(0.20) sintered at 1150 °C for 10 h. The line with $m = 3$ was the most intense and the lines with $m = 4$ were weak. More importantly, the lines with $m = 3.5$ were confirmed. This indicates the formation of $\text{S}_{0.5}\text{BT}$ by a reaction between BiT and SBT. The unknown line at $2\theta = 39.3^\circ$ in Fig. 2a can be assigned to 0016 of $\text{S}_{0.5}\text{BT}$. This indicates that SBT reacts with BiT and changes to $\text{S}_{0.5}\text{BT}$ at relatively low temperatures, i.e. 1000 °C, before densification and grain growth.

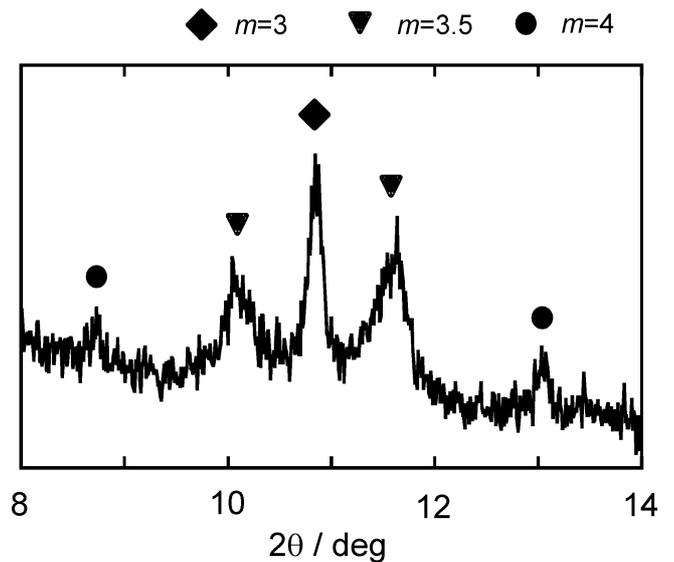


Fig. 7 X-ray diffraction pattern of BiT/SBT(0.20) sintered at 1150 °C for 10 h.

(4) Hetero-TGG using $\text{S}_{0.5}\text{BT}$ as template

It is possible that the change of chemical species of template grains from SBT to $\text{S}_{0.5}\text{BT}$ is responsible for the lack of texture development in BiT/SBT(0.20). Accordingly, the texture development as well as the microstructure development was examined in the BiT/ $\text{S}_{0.5}\text{BT}$ specimen, in which the plate-like $\text{S}_{0.5}\text{BT}$ grains and equiaxed BiT grains were used as template and matrix grains, respectively. Fig. 8 shows the XRD patterns of BiT/ $\text{S}_{0.5}\text{BT}$ with various template volume fractions, sintered at 1150 °C for 10 h. The most intense line was 0014 of BiT at $2\theta = 38.4^\circ$ and the major diffraction lines were 00 l of BiT for the template volume fraction up to 0.075 and 117 of BiT at $2\theta = 30.2^\circ$ for the template volume fractions of 0.10 and 0.20, indicating that the texture developed in the former specimens and that the addition of much $\text{S}_{0.5}\text{BT}$ suppressed the texture development. The texture developed even in BiT/ $\text{S}_{0.5}\text{BT}$ (0.00), i.e., without the template grains. Therefore, the reason for texture development in this specimen was examined first, and then the effect of $\text{S}_{0.5}\text{BT}$ on the texture development was evaluated.

Fig. 9 shows the microstructures of BiT/ $\text{S}_{0.5}\text{BT}$ (0.00) sintered at various temperatures for 2 h; this specimen had no template grains and was prepared with the same

procedure as that used for the preparation of other specimens. The grains developed a plate-like shape at 950°C . Large, plate-like grains were formed at 1050°C , and the size and the number density of the large, plate-like grains increased with an increase in the sintering temperature, as shown in Fig. 9c. A significant number of the large, plate-like grains were oriented with their plate face parallel to the surface of the specimen and the F value was approximately 0.6 at 1150°C . The texture development in this specimen was caused by the growth of relatively large grains in the BiT powder. The BiT powder was not composed of completely equiaxed grains but was composed of somewhat plate-like grains (Fig. 1d). Some large BiT grains with relatively high aspect ratios (approximately 3) were aligned by tape casting and grew to large, plate-like grains at high temperatures, resulting in the texture development.

