

# Texture Engineering of Electronic Ceramics by the Reactive-Templated Grain Growth Method

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## 反応性テンプレート粒成長法による電子セラミックスの配向制御

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**The design and fabrication of textured bulk polycrystals have been one of the key issues for ceramists in their effort to extract the best performances from functional materials through powder processing. Reactive-templated grain growth (RTGG) is a processing method in which reactive template particles are mixed with complementary reactants and aligned, and the product is formed *in-situ* during heat-treatment, preserving the orientation of the template. RTGG has been applied to simple perovskite-type materials, yielding highly textured polycrystals with enhanced piezoelectric properties. The proposed method has also been extended to layer-structured materials, including bismuth layer-structured ferroelectrics and both p- and n-type oxide thermoelectrics with complex compositions. The optimum combination of microstructural and compositional designs is expected to produce outstanding materials with superlative performances.**

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**Key-words :** Textured ceramic, Anisotropic property, Reactive template, Piezoelectric, Thermoelectric

### 1. Introduction

THERE are two types of approaches to developing high-performance electronic ceramics: one is to optimize their compositions, and the other is to tailor ideal microstructures for materials with known compositions. The design and fabrication of highly textured polycrystals is one effective strategy within the latter approach for enhancing the performance of materials with anisotropic properties. Texture control of metals and polymers has been carried out industrially by melt-growth or plastic forming. In the case of ceramics, however, texture engineering has mainly been applied to layer-structured materials such as high- $T_c$  superconductors and bismuth layer-structured ferroelectrics (BLSF) as well as magnetically anisotropic materials.<sup>1)–3)</sup> Hot-forging, i.e., high-temperature heat-treatment of polycrystals with stresses, has been proposed as a processing route for layer-structured materials with a preferred orientation as their weakly bonded planes are aligned parallel to one another.<sup>3)</sup> Hot-pressing and hot-extrusion have also been employed as texture engineering techniques to improve the performance of bismuth telluride-based thermoelectric polycrystals.<sup>4),5)</sup> Nevertheless, hot-working methods have disadvantages with respect to the productivity of polycrystals with uniform density and texture. An alternative processing route for textured ceramics is sintering of a green compact in which anisometric particles are aligned.<sup>2)</sup> In the case of layer-structured materials, plate-like particles have been prepared by molten salt synthesis or other solution growth techniques because of their anisotropic crystal growth characteristics.<sup>6)</sup> The templated grain growth (TGG) technique enables the use of a small fraction of anisometric particles as “seeds” for the alignment of a large amount of fine “matrix” particles.<sup>7)–9)</sup> It is often difficult, however, to synthesize single-crystal particles having a complex composition that would be desirable in term of material performance. Heteroepitaxial templated grain growth on BaTiO<sub>3</sub> and SrTiO<sub>3</sub> was reported to produce <001>-textured Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>–PbTiO<sub>3</sub> and (Bi<sub>1/2</sub>Na<sub>1/2</sub>)TiO<sub>3</sub>–BaTiO<sub>3</sub> ceramics, respectively, with enhanced piezoelectric properties.<sup>10)–13)</sup> Heterotemplate

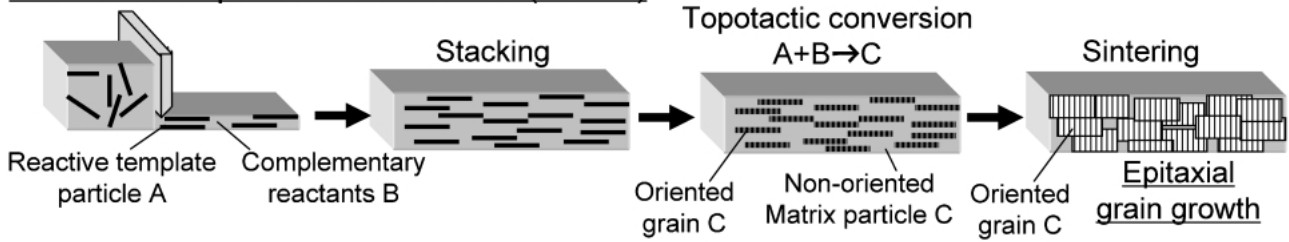
materials could cause compositional deviation or inhomogeneity, which is undesirable from the perspective of ceramic performance.<sup>13)</sup>

The present author has proposed the reactive-templated grain growth (RTGG) method in which reactive template particles are mixed with complementary reactants and aligned by a shear stress, and the product is formed *in-situ* during heat-treatment, preserving the orientation of the template.<sup>14)</sup> This type of reaction sintering for textured bulk ceramics has been known from, for example, the fabrication of cordierite honeycombs with high thermal shock resistance<sup>15)</sup> and spinel-type ferrite magnetic heads with high wear resistance.<sup>16)</sup> The bismuth layer-structured high- $T_c$  superconductor Bi-2223 was also textured by using a Bi2212 anisometric reactive template.<sup>17)</sup> The present author considers RTGG processing to be a key technology for fabricating “high-end” electronic ceramics with performances comparable to those of single crystals. The author and co-workers applied the RTGG method to the design and fabrication of lead-free piezoelectric ceramics with both simple perovskite-type and layered perovskite-type structures.<sup>18)</sup> The technique was extended to the design and fabrication of textured thermoelectric oxide materials with layered structures.<sup>19)</sup> The present paper is a review of the basic research on and applications of the RTGG method as it pertains to lead-free piezoelectric and thermoelectric ceramics.

