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Microstructure development in textured $BaBi_4Ti_4O_{15}$ made by templated grain growth method

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Abstract The effect of template and matrix particle sizes on microstructure development was examined for $BaBi_4Ti_4O_{15}$ textured by the templated grain growth method. Microstructure development was characterized by (1) the shape change of matrix particles from equiaxed to platelike, which resulted in texture development in the matrix phase, and (2) the formation of groups of large platelike grains with parallel alignment. The template particle size determined the size of grains in the final microstructure which was formed by process (2), and the matrix particle size influenced the rate of process (1).

Keywords Barium bismuth titanate · Crystallographic texture · Template grain growth method · Microstructure · Particle size

1 Introduction

One of recent research efforts on piezoelectric ceramics focuses on the development of lead-free compositions. The properties of lead-containing materials, such as $Pb(Zr,Ti)O_3$- and relaxor-based compositions, are so excellent that microstructure refinement as well as the searches for new compositions is necessary to develop lead-free piezoelectric ceramics for practical use [1]. Crystallographic texture is one of the factors constituting microstructure [1], and this paper concerns texture development in $BaBi_4Ti_4O_{15}$ (BBT), which belongs to the family of bismuth layer-structured ferroelectrics (BLSFs) [2]. BLSF is one of the candidates for lead-free piezoelectric ceramics, but texturing is essential to obtain enhanced properties because of its anisotropic crystal structure [2, 3].

One of the most convenient preparation methods of textured BLSF ceramics is the templated grain growth (TGG) method [4]. Although highly textured ceramics are easily obtained, this method inevitably introduces structural inhomogeneity into a green compact because of the use of template and matrix particles with different powder characteristics. Structural inhomogeneity influences sintering behavior and the microstructure of final products [5]. This paper deals with the effects of the template and matrix particle sizes on the microstructure development of textured BBT. The effect of liquid phase on the microstructure is also examined. In the course of this research, we have obtained a new insight into the mechanism of texture development by the close examination of microstructures.

2 Experimental procedure

Two kinds of equiaxed matrix particles and two kinds of platelike template particles with different sizes were used in this experiment. The matrix particles were prepared by the conventional solid state method using reaction (1).

$$BaCO_3 + 2Bi_2O_3 + 4TiO_2 = BaBi_4Ti_4O_{15} + CO_2 \qquad (1)$$

The mixture of starting materials was heated at 1,000 °C for 1 h. The reaction product was ball-milled for 24 h using ZrO_2 balls 15 mm in diameter. This powder was divided into two parts. One was used as large matrix particles (designated as *l*). The other was further ball-milled for additional 48 h using ZrO_2 balls 2 mm in diameter to form small matrix particles (designated as *s*). The particles *l* and *s*

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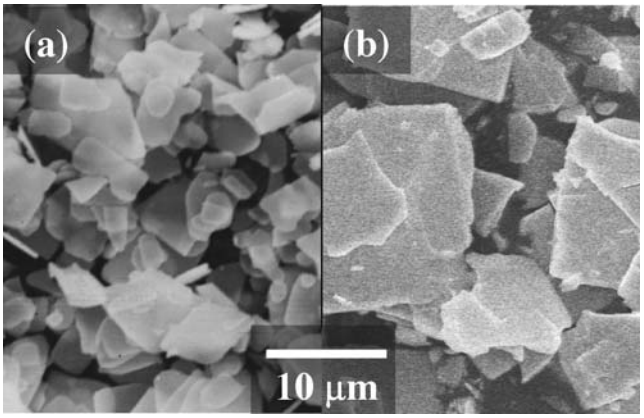

Fig. 1 Photomicrographs of (**a**) small and (**b**) large template particles

were equiaxed and had an irregular shape. The most particles were between 1 and 2 μm in size for *l* and between 0.5 and 1 μm for *s*.

