Microstructure development and texture formation in lead-free piezoelectric ceramics prepared by templated grain growth process

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1. Introduction

The physical properties of sintered ceramics are strongly dependent on density and microstructure. Generally, dense ceramics are preferable, although porous ceramics are used for some applications such as ceramic filters. The elements consisting of the microstructure of single-phase, polycrystalline ceramics are the size, shape, and orientation of grains and the structure of grain boundaries. Many physical properties of a crystal are dependent on the direction of measurement with respect to the crystal axes.¹ Because the orientation of grains in sintered ceramics is random, the measured physical properties are the average value over each grain. Textured ceramics are proposed to improve properties by aligning the orientation of grains in at least one direction. There are various preparation methods for textured ceramics, such as templated grain growth,²³⁴ magnetic alignment,⁵ hot-pressing,⁵ and hot-forging.⁶ The textured ceramics have been extensively reported for piezoelectric applications,⁷ because large increases in the piezoelectric coefficients are achieved over randomly oriented ceramics.²³⁴ This paper addresses the textured lead-free piezoelectric ceramics prepared by the templated grain growth (TGG) method.

The TGG method intends to prepare ceramics with superior properties by aligning grains in a specific direction. In this method, larger grains with an anisometric shape such as a plate or needle and smaller grains with an equiaxed shape are employed. They are called template and matrix grains, respectively. Although various consolidation methods can be applicable to prepare the textured ceramics,⁸¹⁰ tape-casting of a mixture of the template and matrix grains is generally employed.²³⁴ In the cast sheet, the template grains are dispersed in the matrix grains. Shear stresses exerted on the template grains during the casting align the template grains in one direction.¹¹¹² The sheet is cut, laminated, and pressed to form green compacts. When the platelike grains are used as the template grains, the grains are aligned with their plate faces parallel to the sheet surface. Ordinarily, it is recommended to use ceramic powders with submicron particle sizes. However, to align the template grains by shear stresses, sizes larger than 10 μm are required for at least one direction. Molten salt synthesis is a suitable method for preparing anisometric grains with these sizes.¹³ The matrix grains are submicron-sized and are ordinarily prepared by a solid-state method.¹⁴ Sintering densifies the compact and eliminates the matrix grains. Thus, dense textured ceramics are obtained. At first, the presence of a liquid phase was thought to be preferable,¹⁵¹⁶ but later it is found that the liquid phase is not necessarily required.¹⁷¹⁸

Initially, the application of TGG was limited to materials with crystal structures having low crystallographic symmetry, because it was thought that no techniques are applicable for the preparation of anisometric grains for materials with high symmetry.¹⁹ For these materials, Tani proposed the reactive-templated grain growth (RTGG) method.²⁰ In this method,²¹ a precursor of a target compound is used; the precursor must have an anisometric shape and a chemical composition similar to that of the target compound. Complementary compounds are added to form the target compound by a reaction with the precursor. A mixture of the precursor and complementary compounds is formed by tape-casting and calcined at an appropriate temperature. The platelike precursor grains transform to platelike target grains by in situ reaction between the precursor and complementary compounds. By an appropriate design of the composition of...
starting materials, small equiaxed target grains also form. Because the chemical reaction between the precursor and complementary compounds is almost completed in the calcination stage, the compact before sintering is composed of aligned anisometric grains and randomly oriented, equiaxed matrix grains with the same composition. They act as the template and matrix grains as in the TGG process. Therefore, the precursor is called a reactive template.

Because the texture is formed by the elimination of matrix grains, examination of the microstructure development from the green compact to the final sintered compact is important to obtain highly textured ceramics with controlled microstructure, i.e., density, degree of orientation, and grain size. The TGG and RTGG methods are first applied to structure ceramics, and extended to piezoelectric ceramics with the Aurivillius structure, tungsten bronze structure, and perovskite structure. Because materials having the perovskite structure have superior piezoelectric properties, various compounds have been extensively studied. They are \( \text{Bi}_0.5\text{Na}_0.5\text{TiO}_3 \), \( \text{BaTiO}_3 \), and \( \text{K}_0.5\text{Na}_0.5\text{NbO}_3 \)-based materials. For materials containing \( \text{PbO} \), the hetero-templated grain growth method is employed.

Figure 1 shows typical microstructures of textured piezoelectric ceramics. Except for \( \text{BaTiO}_3 \) being composed of grains with round boundaries, grains are all faceted in the other three materials. Therefore, the growth behavior of faceted grains must be considered.

This paper describes the microstructure development in textured piezoelectric ceramics prepared by the TGG and RTGG methods using platelike template grains to understand the mechanism of texture formation and focuses on bismuth layer-structured ferroelectrics. Although the piezoelectric coefficients are not as high as those of materials with the perovskite structure, the bismuth layer-structured ferroelectrics can be potentially used in high-temperature applications because of its high Curie temperature and high electric resistance. Because the crystal structure is highly anisotropic, textured ceramics can be prepared by various methods.

This review paper is organized in the following way. Sections 2 and 3 provide the microstructure development in \( \text{BaBi}_4\text{Ti}_4\text{O}_{15} \), \( \text{Bi}_2\text{Ti}_3\text{O}_7 \), \( \text{K}_0.5\text{Na}_0.5\text{NbO}_3 \), and \( \text{BaTiO}_3 \). The characteristics of the microstructure of the sintered compacts are that the compacts are composed of faceted template and matrix grains. To understand the conditions for the selective growth of the template grains, the principle governing the growth of faceted grains is briefly described in Section 4. Then, the mechanism of grain growth in each material is discussed in Section 5. Finally in Section 6, the effects of the characteristics of template and matrix grains and the chemical composition on the microstructure development and the texture formation are summarized to design optimal preparation conditions.

2. Microstructure development

To obtain highly textured ceramics with controlled microstructure, it is necessary to understand the mechanisms of microstructure development from the green compact to the final product. For textured ceramics, the degree of orientation is a chief concern. Therefore, this section focuses on the microstructure development with a special emphasis on texture formation. The degree of orientation is referred to for several specimens in connection with the microstructure. It is determined by the Lotgering method. \( \text{BaBi}_4\text{Ti}_4\text{O}_{15} \) and \( \text{MBi}_4\text{Ti}_4\text{O}_{15} \) (\( M = \text{Ca}, \text{Sr}, \) and \( \text{Ba} \)) have the Aurivillius structure, which is composed of \( \text{Bi}_2\text{O}_2 \)-layers and pseudo-perovskite blocks. Therefore, these compounds are called bismuth layer-structured ferroelectrics. Although the piezoelectric coefficients are not as high as those of materials with the perovskite structure, the bismuth layer-structured ferroelectrics can be potentially used in high-temperature applications because of its high Curie temperature and high electric resistance. Because the crystal structure is highly anisotropic, textured ceramics can be prepared by various methods.

Here, the microstructure development of the materials prepared by the TGG process is overviewed.

Figure 2 shows the relative density and the degree of orientation of \( \text{BaBi}_4\text{Ti}_4\text{O}_{15} \) containing 20 vol% template grains, heated at 1000, 1050, 1100, and 1130°C for 2 h and at 1130°C for 5, 10, and 15 h. The density increases between 1000 and 1130°C by soaking for 2 h and the degree of orientation increases from 0.46 to 0.73. Prolonged heating at 1130°C does not increase the density, but the degree of orientation continues to increase and

Fig. 1. Typical microstructures of textured (a) \( \text{SrBi}_4\text{Ti}_4\text{O}_{15} \), (b) \( \text{Bi}_2\text{O}_3\text{Sn}_0.5\text{Ti}_4\text{O}_{15} \), (c) \( \text{K}_0.5\text{Na}_0.5\text{NbO}_3 \), and (d) \( \text{BaTiO}_3 \).