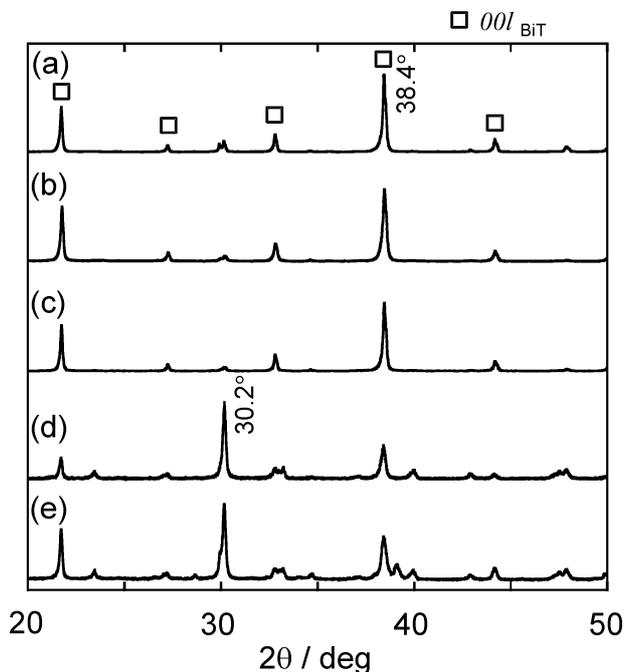


Fig. 8 X-ray diffraction patterns of $\text{BiT}/\text{S}_{0.5}\text{BT}$ with various template volume fractions, sintered at 1150°C for 10 h. The template volume fraction is (a) 0.00, (b) 0.05, (c) 0.075, (d) 0.10, and (e) 0.20.

Fig. 10 shows the microstructures of $\text{BiT}/\text{S}_{0.5}\text{BT}(x)$ with $x=0.075, 0.10$ and 0.20 , sintered at 1150°C for 10 h. $\text{BiT}/\text{S}_{0.5}\text{BT}(0.075)$ was composed of aligned, plate-like grains. The aligned, plate-like $\text{S}_{0.5}\text{BT}$ template grains and the aligned, somewhat plate-like BiT matrix grains were responsible for the texture development in this specimen. In $\text{BiT}/\text{S}_{0.5}\text{BT}(0.10)$ and $\text{BiT}/\text{S}_{0.5}\text{BT}(0.20)$, the matrix grains were plate-like but the orientation was random. The presence of large plate-like grains, which were template $\text{S}_{0.5}\text{BT}$ grains, was confirmed in $\text{BiT}/\text{S}_{0.5}\text{BT}(0.20)$ but their presence was minimal in $\text{BiT}/\text{S}_{0.5}\text{BT}(0.10)$. Furthermore, the sizes of the matrix grains were small-

er in $\text{BiT}/\text{S}_{0.5}\text{BT}(0.10)$ and $\text{BiT}/\text{S}_{0.5}\text{BT}(0.20)$ than in $\text{BiT}/\text{S}_{0.5}\text{BT}(0.075)$.

Fig. 11 shows the XRD diffraction pattern of $\text{BiT}/\text{S}_{0.5}\text{BT}(0.10)$ and $\text{BiT}/\text{S}_{0.5}\text{BT}(0.20)$ sintered at 1150°C for 2 h. The diffraction lines 007 and 0016 of $\text{S}_{0.5}\text{BT}$ were present in $\text{BiT}/\text{S}_{0.5}\text{BT}(0.20)$ but they were not confirmed in $\text{BiT}/\text{S}_{0.5}\text{BT}(0.10)$. This indicates that SrTiO_3 (ST) in $\text{S}_{0.5}\text{BT}$ dissolves in BiT, forming a BiT-ST solid solution, which is called ST-doped BiT. The formation of ST-doped BiT has been confirmed from mixtures of BiT and ST powders and the solubility limit at 1150°C has been estimated to be $0.957\text{BiT}-0.043\text{ST}$ ¹³, which corresponds to the overall composition of $\text{BiT}/\text{S}_{0.5}\text{BT}(0.10)$.