Two kinds of template particles were prepared by molten salt synthesis [6] based on reactions (1) and (2) at 1,120 °C for 1 and 5 h, respectively. Reactions (1) and (2) gave small

$$Bi_4Ti_3O_{12} + BaCO_3 + TiO_2 = BaBi_4Ti_4O_{15} + CO_2 \qquad (2)$$

and large template grains (designated as *S* and *L*), respectively. The salts used in reactions (1) and (2) were KCl and KCl–$BaCl_2$ (2:1), respectively. $Bi_4Ti_3O_{12}$ used in reaction (2) had a platelike shape and was prepared by heating a stoichiometric mixture of Bi_2O_3 and TiO_2 at 1,130 °C for 1 h in the presence of molten NaCl–KCl (1:1) [7]. The products of reactions (1) and (2) were washed with water to remove salt. X-ray diffraction (XRD) measurement indicated that the products were single-phase BBT. Figure 1 shows the photomicrographs of the *S* and *L* particles; they have a platelike shape with an edge length between 2 and 10 μm and a thickness of about 0.4 μm for *S*, and an edge length between 5 and 20 μm and a thickness of about 0.5 μm for *L*.

Powder mixtures containing 20 vol% template and 80 vol% matrix particles were mixed with a solvent (60 vol% toluene−40 vol% ethanol), a binder (poly (vinyl butyral)), and a plasticizer (di-*n*-butyl phthalate), and tape cast to form a sheet in which platelike particles were aligned. The sheets were cut and laminated to form a green compact with a thickness of about 2 mm. The binders were burnt out at 700 °C for 2 h, and then the compacts were sintered under various conditions. The specimens are designated by the notation based on the template/matrix sizes; for example, specimen *L/s* contains the large template and small matrix particles.

Texture development was evaluated by XRD using CuKα radiation. The degree of orientation was evaluated by the Lotgering *F* value [8]; *F*=1 or 0 indicates that the compact is completely textured or random, respectively. The diffraction lines between $2\theta = 10^\circ \sim 50^\circ$ were used for the evaluation. The microstructure was observed with SEM; polished and thermally etched sections were observed for dense specimens, and fractured sections were observed for less dense specimens. Some specimens were etched chemically.

3 Results and discussion

3.1 Densification and texture development

Figure 2 shows the effects of sintering conditions up to and at 1,130 °C on the densification and texture development of four specimens. The densification behavior was almost the same for all specimens. The specimens containing the large template particles had slightly higher density up to 1,130 °C, but the difference became small after 5 h-heating at 1,130 °C. Sintering at 1,130 °C was necessary to obtain sintered compacts with a density of more than 90% of theoretical. The *F* value gradually increased with an increase in

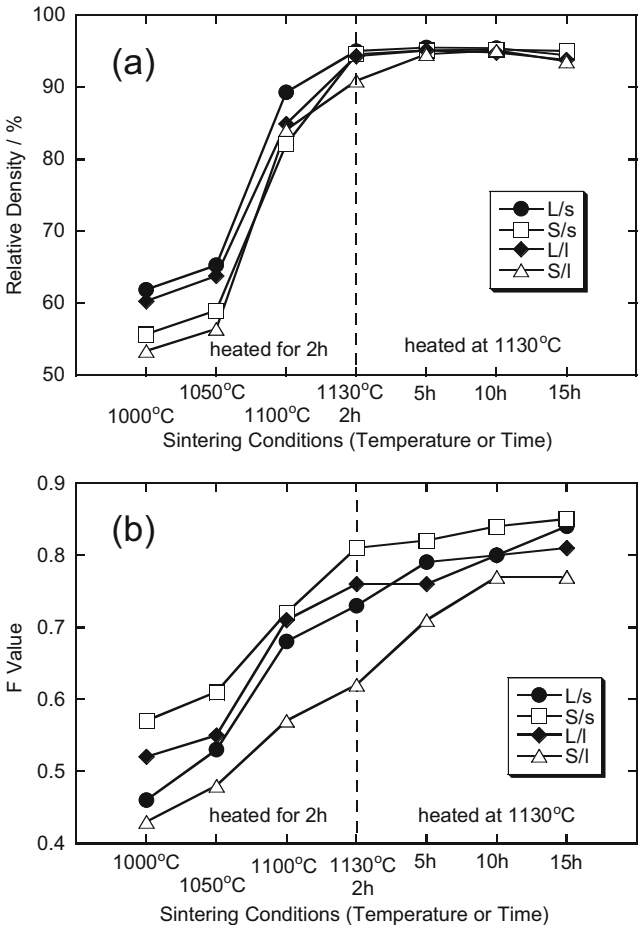

Fig. 2 Effect of sintering conditions on (**a**) densification and (**b**) texture development