Fig. 2. Densification and texture development in \( \text{BaBi}_4\text{Ti}_4\text{O}_{15} \) soaked between 1000 and 1130°C for 2 h and at 1130°C for various periods.
reaches 0.84 by soaking for 15 h. Figure 3 shows the microstructures of several specimens. The specimen heated at 1050°C for 2 h [Fig. 3(a)] is composed of large platelike grains and small equiaxed grains. The platelike grains are template grains and are aligned by shear stresses applied by tape-casting. All matrix grains change their shape to platelike at 1100°C [Fig. 3(b)], while the template grains do not grow to a considerable extent. BaBi₄Ti₄O₁₅ grains have a tendency to become platelike because of its anisotropic crystal structure. The crystallographic c-axis lies perpendicular to the plate face. Therefore, the orientation of c-axis can be judged from the orientation of the plate face. The matrix grains change their shape from equiaxed to platelike even in the absence of the template grains. In this case, the orientation of the platelike grains is random. When the template grains are present [Fig. 3(b)], the plate faces of the matrix grains surrounding the template grains align parallel to those of the template grains. The shape change of matrix grains from equiaxed to platelike under the presence of template grains is responsible for an increase in the degree of orientation from 0.53 to 0.68. A decrease in the thickness of the compact is responsible for an increase in the relative density from 0.65 to 0.89. The large pores in the specimen soaked at 1100°C are caused by the accumulation of pores distributed in the matrix by the formation of face-to-face contact of the platelike grains, but these pores disappear at 1130°C and at this stage the relative density is 0.94 and the degree of orientation is 0.73 [Fig. 3(e)]. Prolonged heating at 1130°C does not cause the growth of large template grains but forms groups of large platelike grains with mutually parallel alignment [Fig. 3(d)]. The size of large platelike grains is almost the same as that of the original template grains. Both the number of grain groups and the number of grains in each group increase with soaking time [Fig. 3(e)]. Finally, the grain groups impinge upon each other [Fig. 3(f)]. This microstructure development from Figs. 3(c) to 3(f) is caused by the growth of small platelike grains under the presence of the template grains. Misoriented matrix grains are consumed by the growing grains with the same orientation as that of the template grains, resulting in an increase in the degree of orientation from 0.73 to 0.84. Similar microstructure development is observed in SrBi₄Ti₄O₁₅ and CaBi₄Ti₄O₁₅.33),53)

The orientation of the c-axis of each grain can be easily determined from the orientation of the plate face, but that of the a-axis cannot be determined by observing the grain shape. Electron back-scatter diffraction (EBSD) can determine the three-dimensional orientation of each grain and grain boundary structure.4) Figure 4 shows one example of EBSD image. The specimen is BaBi₄Ti₄O₁₅ containing 5 vol% template grains (not 20 vol% for the specimen shown in Fig. 3) and heated at 1130°C for 10 h.55) Figure 4(a) is an ordinary EBSD image showing the three-dimensional orientation of grains. The c-axis of many grains is perpendicular to the casting direction but the grains with face-to-face contact do not have their c-axis in the same direction. The boundary between these grains is the twist boundary. The grain boundary energy is dependent on the twist angle. Grain boundaries are not the positions at which the atomic arrangement is completely disordered. Among them, the coincidence site lattice (CSL) has relatively high order and low grain boundary energy.56) Figure 4(b) shows the grain boundary structure. The boundaries shown by the red lines are CSL. The degree of order is expressed by the Σ value, and in general, the boundary with a small Σ value has low grain boundary energy. The population of boundaries with various Σ values is shown in Table 1 for the specimen shown in Fig. 4. About 10% of grain boundaries are CSL with various Σ values. This indicates that the population of grains with low grain boundary energy is low, and these grains can grow at the expense of neighboring grains with high grain boundary energy.
2.2 Bi$_4$Ti$_3$O$_{12}$

The shape change of the matrix grains from equiaxed to platelike is also observed in Bi$_4$Ti$_3$O$_{12}$, but the platelike grains originated from not only the template grains but also the matrix grains grow in the final stage of sintering.\(^{57}\) The growth of the platelike grains in textured Bi$_4$Ti$_3$O$_{12}$ is also reported.\(^{58,59}\) Here, the texture development in the Bi$_4$Ti$_3$O$_{12}$ specimen containing 1 vol% template grains is focused on to show the role of the growth of template grains on the texture formation.\(^{58,59}\) In fact, 1 vol% is not sufficient for texture formation in MBi$_4$Ti$_4$O$_{15}$ (M = Ca, Sr, and Ba). Figure 5 shows the microstructures of the Bi$_4$Ti$_3$O$_{12}$ specimen containing 1 vol% template grains and sintered at various temperatures for 2 h. The specimen sintered at 900°C is composed of large platelike template grains and small equiaxed matrix grains. The relative density is 0.85, and the degree of orientation is 0.21. The matrix grains change their shape to platelike at 950°C, and the relative density reaches 0.95. The degree of orientation is still low at 0.31. Because the template content is low, the orientation of the matrix grains far from the template grains is random as judged from the orientation of plate faces. The number and size of large platelike grains start to increase at above 1000°C, and the degree of orientation abruptly increases to 0.91 at 1000°C and 0.94 at 1050°C. In the BaBi$_4$Ti$_4$O$_{15}$ case, the growth of the template grains is hardly observed. However, a comparison of the microstructures of Bi$_4$Ti$_3$O$_{12}$ at 950, 1100, and 1150°C clearly indicates the growth of the platelike grains in both the radial and thickness directions. The growth of large platelike grains is responsible for an increase in the degree of orientation.

2.3 Bi$_{0.5}$(Na$_{1−x}$K$_x$)$_{0.5}$TiO$_3$

Bi$_{0.5}$(Na$_{1−x}$K$_x$)$_{0.5}$TiO$_3$ is the first textured lead-free piezoelectrics by the RTGG method and is extensively examined among various Bi$_{0.5}$Na$_{0.5}$TiO$_3$-based materials,\(^{57}\) such as Bi$_{0.5}$Na$_{0.5}$TiO$_3$−BaTiO$_3$, Bi$_{0.5}$(Na$_{0.5}$TiO$_3$−Bi$_{0.5}$K$_{0.5}$TiO$_3$−BaTiO$_3$, Bi$_{0.5}$Na$_{0.5}$TiO$_3$−BaTiO$_3$−K$_x$Na$_{0.5}$NbO$_3$, and Bi$_{0.5}$Na$_{0.5}$TiO$_3$−BaZrO$_3$.\(^{60−63}\) Bi$_{0.5}$(Na$_{1−x}$K$_x$)$_{0.5}$TiO$_3$ has the perovskite structure, and anisotropy in the crystal structure is small. Therefore, it is difficult to obtain template grains having a platelike or needlelike shape by molten salt or hydrothermal (solvothermal) synthesis. For this material, the RTGG method is employed to introduce texture.\(^{59}\) Although several materials can be used as the reactive template for Bi$_{0.5}$Na$_{0.5}$TiO$_3$-base materials,\(^{59,60,61,68}\) the microstructure development in Bi$_{0.5}$(Na$_{1−x}$K$_x$)$_{0.5}$TiO$_3$ prepared using Bi$_{0.5}$Ti$_2$O$_5$ is explained here. The reactive template is platelike Bi$_{0.5}$Ti$_2$O$_5$, and the complementary compounds are Bi$_2$O$_3$, Na$_2$CO$_3$, K$_2$CO$_3$, and TiO$_2$. A green compact is prepared by tape-casting. In the green compact, the platelike Bi$_{0.5}$Ti$_2$O$_5$ grains are aligned with their plate face parallel to the casting direction. The green compact is calcined at an appropriate temperature to form Bi$_{0.5}$(Na$_{1−x}$K$_x$)$_{0.5}$TiO$_3$. The platelike Bi$_{0.5}$Ti$_2$O$_5$ grains are transformed to platelike Bi$_{0.5}$(Na$_{1−x}$K$_x$)$_{0.5}$TiO$_3$ grains dispersed in small equiaxed Bi$_{0.5}$(Na$_{1−x}$K$_x$)$_{0.5}$TiO$_3$ grains. In this stage, the platelike grain is not a single crystal but a polycrystal or aggregate of subgrains as shown in Fig. 6.\(^{69}\) When heated at higher temperatures, the surfaces of the platelike grain become smooth, indicating that the polycrystalline grain changes to a single-crystalline grain. Because the topotactic crystallographic orientation is preserved during the transformation from Bi$_{0.5}$Ti$_2$O$_5$ to Bi$_{0.5}$(Na$_{1−x}$K$_x$)$_{0.5}$TiO$_3$, the subgrains in the polycrystal have the same crystallographic orientation and coalesce into one grain, i.e., the single-crystalline grain.