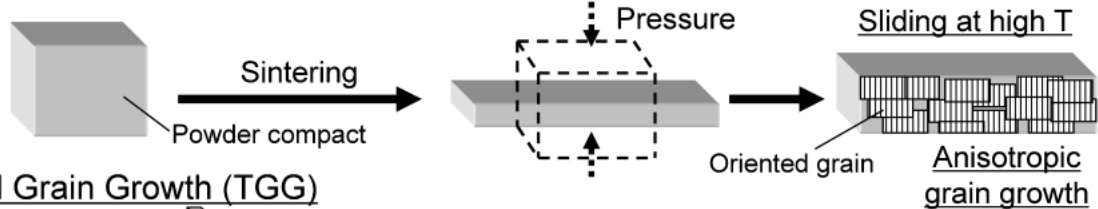
### 2. Design concept for RTGG processing

**Figure 1** schematizes the RTGG processing in comparison with other texture engineering techniques for bulk ceramics. The RTGG method exploits a reactive template material with a crystal structure (at least partially) similar to the target material to be textured. The RTGG method can be a tool for compositional exploration for the best anisotropic performance since the reactive template can be used as a common “seed” material for a series of target materials with various complex compositions.<sup>20)</sup> Another unique characteristic of the RTGG method is that it enables the fabrication of textured

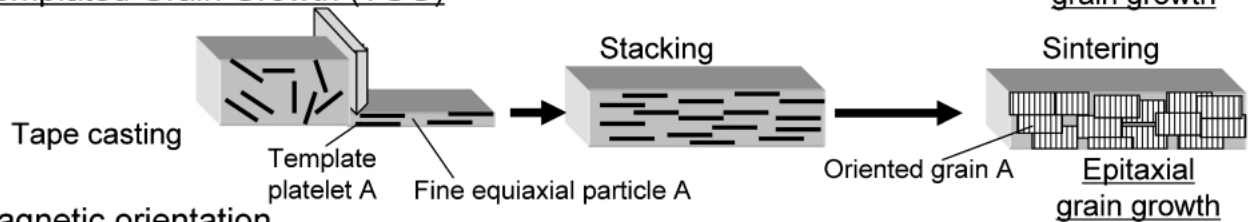
### Reactive Templated Grain Growth (RTGG)



### Hot forge



### Templated Grain Growth (TGG)



### Magnetic orientation

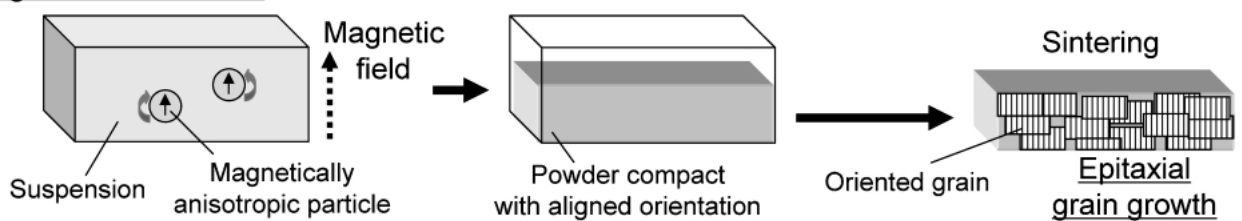


Fig. 1. Schematic diagrams for reactive-templated grain growth and other texture engineering methods.

ceramics even with an (pseudo-)isotropic crystal structure such as a simple perovskite by using a reactive template or its precursor material with an anisotropic crystal structure such as layered perovskite.

On the other hand, there are restrictions on the application of the method; the following conditions must be satisfied:

- (1) A thermodynamically feasible *in-situ* reaction must be designed from a reactive template and complementary reactant(s) to a target material.
- (2) The template and target materials must have epitaxial or topotaxial lattice matching with respect to each other.
- (3) The overall reaction must not have intermediate phases that disturb the crystallographic similarity between the template and target materials.
- (4) The template particles must be able to be prepared in an anisotropic shape.

In other words, it is important to design the most appropriate *in-situ* reaction scheme for the target material on the basis of crystallography and thermodynamics prior to the experiments.