temperature and reached 0.7–0.8 at 1,130 °C with 2 h-heating for all specimens except for *S/l*. Prolonged heating at 1,130 °C increased the *F* value slightly. The increase was most extensive for *S/l* and all specimens had the *F* value between 0.75 and 0.85 by heating at 1,130 °C for 15 h.

3.2 Microstructures

3.2.1 Microstructure development in L/s

Figure 3 shows the microstructures of *L/s* heated at 1,050°, 1,100°, and 1,130 °C for 2 h. The microstructure at 1,050 °C was similar to that after binder burnout and composed of large platelike and small equiaxed particles (template and matrix, respectively). The matrix particles changed their shape to be platelike at 1,100 °C, while template particles

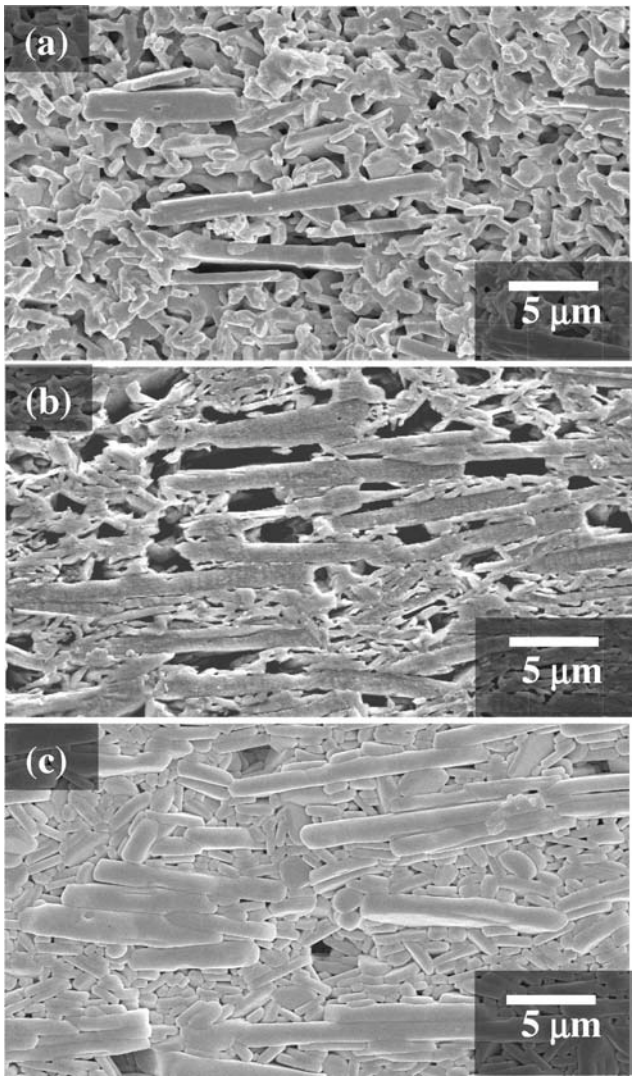

Fig. 3 Microstructures of *L/s* heated at (**a**) 1,050°, (**b**) 1,100°, and (**c**) 1,130 °C for 2 h. The surfaces were (**a**) fractured, (**b**) chemically etched, and (**c**) thermally etched