Figure 7 shows the microstructure of the Bi$_{0.5}$(Na$_{0.5}$K$_{0.5}$)$_{0.5}$TiO$_3$ specimen with a template content of 20 vol% sintered at various temperatures for 2 h, and Fig. 8 shows the density and the degree of orientation.\(^{65}\) The polycrystalline platelike grains change to the single-crystalline grains with smooth surfaces at...
1000°C, with their plate face parallel to the casting direction [Fig. 7(b)]. The (100) axis is perpendicular to the plate face.

The thickness of the platelike grains increases as the sintering temperature is increased from 1000 to 1050°C, and the degree of orientation increases from 0.22 to 0.52 in this temperature interval. However, the relative density is 0.68 at 1000°C and 0.77 at 1050°C. Pores pin the migration of grain boundaries, and grain growth by the grain boundary migration is normally observed in compacts with a relative density higher than 0.9. Therefore, the grains in the specimen shown in Fig. 7(c) grow by a mechanism other than grain boundary migration. This aspect will be addressed in the next section. At 1100°C, almost all the matrix grains are consumed and the degree of orientation reaches 0.70.

2.4 K$_{0.5}$Na$_{0.5}$NbO$_3$

Research on alkali niobates is stimulated by the finding of high piezoelectric properties in the (K,Na,Li)(Nb,Ta,Sb)O$_3$ system.

Textured materials are prepared by the RTGG method using platelike NaNbO$_3$ grains as the reactive template, and are composed of aligned cuboidal grains with a relatively narrow grain size distribution. On the other hand, a non-textured material is composed of randomly oriented cuboidal grains with a wide size distribution.

The basic composition is in the K$_{0.5}$Na$_{0.5}$NbO$_3$–LiTaO$_3$ solid solution. K$_{0.5}$Na$_{0.5}$NbO$_3$ is the solid solution between KNbO$_3$ and NaNbO$_3$, and is located near the morphotropic phase boundary.

Takao et al. examined the microstructure development in a rather simple system, K$_{0.5}$Na$_{0.5}$NbO$_3$ with a sintering aid CuO.

Kikuchihara and Kimura examined the microstructure development in K$_{0.5}$Na$_{0.5}$NbO$_3$ with and without CuO. Here, the microstructure development in K$_{0.5}$Na$_{0.5}$NbO$_3$ without CuO is shown in Fig. 9. The specimen is prepared by the RTGG method using platelike NaNbO$_3$ grains as the reactive template and equiaxed KNbO$_3$ and NaNbO$_3$ grains as the complementary compounds. The template content is designed to be 5 vol%.

The specimen is calcined at 600°C for 2 h and then sintered at various temperatures for 2 h. The microstructure of the specimen soaked at 1000°C is composed of large platelike and small equiaxed grains. The surface of the platelike grains becomes flat, and the shape of the matrix grains is cuboidal at 1000°C. Large cuboidal grains start to form at 1050°C, and the number and the size of large cuboidal grains increase at 1100°C. Finally, all grains become cuboidal at 1150°C. The degrees of orientation are 0.36, 0.71, and 0.90 at 1000, 1050, and 1100°C, respectively. A comparison of the microstructures with the degree of orientation indicates that the formation of large cuboidal grains is responsible for the texture formation.

3. Microstructure development during initial stage of sintering

In an ordinary sintering theory, the microstructure development in each stage of sintering is explained as (1) neck growth and formation of continuous pores on grain edges and corners in the initial stage, (2) reduction in the volume of continuous pores and formation of closed pores in the intermediate stage, and (3) reduction in the volume of closed pores and grain growth in the final stage.

However, faceting of grains occurs in the initial stage and normal neck growth is hardly observed, as shown in Figs. 3, 5, 7, and 9. This section focuses on the microstructure development in the initial stage of sintering.

In the cases of bismuth layer-structured ferroelectrics, the matrix grains change their shape from equiaxed to platelike in an initial stage of sintering [Fig. 3(b) and 5(b)]. The template grain determines the orientation of the platelike matrix grains, which just touch the template grain by forming twist boundaries between the template and matrix grains. These boundaries cannot be formed by neck growth. Close examination of the microstructures gives an insight into the mechanism of the formation of twist boundaries.

Figure 10 shows the microstructures of the Bi$_4$Ti$_3$O$_{12}$ specimen sintered at 960 and 970°C for 2 h.
terraces, hereafter. If the terrace is the neck between the template and matrix grains, its size might be smaller than that of the matrix grain. However, the terrace has a larger size than the matrix grain and increases in size as the sintering proceeds.

The direction of material transport is clearly shown by a model experiment using platelike Bi$_4$Ti$_3$O$_12$ grains as the template and equiaxed SrBi$_4$Ti$_4$O$_13$ grains as the matrix. **Figure 11** shows the microstructure of the specimen in an initial stage of sintering. The terraces having a thin square shape form between the template and matrix grains. The material composed of the terraces is SrTi$_4$Bi$_4$O$_13$. The sides of the terraces are parallel to each other, indicating that the crystallographic orientation of the terraces is the same as that of the template Bi$_4$Ti$_3$O$_12$ grain. These results indicate that the terrace is not formed by neck growth.

**Figure 12** schematically illustrates the shape change of the matrix grain in an initial stage of sintering of bismuth layer-structured ferroelectrics. At first, the matrix grain adheres to the template grain, and forms the grain boundary between these grains [Fig. 12(a)]. The orientation of the c-axis of the template grain is perpendicular to this grain boundary, but that of the matrix grain cannot be specified because the orientation of the matrix grains is random. The grain boundary structure is (001)$_{\text{Temp}}$//$(hk)$$_{\text{M}}$, implying that (001) of the template grain adheres to (hk) of the matrix grain along the grain boundary. Then, the terrace forms between the template and matrix grains [Fig. 12(b)]. The structure of the grain boundary between the template grain and the terrace (Terr) is (001)$_{\text{Temp}}$//$(001)_{\text{Terr}}$. The orientation of the a-axis is not the same for the template grain and terrace, and this boundary is twist boundary.