### 3. Application to piezoelectric ceramics

#### 3.1 Simple perovskite-type ceramics

The development of lead-free piezoelectric ceramics has recently been one of the most significant challenges in the field of electronic materials since most of the industrially-predominant piezoelectric ceramics contain high levels of lead in their compositions.<sup>21)</sup> However, the piezoelectric performance

of lead-free materials is inferior to those of  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT) and related lead-containing materials. The author and co-workers regard texture engineering as one of the most important technologies for enhancing the piezoelectric properties of lead-free compositions.<sup>18)</sup>

$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  (BNT)-based simple perovskite-type materials were selected for texturing as prototype lead-free alternative candidates for PZT-based piezoelectrics.<sup>14)</sup> The present author synthesized  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BiT) plate-like particles in molten salt and used them as reactive templates for BNT-based materials since (1) the target material BNT contains all the elements in the reactive template BiT, (2) the crystal structure of BiT contains unit cells of simple perovskite, and (3) a simple perovskite is generally more stable than a layered perovskite. Textured  $\text{Bi}_{0.5}(\text{Na,K})_{0.5}\text{TiO}_3$  (BNKT) ceramics were prepared by using  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{TiO}_2$  as complementary reactants. **Figure 2** compares X-ray diffraction (XRD) patterns of tape surfaces after casting and sintering.<sup>14)</sup> The BiT template particles were uniaxially aligned with the {001} plane parallel to the casting plane whereas the diffraction peaks of the pseudocubic {100} plane were predominant for the sintered BNKT specimen. High-temperature XRD revealed that the BiT template transformed into a simple perovskite upon heating at 600–800°C and that the development of texture was remarkable above 1000°C.<sup>14)</sup> Transmission electron microscopy (TEM) analysis revealed that the formation of the simple perovskite proceeded topotaxially in the template and epitaxially on the template during the heat-treatment

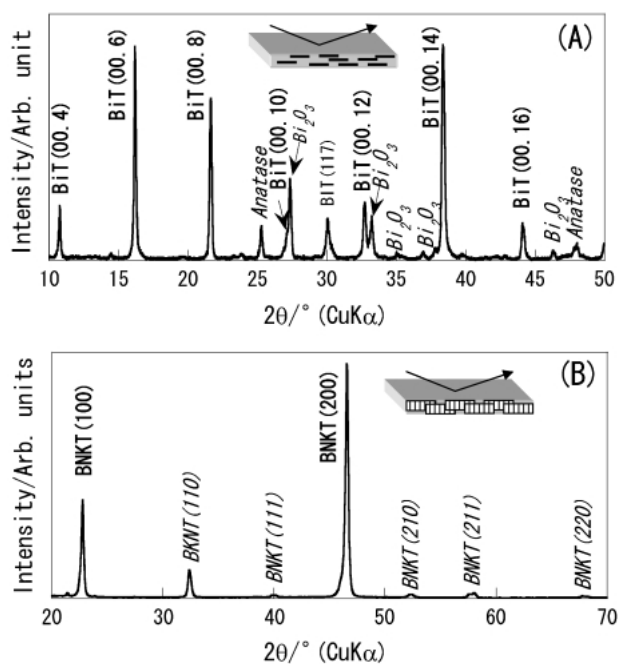


Fig. 2. XRD patterns of (A) a stacked tape containing plate-like  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BiT) with the other reaction gradients for textured  $\text{Bi}_{0.5}(\text{Na,K})_{0.5}\text{TiO}_3$  (BNKT), and (B) a tape after sintering.<sup>14)</sup>

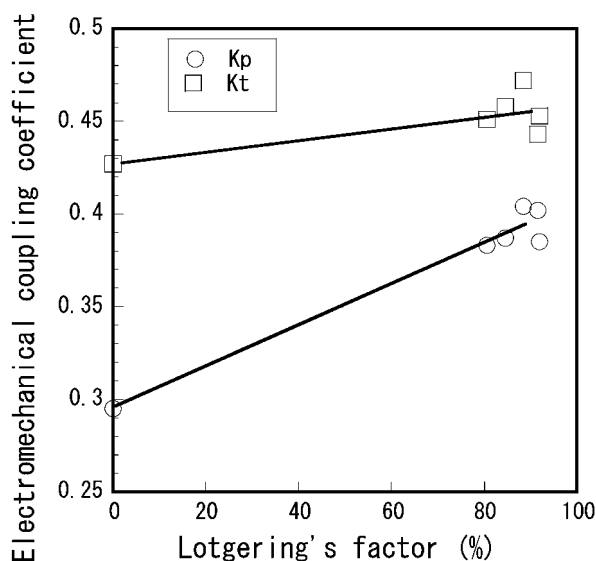


Fig. 3. Electromechanical coupling coefficients of textured and randomly oriented  $\text{Bi}_{0.5}(\text{Na,K})_{0.5}\text{TiO}_3$  (BNKT) ceramics as functions of Lotgering's degree of  $\{100\}$  orientation.<sup>23)</sup>

with the orientation of the developed plane preserved.<sup>22)</sup>

Textured BNKT ceramics with 97–99% in relative density were electroded and poled for piezoelectric measurements. **Figures 3 and 4** plot, respectively, the electromechanical coupling coefficients  $K_p$  and  $K_t$  and piezoelectric constants  $d_{31}$  and  $g_{31}$  as functions of Lotgering's orientation factor for the RTGG- and conventionally-processed BNKT.<sup>23)</sup> The texture had a remarkable effect on the properties: the electromechanical coupling factor  $K_p$  increased by 30–40% and the piezoelectric constants  $d_{31}$  and  $g_{31}$  increased by 40–60% as a result of the texture.