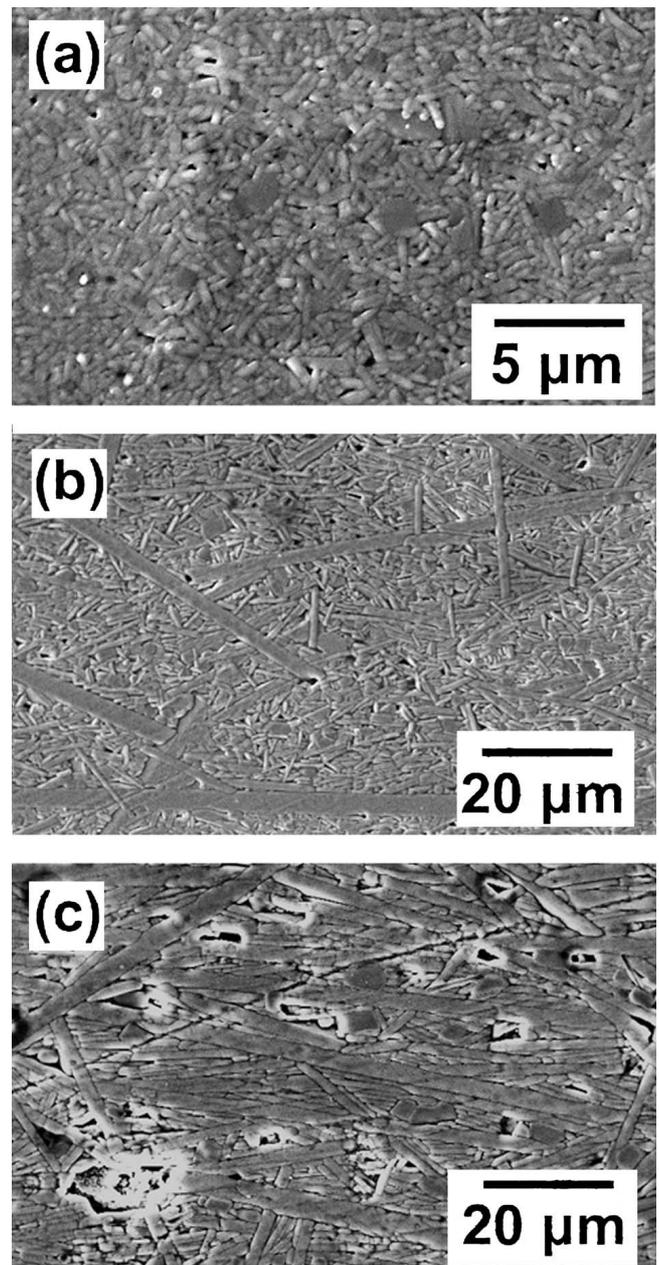


Fig. 9 Microstructures of $\text{BiT}/\text{S}_{0.5}\text{BT}(0.00)$ sintered (a) at 950°C for 2 h, (b) at 1050°C for 2 h, and (c) at 1150°C for 10 h.

The presence of the template grains was not confirmed in BiT/S_{0.5}BT(0.10) sintered at 1150 °C for 10 h (Fig. 10b). The dissolution of ST from template S_{0.5}BT grains in matrix BiT grains disintegrated the template grains. However, this disintegration of the template grains is not the reason for the lack of texture development in BiT/S_{0.5}BT(0.10) and BiT/S_{0.5}BT(0.20), because the template grains were present in BiT/S_{0.5}BT(0.20) (Fig. 10c). The lack of texture development in BiT/S_{0.5}BT(0.10) and BiT/S_{0.5}BT(0.20) is thought to be related to the hindrance in the growth of matrix grains.

Fig. 12 shows the microstructures of ST-doped BiT prepared by isostatic pressing of mixtures of the BiT and ST powders and by sintering at 1150 °C for 2 h. The ST powder was prepared by a solid-state reaction at 1100 °C. The overall compositions were 0.978BiT-0.022ST and 0.957BiT-0.043ST. In the former specimen, the grains grew and had a plate-like shape. The grain growth was suppressed in the latter specimen and the grain shape was plate-like with aspect ratios smaller than those in the first specimen. The dissolution of ST in BiT suppresses grain growth and the development of plate-like shape. The lack of the texture development in BiT/SBT(0.20), as well as in BiT/S_{0.5}BT(0.10) and BiT/S_{0.5}BT(0.20), can be explained based on the effect of ST dissolved in the BiT matrix grains from the SBT or S_{0.5}BT template grains. The overall composition of BiT/SBT(0.20) is 0.856BiT-0.144ST, and the equilibrium phases are the mixture of ST-doped BiT and S_{0.5}BT. This means that the dissolution of ST in BiT changes the matrix composition from pure BiT to ST-doped BiT and the template composition from SBT to S_{0.5}BT. The suppression of both the grain growth of template grains and the morphological change of matrix grains to a plate-like shape is responsible for the lack of the texture development in BiT/SBT(0.20), because these phenomena are the main mechanism of texture development in materials with the Aurivillius structure⁷.