The formation of terraces is also observed in Bi$_{0.5}$-(Na$_{0.5}$K$_{0.5}$)$_{0.5}$TiO$_3$. **Figure 13** shows the microstructure observed in textured Bi$_{0.5}$(Na$_{0.5}$K$_{0.5}$)$_{0.5}$TiO$_3$ soaked at 1000°C for 2 h. The microstructure at low magnification is shown in Fig. 7(b).] Several hills are observed on the platelike template grain and a groove exists half-way up each of the hills. The part below the groove is the terrace, and the matrix grain remains above the groove.

The boundary between the terrace and the matrix grain, i.e., the groove shown in Fig. 13, is not as clear as that observed in Bi$_4$Ti$_3$O$_12$ (Fig. 10). Several model experiments using hetero-templates are conducted to clearly show the presence of terraces in the Bi$_{0.5}$(Na$_{1-x}$K$_x$)$_{0.5}$TiO$_3$ system. (1) Platelike SrBi$_4$Ti$_4$O$_13$ grains used as the template give a (100) texture to matrix Bi$_{0.5}$(Na$_{1-x}$K$_x$)$_{0.5}$TiO$_3$. The film-like terraces of Bi$_{0.5}$-(Na$_{0.5}$K$_{0.5}$)$_{0.5}$TiO$_3$ form on the SrBi$_4$Ti$_4$O$_13$ templates. (2) Equiaxed Bi$_{0.5}$(Na$_{0.5}$K$_{0.5}$)$_{0.5}$TiO$_3$ grains are sprinkled on the surface of a SrTiO$_3$ single-crystalline plate, and the composite is heated. Thin square sheets of Bi$_{0.5}$(Na$_{0.5}$K$_{0.5}$)$_{0.5}$TiO$_3$ (terraces) develop on the single-crystalline plate. The terraces are oriented in an ordered fashion, with the edges parallel to each other. This suggests that the terraces have the same crystallographic orientation as the single-crystalline plate. (3) Bi$_{0.5}$Na$_{0.5}$TiO$_3$ grains are dispersed in 2-methoxyethanol and spin-coated on a polished (100) surface of a SrTiO$_3$ single-crystalline plate. The specimen before heating consists of the SrTiO$_3$ plate and the Bi$_{0.5}$Na$_{0.5}$TiO$_3$ grain layer. The grain layer disappears by heat treatment, leaving a Bi$_{0.5}$Na$_{0.5}$TiO$_3$ single-crystalline, epitaxial film of approximately 1 μm thickness. Evidences (1)–(3) using the hetero-templates indicate that the material consisting of the terrace is supplied from the matrix grains and that the orientation of the terrace is determined by that of the template.

In the case of Bi$_{0.5}$(Na$_{1-x}$K$_x$)$_{0.5}$TiO$_3$, the template grain and terraces have a topotactic crystallographic orientation. Therefore, there is no grain boundary between the template grain and terraces. This means the growth of the template grain. However, this grain growth is not achieved by the migration of grain boundaries. Maurya et al. proposed the material transport via a liquid phase,
state spreading. Microscopically, a direct observation of material transport from a small TiO₂ grain onto the surface of a large TiO₂ grain suggests the material transport mechanism; i.e., the atoms on the surface of matrix grains are transported to the surface of template grain by the flow of groups of atoms. The growth of the template grains in the compacts with low relative densities is caused by this mechanism.

4. Growth of faceted grains

As sintering proceeds, the compacts densify and the pore sizes decrease. This reduces pinning and drag effects of pores on the grain boundary migration. In general, grain growth becomes extensive in compacts with a relative density more than 0.9. Thus, the growth of grains with the same orientation as the template grains results in a further increase in the degree of orientation in the final stage of sintering. Therefore, grain growth by the migration of grain boundaries is an important process. In the cases of BaBi₄Ti₄O₁₅, Bi₄Ti₃O₁₂, Bi₅.5(Na₁₋ₓKₓ)₀.5TiO₃, and K₀.5Na₀.5NbO₃, the grains have faceted boundaries. For these materials, attention must be paid to the effect of grain boundary structure on the grain growth behavior. The migration of grain boundaries is strongly influenced by the grain boundary structure at an atomic level.

Grain growth is caused by addition of atoms (ions) to a growing grain from surrounding grains. In this respect, a material transport route is similar to that occurring in single crystal growth from a liquid phase; that is, (1) adsorption of an atom on a crystal surface, (2) diffusion of the adsorbed atom over the surface, (3) attachment of the atom to a step, (4) diffusion along the step, and (5) integration into the crystal at a kink. Therefore, the growth rate is dependent on the number density of steps, which is determined by the step energy and temperature. The step energy is the energy necessary to form a step and is dependent on the surface orientation. When the step energy is high, the number density of steps is high and the chance of adsorbed atoms to integrate into the crystal is high. Furthermore, the integration of the atoms does not change the number density of steps. Thus, this grain boundary has a high growth rate and the migration rate of grain boundaries is linearly proportional to the driving force for grain growth. This kind of grain surface is called atomically rough, atomically disordered, defaced, or nonsingular. In this paper, “atomically rough” is used. When the step energy is high, the number density of steps is low. Furthermore, growth proceeds by the lateral movement (parallel to the surface) of the steps. When a step reaches the edge of the surface, it disappears. A new step must be formed on the flat surface to continue grain growth. This process requires high activation energy like the twodimensional nucleation in the single crystal growth. Thus, this boundary has a low growth rate and the migration rate is not linearly proportional to the driving force for grain growth. This kind of grain surface is called atomically smooth, atomically ordered, faceted, or singular. In this paper, “atomically smooth” is used.

The grain boundary structure is not determined simply by the material, and processing conditions such as temperature, atmosphere, and dopant induce great effects. Therefore, the grain boundary structure must be determined for each individual specimen. The grain boundary structure at an atomic level can be characterized by direct observation by transmission electron microscopy. However, this procedure is rather laborious and great skill is required. Fortunately, the grain boundary structure at an atomic level can be estimated from the macroscopic grain shape.

The grain boundary structure at an atomic level is closely related to anisotropy in the grain boundary (surface) energy, which determines the macroscopic grain shape. For simplicity, only one grain is considered here. Therefore, the grain boundary energy is equivalent to the surface energy. The anisotropy in surface energy is depicted by the Wulff plot (Fig. 14). The surface energy is expressed by a vector; the direction of the vector is perpendicular to the vector. The length of the vector is proportional to the surface energy of this surface. The Wulff plot is a locus of the apex of the vector. An equilibrium grain shape is derived from the Wulff plot. A vertical plane is drawn at the apex of each vector, and the innermost envelope of these planes constructs the equilibrium grain shape. Conversely, information on the anisotropy in surface energy is obtained from the grain shape. If a grain is faceted, there is a cusp in the Wulff plot in the direction perpendicular to this surface. If the cusp is shallow, the center of the face is faceted but the corners and edges are rounded. If the cusp is deep, the corners and edges are sharp. Therefore, the surface morphology gives information on the depth of cusp in the Wulff plot.

The surface structure at an atomic level is determined by the magnitude of step energy. Figure 15(a) shows the structures of (001) and (hkl), which inclines from (001) by angle θ. The (hkl) face has steps, and the atoms on the steps have more missing bonds than those on (001), resulting in higher surface energy. This energy is called step energy. The step energy is depicted in the Wulff plot; the difference between the vectors (001) and (hkl) in Fig. 15(b) is proportional to the step energy for (001). Therefore, a deeper cusp in the Wulff plot means higher step energy. Consequently, a surface with high step energy is a surface with an atomically smooth structure and a macroscopically faceted surface. Thus, the faceted grains in BaBi₄Ti₄O₁₅, Bi₄Ti₃O₁₂, Bi₅.5(Na₁₋ₓKₓ)₀.5TiO₃, and K₀.5Na₀.5NbO₃ have high step energy and atomically smooth boundary structure.