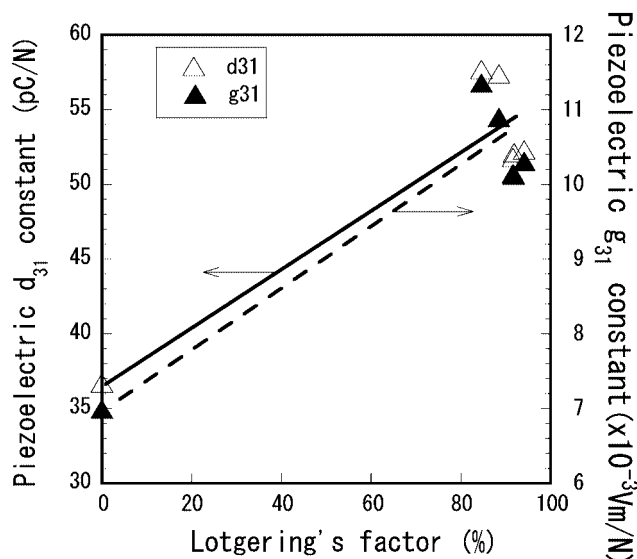


Fig. 4. Piezoelectric  $d_{31}$  and  $g_{31}$  constants of textured and randomly oriented  $\text{Bi}_{0.5}(\text{Na,K})_{0.5}\text{TiO}_3$  (BNKT) ceramics as functions of Lotgering's degree of  $\{100\}$  orientation.<sup>23)</sup>

Table 1. Textured Perovskite-Type Materials and Their Reactive Templates

Reactive template	Target perovskite composition	Reference
{001} $\text{Bi}_4\text{Ti}_3\text{O}_{12}$	{100} $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$	[14,24]
	{100} $\text{Bi}_{0.5}(\text{Na,K})_{0.5}\text{TiO}_3$	[14,25]
	{100} $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-BaTiO}_3$	[12,26]
	{100} $\text{Bi}_{0.5}(\text{Na,K})_{0.5}\text{TiO}_3\text{-Pb(Zr,Ti)O}_3$	[27]
	{100} $(\text{Pb}_{1/2}\text{Bi}_{1/2})(\text{Ni}_{1/4}\text{Ti}_{3/4})\text{O}_3$	[28]
	{100} $\text{BaTiO}_3$	[29]
{001} $\text{Sr}_2\text{Ti}_2\text{O}_7$	{100} $\text{SrTiO}_3$	[30]
	{100} $(\text{Pb,Sr})(\text{Zr,Ti})\text{O}_3\text{-Pb(Ni,Nb)O}_3$	[28]
{100} $\text{NaNbO}_3$	{100} $(\text{K,Na,Li})(\text{Nb,Ta,Sb})\text{O}_3$	[31]
{010} $\text{Sr}_2\text{Nb}_2\text{O}_7$	{110} $(\text{Pb,Sr})\{(\text{Zr,Ti,Ni,Nb})\text{O}_3\}$	[27]
{001} $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$	{111} $\text{BaTiO}_3$	[32]

Texture engineering through the RTGG method has been extended to other simple perovskite-type material systems: **Table 1** lists the combination of reactive templates and target perovskite-type materials, reported in the literature. Ruddlesden–Popper-type layer-structured compounds as well as bismuth layer-structured compounds are candidate reactive template materials for simple perovskite-type ceramics with the pseudocubic  $\{100\}$  plane aligned, as schematized in **Fig. 5**.<sup>28),30)</sup>  $\text{Sr}_2\text{Nb}_2\text{O}_7$ -type layered compounds work as reactive template materials for  $\{110\}$ -textured simple perovskite-type ceramics.<sup>28)</sup> Furthermore, simple perovskite-type ceramics with the  $\{111\}$  plane aligned are designed and fabricated with reactive template materials having a lattice matching plane with the perovskite  $\{111\}$ .<sup>32)</sup>

Texture development for RTGG-processed perovskite-type materials is found to depend on their compositions. Since the driving force for templated grain growth is the size difference between particles, the size of templates must be larger than that of neighboring matrix particles for the texture to develop. Pure BNT composition, for example, is difficult to texture since the fine matrix grains tend to grow rapidly before the epitaxial grain growth starts on the aligned large templates. The grain growth was suppressed by the substitution of 10–15% K for Na or the introduction of excess amounts of  $\text{Bi}_2\text{O}_3$

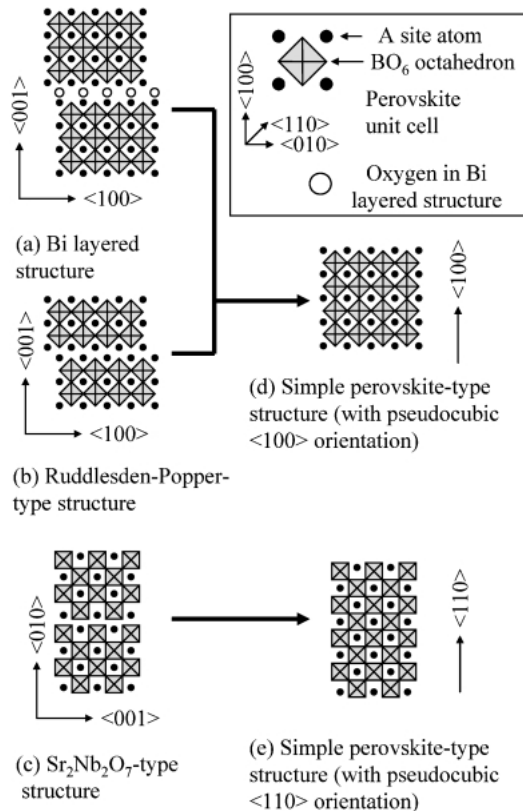


Fig. 5. Schematic crystal structures of reactive templates for {100}- and {110}-textured simple perovskite-type ceramics.<sup>28)</sup>