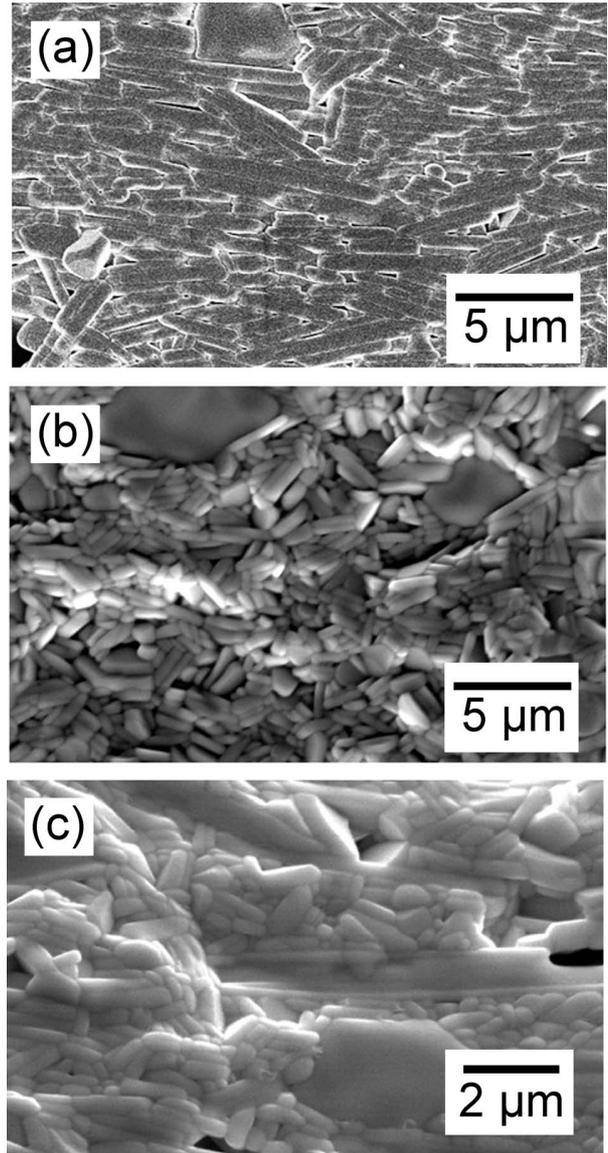


Fig. 10 Microstructures of (a) BiT/S_{0.5}BT(0.075), (b) BiT/S_{0.5}BT(0.10), and (c) BiT/S_{0.5}BT(0.20) sintered at 1150 °C for 10 h.