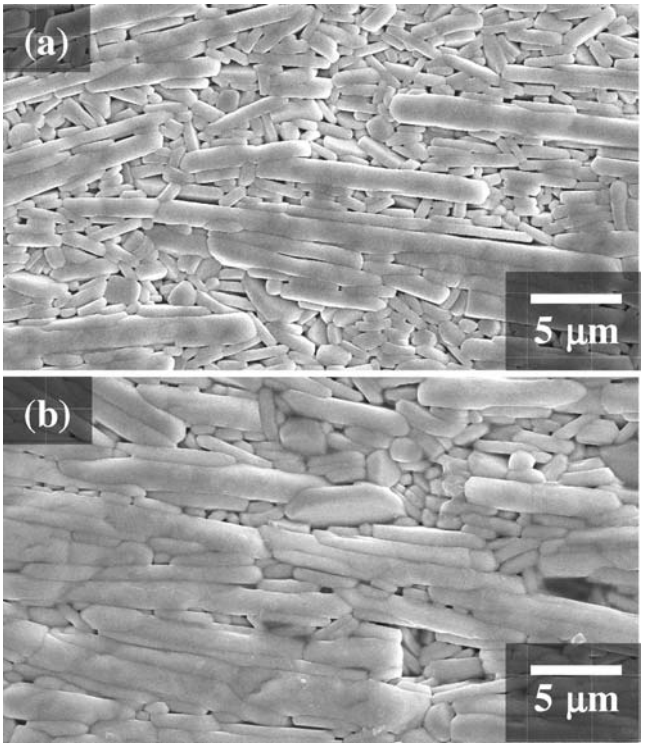

Fig. 4 Microstructures of *L/s* heated at 1,130 °C for (**a**) 5 and (**b**) 15 h. The surfaces were thermally etched

did not grow to a considerable extent. During this shape change, the plate faces of small matrix particles came in contact with that of template particles, forming "face-to-face contact". The "face-to-face contact" formed not only between template and matrix particles but also between matrix particles. Because the plate face is perpendicular to the crystallographic <001> direction, newly formed platelike particles have their <001> parallel to the <001> of template particles. Thus, texture was developed in the matrix phase, resulting in an increase in the *F* value (Fig. 2). Further heating reduced the volume of pores present in the matrix phase, and dense ceramics were obtained at 1,130 °C.

Prolonged heating at 1,130 °C caused another microstructure change. Figure 4 shows the microstructures of *L/s* heated at 1,130 °C for 5 and 15 h. A remarkable characteristic is the formation of groups of the large platelike grains with parallel alignment. This microstructure is developed by the growth of small platelike grains in touch with large platelike grains at the stage shown in Fig. 3(c). At this stage, a small platelike grain makes the "face-to-face contact" with a large template grain. Two grains have a relationship of $<001>_{large}$// $<001>_{small}$; this kind of grain boundary is called a twist boundary. The energy of twist boundary depends on the twist angle. Therefore, there are some small platelike grains with low grain boundary energy, and these grains can grow at the expense of neighboring small platelike grains. The diameter of the growing matrix grains is limited to the diameter of the large platelike grain, because the growing