over the stoichiometry of BNT.<sup>24),25)</sup>

Another factor affecting the texture of a target material is the possible formation of intermediate phases that could disturb the succession of the crystallographic framework. Piezoelectric  $(\text{Pb}_{1/2}\text{Bi}_{1/2})(\text{Ni}_{1/4}\text{Ti}_{3/4})\text{O}_3$  (PBNT) ceramics were prepared by using BiT platelets as reactive templates similarly to BNKT, and PbO, NiO, and  $\text{TiO}_2$  as complementary reactants.<sup>28)</sup> RTGG-prepared PBNT ceramics were fully dense, but poorly textured after sintering at  $1150^\circ\text{C}$ . High-temperature XRD in the temperature range of  $500\text{--}800^\circ\text{C}$  revealed the formation of a Bi–Pb–O phase with a crystal structure similar to that of  $\gamma\text{-Bi}_2\text{O}_3$  which does not have lattice matching with simple perovskite (Fig. 6). Rapid heating of the specimen up to  $800\text{--}900^\circ\text{C}$  suppressed the formation of the unfavourable intermediate compound and directly yielded the perovskite, with the aligned plane preserved.

The  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  (KNN) system has a higher Curie temperature ( $T_c$ ) than BNT and  $\text{BaTiO}_3$ -based materials as well as favorable piezoelectric properties for a lead-free material. Saito et al. recently reported that the combination of texture engineering and compositional design in KNN produced lead-free piezoelectric ceramics whose  $T_c$ , piezoelectric properties and high-field strain properties were all comparable to those of commercial PZT-based materials.<sup>31)</sup> They first synthesized  $\text{Bi}_{2.5}\text{Na}_{3.5}\text{Nb}_5\text{O}_{18}$  (BiNN5) platelets as a precursor material by a molten salt method and then in a second molten salt reaction the BiNN5 platelets were converted into  $\text{NaNbO}_3$  platelets which were to be used as a reactive template for {100}-textured KNN ceramics.

### 3.2 Layered perovskite-type ceramics

BLSF ceramics are candidate materials for temperature-stable lead-free piezoelectric resonator, filter and sensor applica-

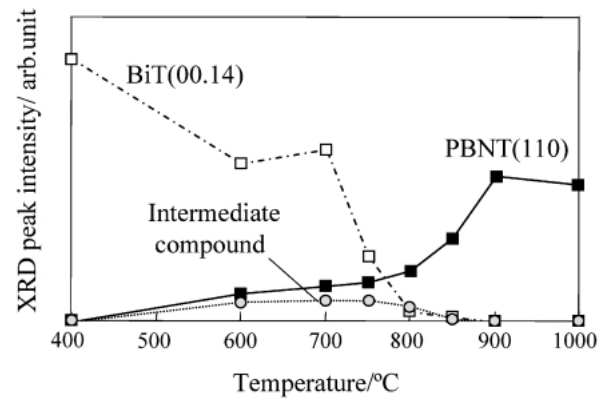


Fig. 6. High temperature XRD peak intensities for representative crystallographic phases of reactive template  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BiT), target material  $(\text{Pb}_{1/2}\text{Bi}_{1/2})(\text{Ni}_{1/4}\text{Ti}_{3/4})\text{O}_3$  (PBNT), and intermediate compound in the RTGG processing.<sup>28)</sup>

tions because of their high  $T_c$  and high mechanical quality factors ( $Q_m$ ).<sup>33)–35)</sup> The candidate materials include  $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$  (CBT),  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  (SBT),  $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$  (NBT), and  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  (SBN). Textured CBT and SBN ceramics were fabricated by the TGG method, and were reported to have excellent temperature coefficients of resonant frequency suitable for resonator applications.<sup>34),35)</sup>

The author and co-workers used BiT platelets as reactive templates and prepared three types of four-layered BLSF ceramics, namely Ca-doped  $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$  (NBT),  $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$  (CBT) and  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  (SBT) ceramics.<sup>18)</sup> Extrusion as well as tape casting were applied for the alignment of the template particles. Figure 7 schematizes the processing and evaluation of CBT ceramics.<sup>36),37)</sup> Fully dense and single-phase ceramics were obtained for NBT and CBT with a high degree of <001> orientation ( $>0.9$ ); the piezoelectric properties of these ceramics were evaluated. The SEM images in Fig. 8 reveal the microstructure of a textured CBT ceramic in which plate-like grains are aligned parallel to the original casting plane.