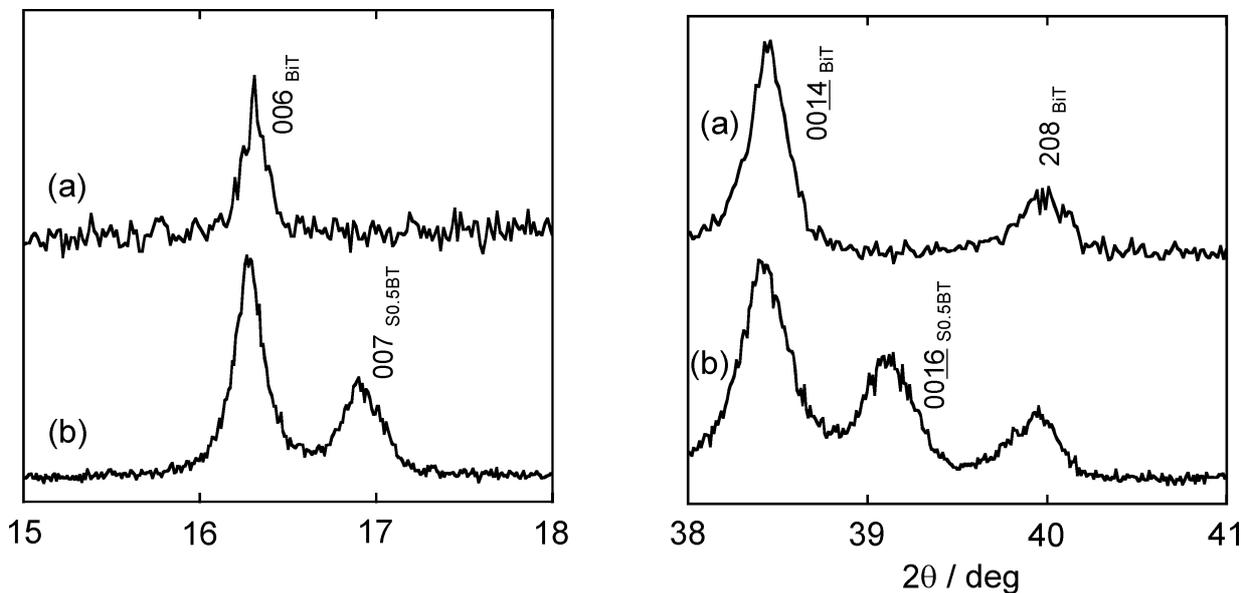


Fig. 11 X-ray diffraction patterns of (a) BiT/S_{0.5}BT (0.10) and (b) BiT/S_{0.5}BT (0.20) sintered at 1150 °C for 2 h.

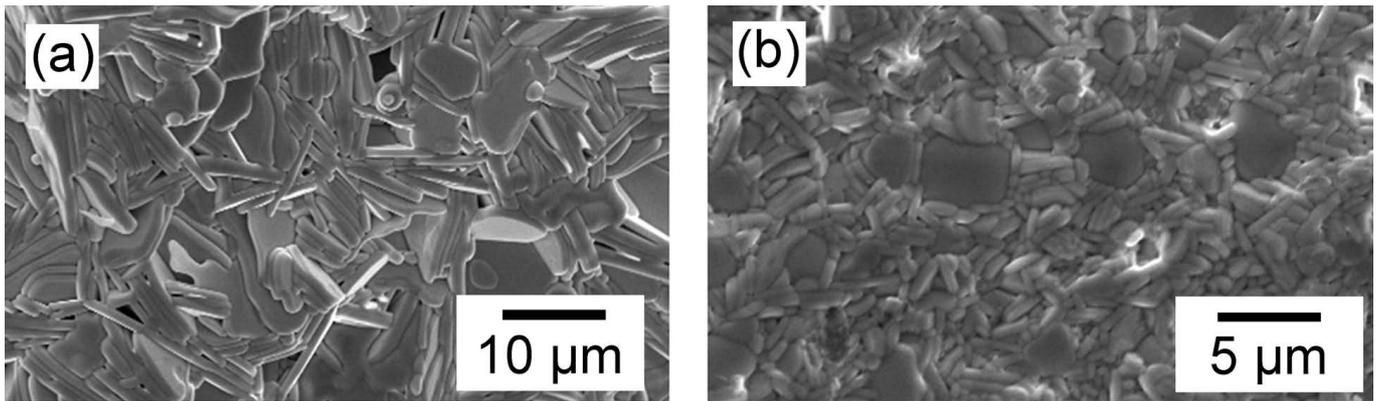


Fig. 12 Microstructures of ST-doped BiT sintered at 1150 °C for 2 h. The overall compositions are (a) 0.978BiT-0.022ST and (b) 0.957BiT-0.043ST.

IV. Summary and Conclusions

The hetero-templated grain growth process developed texture in SBT/BiT(0.20) but did not develop in BiT/SBT(0.20). The reason for the lack of texture development in BiT/SBT(0.20) was examined from two points of view, namely, solid-state spreading and chemical reaction. Solid-state spreading was found to be operative in both specimens because the formation of terraces, which were formed by solid-state spreading, was confirmed in both specimens. Next, the possibility of a chemical reaction between SBT and BiT was examined and the formation of $\text{SrBi}_8\text{Ti}_7\text{O}_{27}$ ($\text{S}_{0.5}\text{BT}$) was confirmed. This means that the template grains changed from SBT to $\text{S}_{0.5}\text{BT}$ in BiT/SBT(0.20). Therefore, texture development in BiT/ $\text{S}_{0.5}\text{BT}$ was examined, and it was found that an increase in the template volume fraction resulted in the suppression of texture development. SrTiO_3 in the template $\text{S}_{0.5}\text{BT}$ grains dissolved in BiT matrix grains and suppressed the growth and morphological change of the matrix grains, resulting in the suppression of texture development. It can therefore be concluded that the dissolution of a high concentration of SrTiO_3 in BiT matrix grains was the reason for the lack of texture development in BiT/SBT(0.20), as well as in BiT/ $\text{S}_{0.5}\text{BT}$ with a large amount of template grains.

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