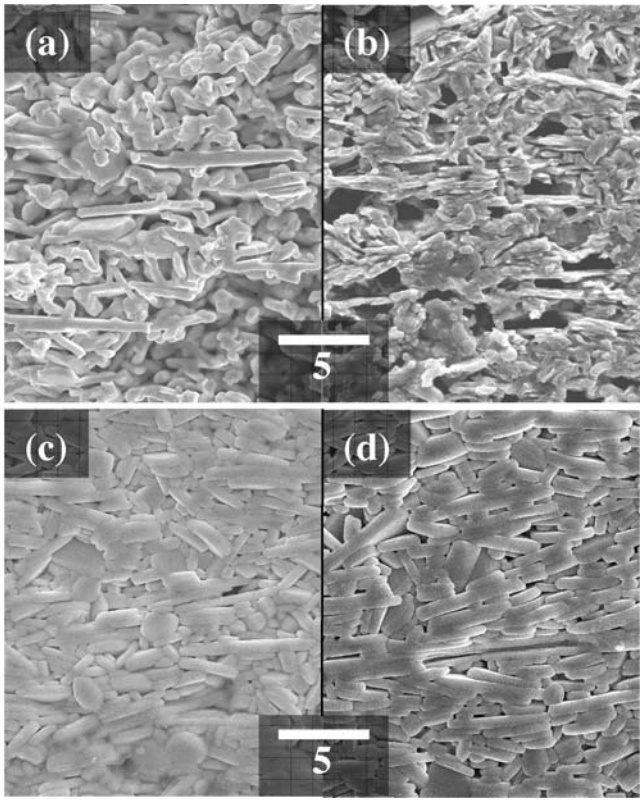

Fig. 5 Microstructures of *S/l* heated at (**a**) 1,050°, (**b**) 1,100°, and (**c**) 1,130 °C for 2 h and (**d**) at 1,130 °C for 15 h. The surfaces were (**a**) fractured, (**b**) chemically etched, and (**c**) and (**d**) thermally etched

grain grows along the plate face of the large grain. Thus, the groups of large platelike grains with parallel alignment are formed.

Microstructure development in *L/l* was almost the same as that in *L/s*, as shown in Section 3.2.3. The characteristics of microstructure development in the specimens containing *L* particles are summarized as follows: (1) the shape change of matrix particles from equiaxed to platelike and the formation of "face-to-face contact" between template and matrix particles and between matrix particles, and (2) the growth of small platelike matrix grains in touch with large platelike grains to form a group of large platelike grains with parallel alignment. Texture development is not caused by the growth of template grains but by the formation of platelike matrix particles with plate faces parallel to that of template grains, mainly during process (1).

3.2.2 Effect of template particle size

Processes (1) and (2) proceeded also in the specimens containing *S* particles. Figure 5 shows the microstructures of *S/l* specimen heated at 1,050°, 1,100°, and 1,130 °C for 2 h and at 1,130 °C for 15 h. The change of matrix grains from an equiaxed to platelike shape is clearly indicated in Fig. 5(b). Process (2) occurred during heating at 1,130 °C

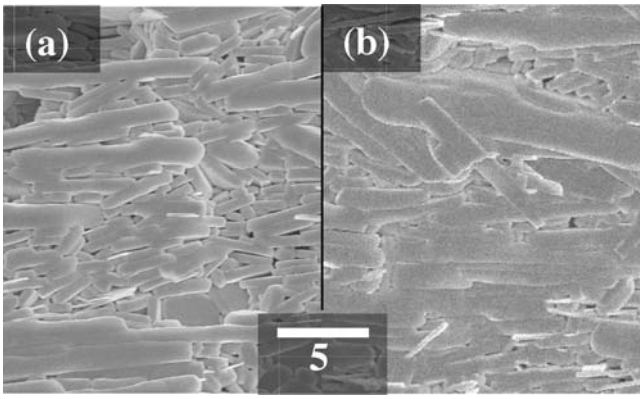

Fig. 6 Microstructures of *L/l* heated at 1,130 °C for (**a**) 2 h and (**b**) 15 h. The surfaces were thermally etched

Fig. 5(d), but the distinction between large and small platelike gains was not clear as in *L/s*. Figures 3, 4 and 5 indicate that template grains do not grow to a considerable extent during processes (1) and (2), and determine the size of platelike grains after process (2) (Figs. 4(b) and 5(d)). Thus, the compacts composed of small platelike grains with a relatively narrow size distribution were obtained by using *S* particles.

3.2.3 Effect of matrix particle size

Figure 6 shows the microstructures of *L/l* heated at 1,130 °C for 2 and 15 h. The comparison of microstructures between *L/s* and *L/l* (between Figs. 3(c) and 6(a) and between Figs. 4(b) and 6(b)) indicates that these specimens have the microstructures with the same characteristics, indicating that the matrix particle size has little effect on microstructure development in the specimens with a large size difference between template and matrix particles.