Table 2 gives the piezoelectric and dielectric properties of textured CBT ceramics prepared by the RTGG method and randomly-oriented CBT prepared by the conventional method.<sup>36),37)</sup> The electromechanical coefficients  $k_t$  and  $k_{33}$  of the RTGG-processed specimen were more than three times as high as those of the randomly oriented specimen and the values exceeded 50% when processed by tape-casting. The piezoelectric constants  $d_{33}$  and  $g_{33}$  of the textured BLSF were also remarkably higher than those of the randomly oriented ceramics. Unidirectionally textured CBT ceramics processed by extrusion in the RTGG method also showed enhanced piezoelectric properties when compared with the randomly oriented ceramics.

## 4. Application to thermoelectric ceramics

### 4.1 p-type layered cobaltite ceramics

The recovery of energy from waste heat by thermoelectric power generation has been desired as a technology to contribute to the reduction of carbon dioxide emissions. Layered oxide materials have recently attracted attention as candidate materials for thermoelectric devices because they are chemically stable at high temperatures in air.<sup>38)–40)</sup> The fabrication of thermoelectric power generation modules requires high-performance bulk elements. The figure of merit for thermoelec-

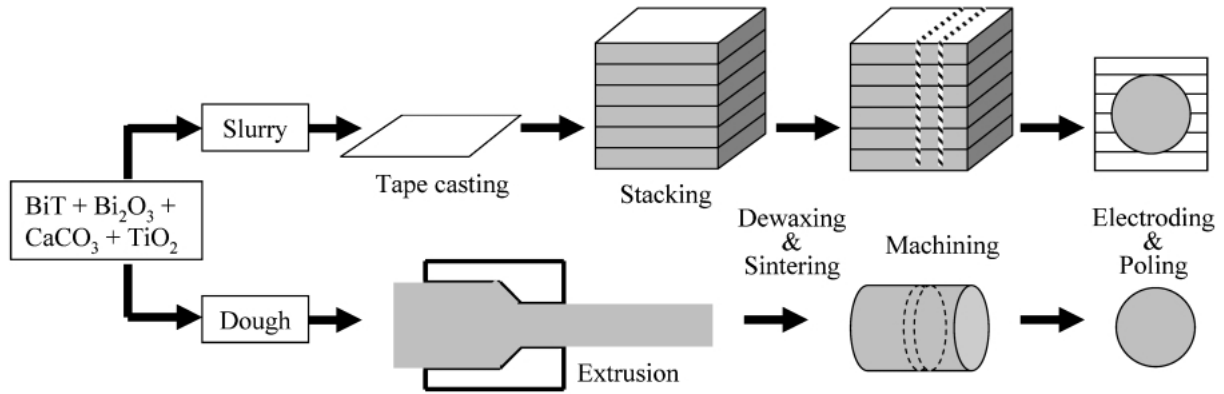


Fig. 7. Schematic diagram of two preparation routes for textured bismuth layer-structured ferroelectric (BLSF) ceramics by the RTGG method.<sup>36),37)</sup>

Sintered sheet stack

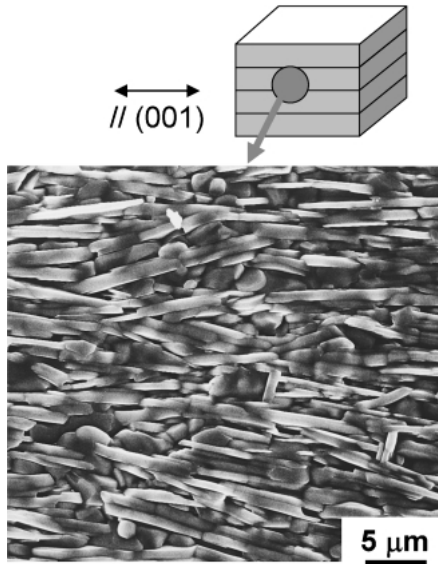


Fig. 8. SEM image of polished and etched surface of RTGG-processed  $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$  (CBT) ceramic perpendicular to the original tape-casting plane.<sup>36)</sup>

Table 2. Piezoelectric and Dielectric Properties of the Textured  $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$  (CBT) Ceramics Prepared by the RTGG Method and of Randomly-Oriented CBT Prepared by a Conventional Method<sup>36),37)</sup>

Specimen	RTGG/ tape casting	RTGG/ extrusion	Conventional
density ( $\text{g/cm}^3$ )	7.205	7.100	7.206
$\epsilon_{33}^T/\epsilon_0$	139	143	149
$\tan\delta$ (%)	0.09	0.10	0.13
$k_p$ (%)	4.8	5.9	4.7
$k_{31}$ (%)	3.2	3.9	2.9
$k_t$ (%)	53.4	41.4	16.2
$k_{33}$ (%)	53.5	41.8	16.9
$-d_{31}$ ( $\times 10^{-12}$ C/N)	2.8	3.5	2.8
$d_{33}$ ( $\times 10^{-12}$ C/N)	45	35	15
$-g_{31}$ ( $\times 10^{-3}$ Vm/N)	2.3	2.8	2.1
$g_{33}$ ( $\times 10^{-3}$ Vm/N)	36.5	27.7	11.4