In the final stage of sintering, grain growth is caused by grain boundary migration. An atomically rough boundary is ordinarily rounded and moves toward the center of curvature. The migration of an atomically smooth boundary is different from that of an atomically rough boundary. Because the activation
energy for grain boundary migration is high, high driving force is necessary for grain growth. The relation between the driving force and an intrinsic growth rate is shown in Fig. 16. The intrinsic growth rate is the growth rate in a fully dense compact; there are no pores to pin and drag the grain boundary. There is critical driving force for an appreciable growth rate (below the critical value, the growth rate is essentially zero). Kang et al. categorized the grain growth behavior into four types in terms of the relative values of the critical and maximum driving forces, $\Delta g_c$ and $\Delta g_{\text{max}}$, respectively: (1) normal grain growth ($\Delta g_c = 0$), (2) pseudo-normal grain growth ($0 < \Delta g_c < \Delta g_{\text{max}}$), (3) abnormal grain growth ($0 < \Delta g_c \sim \Delta g_{\text{max}}$), and (4) stagnant grain growth ($\Delta g_c \gg \Delta g_{\text{max}}$). This behavior has been experimentally confirmed for various systems. An excellent example is observed in a model system of BaTiO$_3$; the grain boundary structure is continuously controlled by oxygen partial pressure. The criteria using the relative values of the critical and maximum driving forces can be applicable to the system with mono-modal grain size distribution. In the TGG cases, the grain size distribution is bi-modal, and the maximum driving force is equivalent to the driving force of the template grains. The driving force for grain growth is caused by the reduction in free energy. The free energy is a function of energy and entropy. In the grain growth process, the energy term is dominant over the entropy term. Therefore, grain growth is driven by a reduction in the total boundary energy. In the present cases, the important origins of the reduction in the total boundary energy are a decrease in the grain boundary area, the substitution of low-energy boundaries for high-energy boundaries, and the approach of the grain shape to an equilibrium shape. The first origin results in the growth of large grains at the expense of small grains. Therefore, the driving force caused by the decrease in the grain boundary area is equivalent to that caused by the difference in grain sizes. The importance of the last origin is exemplified in the shape change of the grains in the bismuth layer-structured ferroelectrics. The matrix grains are prepared by solid-state reaction and have an irregular shape. The grain shape changes to platelike during sintering [Fig. 3(b)]. This shape change also occurs in the compact without the template grains. Therefore, the deviation from an equilibrium shape contributes to the driving force for grain growth.

5. Mechanisms of microstructure development in connection with texture formation

Sections 2 and 3 illustrate the microstructure development in textured BaBi$_4$Ti$_4$O$_{15}$, Bi$_4$Ti$_3$O$_{12}$, Bi$_8$Sc(Na$_{1-x}$K$_x$)$_{5-x}$Ti$_5$O$_{27}$, and K$_{0.5}$Na$_{0.5}$NbO$_3$. These materials are composed of faceted grains. Section 4 provides the basic concept of the growth of the faceted grains. In this section, the mechanisms of the microstructure development are discussed.

5.1 Bismuth layer-structured ferroelectrics

In Bi$_4$Ti$_3$O$_{12}$, the template grains grow both in the radial and thickness directions (Fig. 5) but they do not grow in BaBi$_4$Ti$_4$O$_{15}$ (Fig. 3). Figure 17 shows the shape of grains prepared by molten salt synthesis. The plate faces are smooth for both materials. The side faces are linear in the top view for BaBi$_4$Ti$_4$O$_{15}$, indicating that they are atomically smooth. On the other hand, the side faces are rounded for Bi$_4$Ti$_3$O$_{12}$, i.e., the side faces of platelike Bi$_4$Ti$_3$O$_{12}$ grains are atomically rough. The critical driving force for the migration of the side faces of Bi$_4$Ti$_3$O$_{12}$ is small as compared to that for the side faces of BaBi$_4$Ti$_4$O$_{15}$ as well as the plate faces of Bi$_4$Ti$_3$O$_{12}$ and BaBi$_4$Ti$_4$O$_{15}$. The size difference between the template and matrix grains derives enough driving force for the migration of the side faces for Bi$_4$Ti$_3$O$_{12}$. The platelike Bi$_4$Ti$_3$O$_{12}$ grains increase their dimension in the radial direction. This results in an increase in the aspect ratio, i.e., a deviation from the equilibrium shape. The growth in the radial direction derives the driving force for the growth in the thickness direction, which exceeds the critical driving force for the migration of plate face. Thus, the platelike Bi$_4$Ti$_3$O$_{12}$ grains continue to grow, and the growth of the template grains at the expense of the matrix grains is the origin of texture formation.

In BaBi$_4$Ti$_4$O$_{15}$, the driving force caused by the size difference between the template and matrix grains is less than the critical driving force both in the radial and thickness directions. The growth behavior is in the stagnant grain growth region for the template grains. The microstructure development is not caused by the growth of the template grains but by the shape change and growth of the matrix grains. The origins of the driving force for these processes are the substitution of low-energy boundaries for high-energy boundaries and the approach to the equilibrium shape. Figure 18 schematically illustrates the shape change and growth of the matrix grains in the vicinity of the template grains. In the compact in an initial stage of sintering, the terraces form on the template grains (Fig. 12) due to the formation of low-energy boundary (twist boundary) between the template grains and the terraces as well as the tendency of the matrix grains to have a platelike shape. Then, the matrix grains with irregular shapes just surrounding the terraces start to change their shape to platelike using the surfaces of the terraces. Thus, the terraces form around the template grains [Fig. 18(b)]. The grain boundaries between the template grains and terraces and between the terraces are twist boundaries with various twist angles, i.e., various boundary energies. The next step is the growth of the terraces attached to the template grains. The terrace with the lowest grain boundary
energy [grain 1 in Fig. 18(b)] starts to grow parallel to the surface of the template grain. In this case, the driving force is derived by the substitution of high-energy boundaries by the low-energy boundary. Thus, a thin grain [grain 1 in Fig. 18(c)] is formed on the template grain. Because the aspect ratio of the thin grain is far deviated from an equilibrium value, grain 1 has the driving force for growth toward the thickness direction. This driving force for growth exceeds the critical value. Thus, grain 1 increases its thickness and reaches the equilibrium aspect ratio [Fig. 18(d)]. Then, the driving force decreases to the critical value and the growth of grain 1 ceases. There are several small terraces on grain 1 and the terrace with the lowest grain boundary energy [grain 2 in Fig. 18(d)] starts to grow to increase its diameter [Fig. 18(e)] and thickness [Fig. 18(f)]. Thus, grain groups form with mutually parallel orientation [Fig. 18(d)], and this is the origin of the texture formation in BaBi$_4$Ti$_4$O$_{15}$. The same situation is also observed in CaBi$_4$Ti$_4$O$_{15}$ and SrBi$_4$Ti$_4$O$_{15}$.