Figure 7 shows the microstructures of *S/s* heated at 1,130 °C for 2 and 15 h. The comparison of microstructures between *S/l* and *S/s* just after process (1) (Figs. 5(c) and 7(a)) indicates that the aspect ratio of small grains, which are matrix grains, is

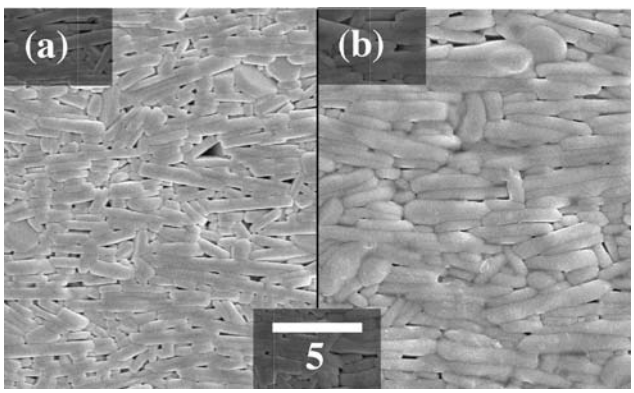

Fig. 7 Microstructures of *S/s* heated at 1,130 °C for (**a**) 2 h and (**b**) 15 h. The surfaces were thermally etched

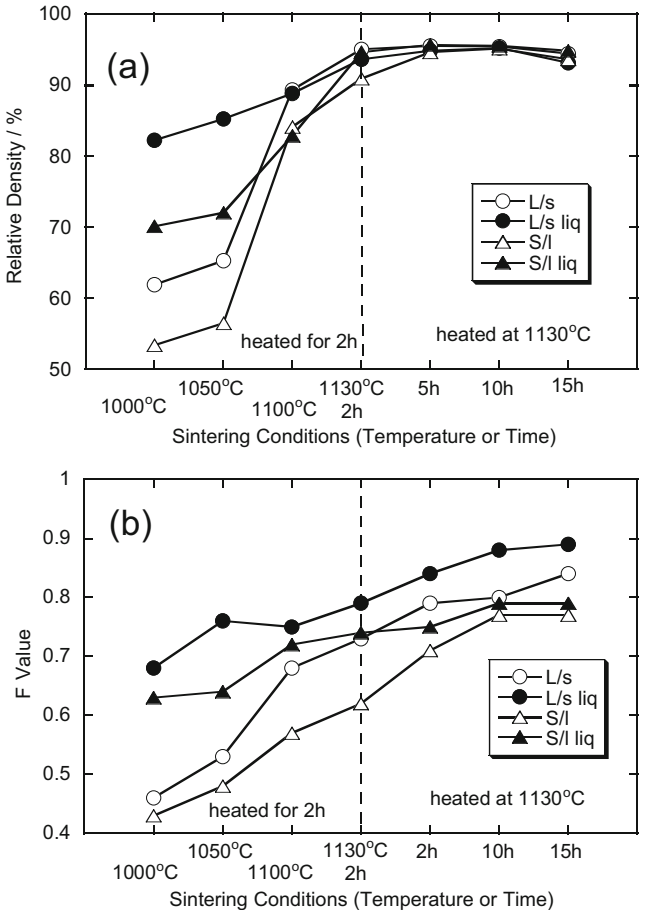

Fig. 8 Effects of liquid phase on (**a**) densification and (**b**) texture development

larger in *S/s* than *S/l*, indicating that smaller *s* particles more easily change their shape from equiaxed to platelike than larger *l* particles. The microstructures after process (2) (Figs. 5(d) and 7(b)) had almost the same characteristics, indicating that the matrix particle size had little effect on process (2). These results are summarized as follows. When the size difference between template and matrix particles is small as in the specimens containing *S* particles, large matrix particles have a small tendency to form "face-to-face contact," resulting in the formation of matrix grains with small aspect ratios. The limitation of the formation of "face-to-face contact" results in a small *F* value (Fig. 2).