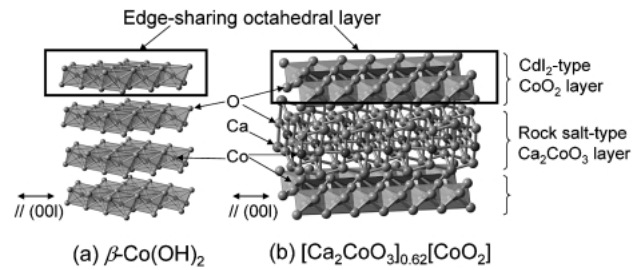
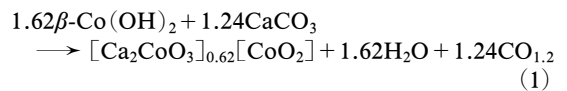


Fig. 9. Schematic diagram on structural similarity between  $\beta\text{-Co}(\text{OH})_2$  (reactive template) and  $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$  (target material).<sup>49)</sup>

tric materials is expressed as  $Z$ , or  $S^2\sigma/\kappa$ , where  $S$  is thermoelectric power or Seebeck coefficient,  $\sigma$  is electrical conductivity, and  $\kappa$  is thermal conductivity. Layered conductor materials generally possess strong anisotropy in electrical conductivity so that the preparation of textured polycrystals is important for high performance, similarly to the fabrication of  $\text{Bi}_2\text{Te}_3$ -based thermoelectric polycrystals.<sup>41)</sup>

A series of layered cobaltite materials have been proposed as p-type thermoelectric oxides with high  $\sigma$  values parallel to a common  $\text{CdI}_2$ -type  $\text{CoO}_2$  layer composed of edge-sharing  $\text{CoO}_6$  octahedra. This material group includes  $\text{Na}_x[\text{CoO}_2]$ ,<sup>39)</sup>  $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$  (denoted as CCO),<sup>42),43)</sup>  $[\text{Ca}_2(\text{Co}_{0.65}\text{Cu}_{0.35})_2\text{O}_4]_{0.624}[\text{CoO}_2]$ ,<sup>44)</sup> and  $[\text{Bi}_2\text{M}_{2-x}\text{O}_4]_p[\text{CoO}_2]$  ( $\text{M} = \text{Sr}$ , or  $\text{Ca}$ ).<sup>45)–47)</sup> The author and co-workers have noticed that the crystal structure of  $\beta\text{-Co}(\text{OH})_2$  is also composed of edge-sharing octahedral layer stacking along the  $c$ -axis, as illustrated in Fig. 9. Plate-like particles of  $\beta\text{-Co}(\text{OH})_2$  are synthesized by a precipitation method and used as a reactive template for layered cobaltite ceramics.<sup>48)</sup> A typical example of a reaction scheme for textured CCO is:



In the actual RTGG processing, plate-like  $\beta\text{-Co}(\text{OH})_2$  particles were mixed with  $\text{CaCO}_3$ , aligned by tape-casting, and heat-treated up to sintering temperatures.<sup>49)</sup> During the heat treatment,  $\beta\text{-Co}(\text{OH})_2$  particles first decomposed into spinel-type  $\text{Co}_3\text{O}_4$ , then reacted with  $\text{CaCO}_3$  or  $\text{CaO}$  to form  $\beta\text{-Na}_x\text{CoO}_2$ -type  $\text{Ca}_x\text{CoO}_2$ , and finally transformed into CCO, as revealed by the changes in XRD patterns in Fig. 10.<sup>50)</sup> The

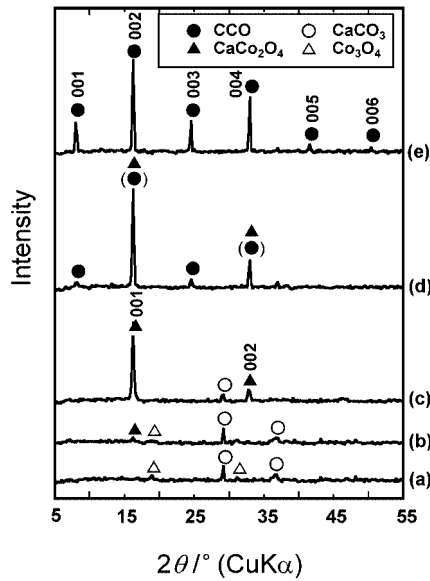


Fig. 10. XRD patterns for tape-cast powder mixture of plate-like  $\beta$ -Co(OH) $_2$  and CaCO $_3$  for  $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$  (CCO) heat-treated at (a) 673 K, (b) 913 K, (c) 973 K, (d) 1103 K and (e) 1163 K.<sup>50)</sup>