5.2 Perovskites

In Bi$_{0.5}$(Na$_{1-x}$K$_x$)$_{0.5}$TiO$_3$ (x between 0.1 and 0.5) and K$_{0.5}$Na$_{0.5}$NbO$_3$, the growth of the template grains is responsible for the texture formation, but the relative growth rates between the template and matrix grains are different. In K$_{0.5}$Na$_{0.5}$NbO$_3$ (Fig. 9), large cuboidal grains with the aspect ratio of about unity emerge at 1100°C [Fig. 9(c)]. Figure 19 shows the microstructures of the K$_{0.5}$Na$_{0.5}$NbO$_3$ specimens with and without the template grains, soaked at 1085°C for 2 h. This indicates that the driving force for the growth of the matrix grains is less than the critical driving force and the growth behavior of the matrix grains is in the stagnant region. The template grains have higher driving force than the matrix grains due to the deviation from the equilibrium shape (the template grains are platelike) as well as the size difference between the template and matrix grains. The template grains can grow at the expense of the matrix grains, if the mobility is high and the pore volume is low. Takao et al. reported that the elimination of pores to less than 10 vol% is necessary for the growth of the template grains. This means that the pores hinder the grain boundary migration. When the pore volume decreases to less than 10 vol%, the pinning and drag effects of pores diminish. The intrinsic mobility of grain boundaries is determined by temperature. The template grains have sufficient mobility at a temperature at which the relative density reaches a value more than 0.9 within a reasonable period of time. Thus, the template grains can grow to cuboidal grains in a short period of time. Prolonged heating results in slow growth of the cuboidal grains. The growth of the cuboidal grains ceases when the growing grains collide with other cuboidal grains and the porous matrix regions.

In Bi$_{0.5}$(Na$_{1-x}$K$_x$)$_{0.5}$TiO$_3$, the matrix grains also grow with the growth of the template grains. This indicates that the grain growth behavior is in the pseudo-normal growth region for both the template and matrix grains and the driving force for growth of both grains is fairly higher than the critical value. The growth of matrix grains reduces the driving force for the growth of the template grains. Thus, the template grains cannot have enough time to grow to become cuboidal (the equilibrium shape). The effectiveness of the template grains to consume the matrix grains is limited only in the vicinity of the template grains. Therefore, a template content of 20 vol% is necessary for effective consumption of the matrix grains. In contrast, a template content of 5 vol% is sufficient for K$_{0.5}$Na$_{0.5}$NbO$_3$.

6. Processing design of textured ceramics

It is necessary to optimize the processing procedure to prepare highly textured piezoelectrics with controlled microstructure. The processing parameters include selections of the chemical composition including additives, powder characteristics of the template and matrix grains, template content, and sintering conditions. Ordinarily, the chemical composition is determined from the demand of applications. The phenomena occurring during sintering are caused by the material transport by diffusion, and the diffusion rate is a function of sintering temperature. Therefore, the sintering temperature is determined to obtain the products in a reasonable period of time. If the sintering temperature is above an optimum temperature, over-firing deteriorates the rates the properties of the products. The first half of this section addresses the effects of the sizes of the template and matrix grains and the template content on texture formation. In the latter half, topics relating to the chemical compositions of the specimens are addressed.

6.1 Template grain size

The size of template grains is important in the microstructure development from several aspects. It determines (1) the degree of alignment of the template grains in the cast sheets, (2) the number density of the template grains, (3) the size difference between the template and matrix grains, and (4) the size of the grains in textured MBi$_4$Ti$_4$O$_{15}$ (M = Ca, Sr, and Ba).

The template grains must be aligned in the right direction in the cast sheets. The origin of the grain alignment is the shear stresses exerted on the platelike grains during casting. Although there is
no report available on the relation between the size of platelike grains and the degree of grain alignment in the cast sheets, it is the author's experience that the degree of grain alignment in the cast sheets is increased as the template grain size increases.65)

When the growth of template grains is slow, the size of the template grains determines the size of grains in the final products. In MBi4Ti4O15, the template grains do not grow, and the shape change and growth of the matrix grains are the main routes of the microstructure development. The final products are composed of groups of grains with mutually parallel orientation, and the size of the grains is almost the same as that of the template grains; i.e., the template grains determine the size of grains in the final products (Fig. 3). Therefore, the size of grains in textured MBi4Ti4O15 can be controlled by selecting the template grain size.53)

In the preparation of Bi0.5(Na1-xKx)0.5TiO3 (0.1 < x < 0.5) by the RTGG process, the Bi4Ti3O12 grain size determines the template grain size. Figure 20 shows the microstructure of the Bi0.5(Na0.5K0.5)0.5TiO3 compacts soaked at 1100°C for 2 h, the same conditions as that shown in Fig. 7(d).65) These three specimens are prepared under the same conditions except for the Bi4Ti3O12 size. The Bi4Ti3O12 grains are prepared at 950°C [Fig. 7(d)], 1050°C [Fig. 20(a)], and 1130°C [Fig. 20(b)]. The size of Bi4Ti3O12 grains increases as the preparation temperature is increased.82) As the Bi4Ti3O12 grain size increases, the template Bi0.5(Na0.5K0.5)0.5TiO3 grain size increases. In these cases also, the template grain size determines the size of grains in the final products.65) In addition, the template grain size determines the rate of texture formation. When the template grain size is small, all matrix grains are consumed by soaking at 1100°C for 2 h [Fig. 7(d)], but a fairly large amount of the matrix grains remains in the cases using medium- and large-sized template grains (Fig. 20). An increase in the sintering temperature increases the growth rate of the template grains and accelerates the consumption of the matrix grains. The matrix grains disappear by soaking at 1200°C for 2 h for medium-sized template grains, but still exist in the specimen containing large-sized template grains.65) This example indicates that the number density of template grains is important to obtain highly textured Bi0.5(Na0.5K0.5)0.5TiO3 and the use of small-sized template grains is preferable.85)

The reverse result is observed in Bi0.5(Na0.5K0.5)0.5TiO3 (0.1 < x < 0.5).83) In this case, the step energy is lower than that for Bi0.5(Na0.5K0.5)0.5TiO3, and both the template and matrix grains increase their sizes during sintering. This decreases the driving force for the growth of the template grains derived from the difference between the template and matrix grain sizes. Enough size difference can be maintained when large-sized template grains are used, resulting in a high degree of orientation. When small-sized template grains are used, the size difference is no more sufficient to cause the selective growth of template grains and textured Bi0.5-(Na0.5K0.5)0.5TiO3 with a high degree of orientation is hardly obtained.83)

6.2 Matrix grain size
The matrix grain size influences the texture development from two aspects. One aspect relates to the orientation of template grains in a green sheet made by tape-casting. Large matrix grains hinder the alignment of template grains. One example is reported for CaBi4Ti4O15.27),84) When the template grains (20 vol %) with a diameter of about 5 μm are used, the matrix grains with an average grain diameter of about 0.5 and 1.0 μm result in the degree of orientation of 0.57 and 0.25, respectively, in the calcined compacts.

Another aspect relates to the formation of the grain groups. Figure 21 shows the microstructures of SrBi4Ti4O13 prepared using platelike grains with a diameter of about 10 μm, thickness of about 0.4 μm, and a template content of 20 vol %.85) When the matrix grains with an average size of 0.32 μm are used, groups of platelike grains with the same orientation are formed and the degree of orientation reaches 0.90 by soaking at 1200°C for 10 h [Fig. 21(a)]. However, groups of platelike grains with the same orientation do not extensively form in the specimen using the matrix grains with an average grain size of 1.5 μm [Fig. 21(b)]. The degree of orientation is 0.24 for the specimen soaked at 1200°C for 10 h. Small matrix grains change their shape from equiaxed to platelike under the influence of the template grains, resulting in a high degree of orientation. Large matrix grains, on the other hand, change their shape without the influence of the template grains, and do not contribute to texture formation.

The disadvantage of using large matrix grains is also observed in Bi0.5(Na0.5K0.5)0.5TiO3 prepared by the RTGG process.65) The specimen shown in Fig. 7 has been prepared using TiO2 with an average grain size of 70 nm. When the specimen is prepared under the same conditions except for TiO2 with an average grain size of 150 nm, the density and the degree of orientation decrease. For example, the specimen shown in Fig. 7 has a relative density of 0.97 and the degree of orientation of 0.83 by soaking at 1150°C for 2 h (Fig. 8) but the specimen using large TiO2 grains has values of 0.75 and 0.60, respectively, for these quantities.