3.3 Effect of liquid phase

A liquid phase plays an important role in microstructure development in Al_2O_3 textured by the TGG process [4]. In the Al_2O_3 case, a liquid phase promotes the growth of template grains at the expense of matrix grains, resulting in the formation of highly-textured microstructure [9]. In the present BBT case, we have examined whether a liquid

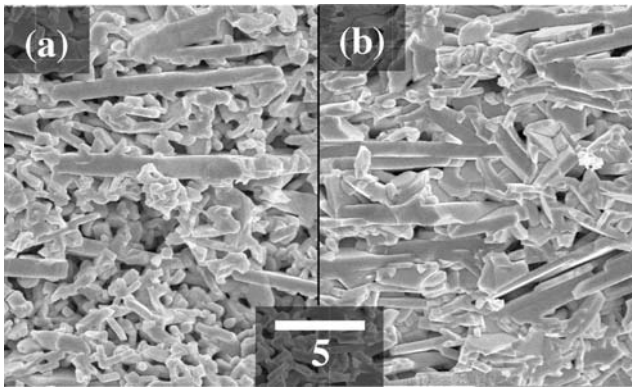

Fig. 9 Microstructures of *L/s* (**a**) without and (**b**) with liquid phase, heated at 1,000 °C for 2 h. The surfaces were fractured

phase promotes the growth of template grains by adding 1 wt.% Bi_2O_3.

Figure 8 shows the densification and texture development of the *L/s* and *S/l* specimens with and without the liquid phase. The liquid phase promoted densification up to 1,100 °C, but did not at 1,130 °C. The promotion of texture development was also effective up to 1,100 °C.

Figure 9 shows the microstructures of *L/s* with and without the liquid phase, heated at 1,000 °C for 2 h. The comparison of microstructures indicates that the liquid phase promotes the shape change of matrix grains from equiaxed to platelike; the matrix particles in the specimen without the liquid phase are equiaxed but those in the specimen with the liquid phase are platelike. This shape change increased density and texture development. The same microstructural characteristics were observed in *S/l*. The microstructures of specimens heated at 1,130 °C were not markedly changed by the presence of liquid phase, as exemplified by the comparison between Figs. 10(a) and 3(c) and between Figs. 10(b) and 5(c). As a whole, the Bi_2O_3 liquid phase did not change the mechanisms of microstructure development; it promoted process (1) but had little effect on process (2).

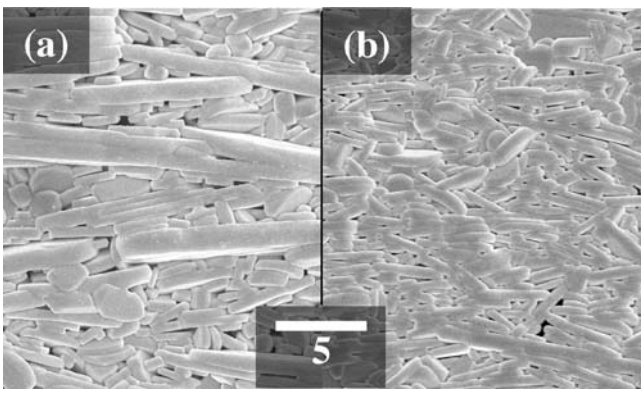

Fig. 10 Microstructures of (**a**) *L/s* and (**b**) *S/l* with liquid phase, heated at 1,130 °C for 2 h. The surfaces were thermally etched

4 Conclusions

The green compacts were composed of aligned, platelike template particles and randomly oriented, small equiaxed matrix particles. During sintering, the shape of matrix particles changed from equiaxed to platelike at the first stage. The presence of aligned template particles determined the orientation of plate faces of matrix particles by forming "face-to-face contact" between template and matrix particles. The formation of "face-to-face contact" extended to the matrix; the contact was formed between matrix particles. Thus, the textured region developed in the matrix phase at this stage. When the template size was small, the matrix particle size determined the extent of the "face-to-face contact" formation. Prolonged heating at high temperature did not increase the degree of texture development to a considerable extent, but caused the growth of matrix grains in contact with large template grains, resulting in an increase in microstructural homogeneity. In the final stage, the grain size was determined by the size of template particles. The use of the Bi_2O_3 liquid phase did not alter the mechanisms of microstructure development; it only promoted the shape change of matrix particles.

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