6.3 Template content
The template content is determined from the growth behavior of the template grains. When the growth of the template grains is fast, as in Bi2Ti4O12, the template grains can consume the matrix grains present far from the template grains, and a high template content is not necessary. In an extreme case, 1 vol % of template
content is sufficient to obtain highly textured Bi$_4$Ti$_3$O$_{12}$ (Fig. 5). The grain size in the final product is determined by the sintering conditions, i.e., soaking temperature and period.\(^{56}\)

In K$_{0.5}$Na$_{1-x}$Nb$_x$O$_3$, the template grains with 0.5 μm thickness and 10–15 μm side length grow to cuboidal grains of size 10–20 μm.\(^{56}\) The growth perpendicular to the plate faces can consume a fairly large volume of the matrix grains and a template content of 5 vol% is normally used.\(^{60,62,63,66}\)

When the growth of the template grains is stagnant or slow, the template grains consume a small volume of the matrix grains. In Bi$_2$Ti$_2$O$_7$ (M = Ca, Sr, and Ba) the texture is obtained by the formation of groups of grains with mutually parallel alignment adjacent to the template grains, and a suitable template content is necessary to obtain a highly textured material under reasonable sintering conditions. For the Bi$_2$Ti$_2$O$_7$ cases, 20 vol% template content is used.\(^{33,51,66}\) In Bi$_2$Ti$_2$(Na$_{1-x}$K$_x$)$_2$O$_3$ (0.1 < x < 0.5), the matrix grains are consumed by slow growth of the template grains. Therefore, the template grains can consume the nearby matrix grains within a reasonable soaking period, and the number density of the template grains is important to ensure total consumption of the matrix grains. One example is reported for Bi$_2$Ti$_2$(Na$_{0.35}$K$_{0.15}$)$_2$O$_3$.\(^{66}\) By soaking at 1200°C for 10 h, the degree of orientation reaches 0.89 when the template content is 20 vol%. This value decreases to 0.77 and 0.62 for template contents of 10 and 5 vol%, respectively.

### 6.4 Formation of template grains in RTGG

In the RTGG process, the template grains are formed during calcination by the in situ reaction between the reactive template and complementary compounds. The atoms in the complementary compounds must diffuse into the reactive template grains. If the direction of diffusion is opposite, the reactive template grains dissolve in the matrix phase and the texture does not form. This phenomenon is observed in the Bi$_2$Ti$_2$(Na$_{0.35}$K$_{0.15}$)$_2$O$_3$–Pb(Zr$_{0.1}$Ti$_{0.9}$)O$_3$, Bi$_2$Na$_{0.5}$Ti$_2$O$_7$–BaTiO$_3$, and Bi$_2$Na$_{0.5}$Ti$_2$O$_7$–BiFeO$_3$ systems.\(^{89,91}\) Interesting phenomena are observed in K$_{0.5}$Na$_{0.5}$NbO$_3$. In the preparation of textured K$_{0.5}$Na$_{0.5}$NbO$_3$ by the RTGG method, the reactive template consists of plate-like NaNbO$_3$ grains derived from Bi$_2$Na$_2$Nb$_2$O$_6$ by two-step molten salt synthesis.\(^{16,32}\) The plate-like NaNbO$_3$ grains can be prepared by single-step molten salt synthesis.\(^{92,93}\) Although the NaNbO$_3$ grains prepared by the single-step method provide reproducible results in the texture formation, those prepared by the single-step method are irreproducible.\(^{35}\) Figure 22 shows the microstructures of the specimens for different experimental runs using the NaNbO$_3$ grains prepared by the single-step method. In both specimens, the NaNbO$_3$ reactive template grains dissolve in the matrix phase, leaving large voids. In the specimen shown in Fig. 22(a), dense regions develop around large voids. These regions are formed on the NaNbO$_3$ reactive template grains before the dissolution and have the same orientation as that of the NaNbO$_3$ grains. These regions act as the template, resulting in the formation of textured K$_{0.5}$Na$_{0.5}$NbO$_3$. In the specimen shown in Fig. 22(b), on the other hand, the NaNbO$_3$ reactive template grains dissolve before the formation of dense regions around these grains, and textured K$_{0.5}$Na$_{0.5}$NbO$_3$ does not form. Slow diffusion of potassium ions into the NaNbO$_3$ reactive template grains is responsible for the dissolution of the NaNbO$_3$ reactive template grains prepared by the single-step method.\(^{16,66}\) By heating at 1000°C before sintering to transform NaNbO$_3$ to (K$_{1-x}$Na)$_x$NbO$_3$, textured K$_{0.5}$Na$_{0.5}$NbO$_3$ is obtained.\(^{93}\)

The formation of large rectangular voids is reported in textured (K$_{0.47}$Na$_{0.53}$)(Nb$_{0.35}$Ta$_{0.65}$)O$_3$ prepared using the NaNbO$_3$ reactive template grains prepared by the two-step method.\(^{37}\) The voids are formed at the centers of large aligned grains and their shape and size are almost the same as those of the reactive template grains. The dense regions are formed around the reactive NaNbO$_3$ template grains before the transformation of NaNbO$_3$ to (Na,K)(Nb,Ta)O$_3$, probably due to slow diffusion of Ta ions. After the formation of the dense regions, the reactive template grains dissolve in these regions, leaving large rectangular voids behind.

The formation of textured ceramics by the RTGG process, the reactive template and complementary compounds are used. Another possibility is the use of pre-reacted matrix grains,\(^{35,60,95,96}\) but they lower the degree of orientation in K$_{0.47}$Na$_{0.52}$NbO$_3$ and Bi$_2$Ti$_2$(Na$_{0.35}$K$_{0.15}$)$_2$O$_3$. In the K$_{0.47}$Na$_{0.52}$NbO$_3$ case with a template content of 5 vol%, the degrees of orientation are 0.96 and 0.67 for the specimens using a mixture of KNbO$_3$ and NaNbO$_3$ and pre-reacted K$_{0.5}$Na$_{0.5}$NbO$_3$, respectively, when soaked at 1115°C for 2 h.\(^{35}\) The specimen using the mixture of KNbO$_3$ and NaNbO$_3$ exhibits a homogeneous microstructure, whereas the microstructure of the specimen using pre-reacted K$_{0.5}$Na$_{0.5}$NbO$_3$ is inhomogeneous and contains large cuboidal grains (Fig. 23). In the Bi$_4$Ti$_3$(Na$_{0.5}$K$_{0.15}$)$_2$O$_3$ case, the degrees of orientation for the specimens using the mixture of raw materials and pre-reacted Bi$_4$Ti$_3$(Na$_{0.5}$K$_{0.15}$)$_2$O$_3$ are 0.93 and 0.44, respectively, when soaked at 1200°C for 2 h.\(^{95}\) It is possible that the magnitude of the critical driving force for grain growth is dependent on the combination of the template and matrix grains. When the mixture of KNbO$_3$ and NaNbO$_3$ is used, a large number of the template grains have the driving force beyond the critical value, and almost all template grains can grow. When the pre-reacted matrix grains are used, a limited number of the template grains can have the driving force which
The effectiveness of the application of the RTGG process to prepare Bi$_{0.5}$Na$_{0.5}$TiO$_3$ is controversial. Initially, Tani reported that RTGG is effective but subsequent studies reveal that the texture does not develop in Bi$_{0.5}$Na$_{0.5}$TiO$_3$ using a method similar to that employed by Tani. The origin of this discrepancy is found to be a slight deviation in the stoichiometry. When pre-heating, potassium ions in the pre-reacted matrix grains diffuse into the NaNbO$_3$ reactive template grains, which transform to the (K,Na)NbO$_3$ template grains. In the Bi$_{0.5}$(Na$_{0.85}$K$_{0.15}$)$_{0.5}$TiO$_3$ case, the Bi$_2$Ti$_2$O$_7$ reactive template grains react with Na$_2$CO$_3$ and K$_2$CO$_3$, and the concentration of these compounds is reduced by the use of pre-reacted Bi$_{0.5}$(Na$_{0.85}$K$_{0.15}$)$_{0.5}$TiO$_3$. The effect of the template formation rate on the characteristics of the template grains is not yet understood. This knowledge is necessary to determine the conditions to form good template grains, i.e., single-crystalline grains with the same size as the reactive template grains.

### 6.5 Deviation from stoichiometry

The effectiveness of the application of the RTGG process to prepare Bi$_{0.5}$Na$_{0.5}$TiO$_3$ is controversial. Initially, Tani reported that RTGG is effective but subsequent studies reveal that the texture does not develop in Bi$_{0.5}$Na$_{0.5}$TiO$_3$ using a method similar to that employed by Tani. The origin of this discrepancy is found to be a slight deviation in the stoichiometry. When pre-heating, potassium ions in the pre-reacted matrix grains diffuse into the NaNbO$_3$ reactive template grains, which transform to the (K,Na)NbO$_3$ template grains. In the Bi$_{0.5}$(Na$_{0.85}$K$_{0.15}$)$_{0.5}$TiO$_3$ case, the Bi$_2$Ti$_2$O$_7$ reactive template grains react with Na$_2$CO$_3$ and K$_2$CO$_3$, and the concentration of these compounds is reduced by the use of pre-reacted Bi$_{0.5}$(Na$_{0.85}$K$_{0.15}$)$_{0.5}$TiO$_3$. The effect of the template formation rate on the characteristics of the template grains is not yet understood. This knowledge is necessary to determine the conditions to form good template grains, i.e., single-crystalline grains with the same size as the reactive template grains.

### 6.6 Additives

The role of CuO in the texture formation in K$_{0.5}$Na$_{0.5}$NbO$_3$ is examined using the platelike Na$_4$NbO$_3$ grains as the reactive template and the mixture of K$_2$O and Na$_2$O as complementary compounds. The specimen used as reference is the one shown in Fig. 9. The addition of 1 mol% CuO improves the degree of orientation below 1100°C. When CuO is absent, the degree of orientation is 0.36 and 0.71 at 1000°C and 1050°C, respectively. These values are increased to 0.55 and 0.86, respectively, as a result of the CuO addition. However, the degree of orientation is 0.90 at 1100°C for both specimens. Figure 24 shows the microstructure of the specimen containing CuO, soaked at 1050°C for 2 h. Comparison with the specimen without CuO reveals that the addition of CuO increases the degree of orientation.

![Fig. 24](image-url)

**Fig. 24.** Microstructure of K$_{0.5}$Na$_{0.5}$NbO$_3$ with CuO, soaked at 1050°C for 2 h.
CuO [Fig. 9(b)] indicates that CuO promotes the formation of large cuboidal grains, which is responsible for the texture development. At 1100°C, the number of large cuboidal grains increases in the specimen without CuO [Fig. 9(c)], resulting in the same degree of orientation irrespective of the presence of CuO. The fact that CuO does not have a large influence on the relationship between the relative density and the degree of orientation indicates that CuO addition lowers the sintering temperature by promoting densification.16,86

7. Summary and conclusions

Texture engineering is one of the methods to improve the properties of sintered ceramics. The TGG and RTGG methods are widely applied to piezoelectric ceramics. In the TGG and RTGG methods, compacts containing aligned template grains and randomly oriented matrix grains are sintered. During sintering, the degree of orientation is increased by the elimination of the matrix grains. Optimum preparation conditions must be selected to prepare highly textured ceramics with controlled microstructures. To determine the preparation conditions, it is necessary to observe the microstructures from a green compact to a final sintered compact and to understand the underlying mechanisms in the microstructure development. This review paper focuses on BaBi₄Ti₄O₁₅ and Bi₄Ti₃O₁₂ textured by the TGG method and on Biₓ₀.₅(Naₓ₋₀.₅Kₓ)₀.₅TiO₃ and K₀.₅Na₀.₅NbO₃ textured by the RTGG method. The reason to select these materials is that they have faceted grain boundaries but the grain growth behavior is different. The characteristics of the microstructure development in the materials mentioned above are that the green compacts contain two kinds of grains with fairly large size differences and the grain boundaries are faceted. The growth of faceted grains requires that the driving force for growth be higher than the critical driving force. Therefore, the relative magnitude of the driving force of the template grains and the critical driving force determines the mode of the microstructure development.

In the BaBi₄Ti₄O₁₅ case, the critical driving force is higher than the driving force of the template grains and the growth of the template grains is hindered. The origins of the texture formation are the shape change and growth of the matrix grains. In the Bi₄Ti₃O₁₂ case, the template grains and large platelike grains derived from the matrix grains can grow at the expense of the matrix grains. The difference in the grain growth behavior between BaBi₄Ti₄O₁₅ and Bi₄Ti₃O₁₂ is caused by the grain boundary structure of the side faces of the platelike grains. The side faces are faceted in BaBi₄Ti₄O₁₅ with high critical driving force, resulting in hindrance of the template grain growth. The side faces of Bi₄Ti₃O₁₂ are rounded and the critical driving force is low. The growth of the side faces drives the driving force for growth perpendicular to the plate faces. Thus, continuous growth of the platelike grains consumes misoriented matrix grains and increases the degree of orientation.

In the Biₓ₀.₅(Na₋₀.₅Kₓ)₀.₅TiO₃ case, the step energy increases as the potassium concentration (x value) increases. The structure of the grain boundaries of Biₓ₀.₅NaₓTiO₃ is atomically rough and the grain boundaries are rounded. Both the template and matrix grains can grow. The matrix grains around the template grains consume the growth of the template grains. However, the matrix grains far from the template grains grow to a considerable extent, and the consumption of these grains by the template grains is difficult. Therefore, a template content of 37.5 vol% is necessary to obtain highly textured Bi₀.₅Na₀.₅TiO₃. When the x value is more than 0.10, the grain boundary structure is atomically smooth and the grains are faceted. The grain growth rate is decreased as the potassium concentration is increased. In Biₓ₀.₅(Na₋₀.₅Kₓ)₀.₅TiO₃, both the template and matrix grains can grow but the growth of the template grains is faster than that of the matrix grains. The volume of the matrix in which the template grains can consume the matrix grains is higher than that of Bi₀.₅Na₀.₅TiO₃, and an optimum template content is reduced to 20 vol%. In Biₓ₀.₅NaₓKₓ₀.₅TiO₃, the growth of the matrix grains is stagnant and that of the template grains is sluggish. To consume all matrix grains, optimum selection of the template grain size and the template content is required.

In the Kub₄Na₀.₅NbO₃ case, the template grains have enough driving force for growth but pores pin and drag the grain boundary. When the relative density reaches more than 0.9, the pores cannot pin the grain boundaries and the template grains extensively grow to cuboidal grains. The migration rate of the grain boundaries is higher than the mobility of the pores, resulting in the formation of intragrain pores in the cuboidal grains. Because the reduction in the pore volume is important for the growth of the template grains, which is directly related to the texture formation, one of the criteria to select additives is the ability to promote densification.

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