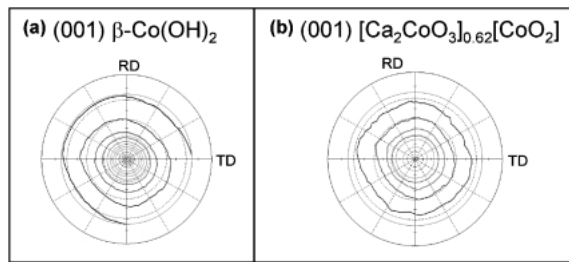


Fig. 11. Pole figure measurements for (a) (001) plane of  $\beta$ -Co(OH) $_2$  templates in a green compact and (b) (002) plane of  $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$  (CCO) in a sintered ceramic.<sup>50)</sup>

intermediate  $\text{Ca}_x\text{CoO}_2$  is composed of alternately stacking  $\text{CoO}_2$  layers of edge-sharing  $\text{CoO}_6$  octahedra and Ca cation layers along the  $c$ -axis. The spinel-type  $\text{Co}_3\text{O}_4$  contains similar edge-sharing  $\text{CoO}_6$  octahedra parallel to all the  $\{111\}$  planes. XRD pole figure measurements revealed that the preferred orientation parallel to the tape casting plane of the specimen changed from (001) for  $\beta$ -Co(OH) $_2$  to  $\{111\}$  for  $\text{Co}_3\text{O}_4$ , (001) for  $\text{Ca}_x\text{CoO}_2$ , and  $\{001\}$  for CCO. **Figure 11** shows the pole figure patterns of the (001) plane of  $\beta$ -Co(OH) $_2$  templates in a green compact and (b) (002) plane of  $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$  (CCO) in a sintered ceramic.<sup>49)</sup> The mechanism of the texture preservation is thought to be topotactic conversion with maintained common (or similar)  $\text{CoO}_2$  layers. TEM observations confirmed that the relationship between the crystallographic orientations was (001)  $\beta$ -Co(OH) $_2$ // $\{111\}$   $\text{Co}_3\text{O}_4$ //(001)  $\text{Ca}_x\text{CoO}_2$ //(001) CCO.<sup>50)</sup>

The textured CCO ceramic prepared by the RTGG method showed anisotropies in  $\sigma$ ,  $S$  and  $\kappa$ , and exhibited an improved  $Z$  value in the direction parallel to the aligned (001) plane.<sup>48)</sup> In particular, the value of electrical conductivity of the textured CCO ceramic reached about 60% of that of a single crystal. Textured ceramics for other layered cobaltite compositions were also prepared as designed by the RTGG method with  $\beta$ -Co(OH) $_2$  or its derivative used as the reactive

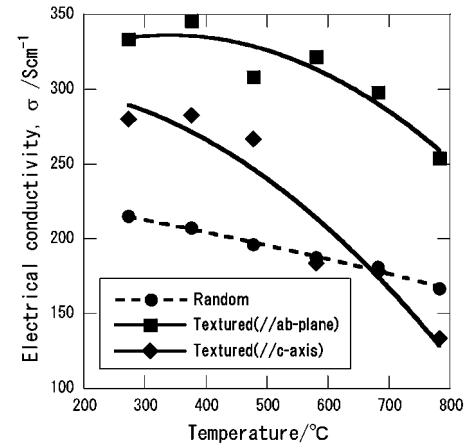


Fig. 12. Temperature dependence of electrical conductivity of Ca-doped textured and randomly oriented  $(\text{ZnO})_m\text{In}_2\text{O}_3$  ceramics ( $m = 3$  and 4).<sup>56)</sup>

template.<sup>20),51)</sup> It should be noted that transport properties in ceramics of layered thermoelectric materials, such as the electrical conductivity, are remarkably sensitive to the degree of orientation.<sup>52)</sup> Thus, the fabrication of ceramics with “ultimate” texture is essential for the application of layered thermoelectric oxides to high-performance devices.

#### 4.2 n-type homologous compound ceramics

Homologous compounds,  $(\text{ZnO})_m\text{In}_2\text{O}_3$  (denoted as  $Z_m\text{IO}$  where  $m$  is an integer  $\geq 3$ ), were reported as n-type layered oxide materials with low thermal conductivity as well as relatively high electrical conductivity.<sup>38)</sup> An investigation on sputter-deposited  $(\text{ZnO})_5\text{In}_2\text{O}_3$  thin films with preferred orientations revealed that this compound is highly anisotropic in electrical conductivity owing to its high carrier mobility along the  $ab$ -plane.<sup>53)</sup> Textured  $Z_m\text{IO}$  ceramics with a preferred  $\{001\}$  plane were prepared by using plate-like  $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2$  as a reactive template and  $\text{In}_2\text{O}_3$  as a complementary reactant through a similar processing scheme to that for a textured CCO ceramic.<sup>54)</sup> Moreover, compositional investigation into the  $Z_m\text{IO}$  system was also carried out to find the optimum  $m$ -value (3–4) and dopant (Ca for In site) for the combination of a high thermoelectric power factor,  $S^2\sigma$ , and low  $\kappa$ .<sup>55)</sup> RTGG processing gave  $Z_m\text{IO}$  ceramics with further improved  $\sigma$  in the direction parallel to the aligned (001) plane (**Fig. 12**).<sup>56)</sup> The resultant dimensionless figure of merit ( $ZT$ ) for a Ca-doped and textured  $Z_m\text{IO}$  ( $m = 3$  and 4) ceramic was 0.31, which is 30% higher than that of a randomly-oriented ceramic with the same composition (**Fig. 13**).<sup>56)</sup>

Asahi et al. designed and fabricated an all-oxide bridge-type thermoelectric module to minimize contact problems under thermal stress and to collect the heat efficiently with exposure of the high-temperature joint to hot air.<sup>57),58)</sup> Textured p-type CCO and n-type  $Z_m\text{IO}$  ceramics were prepared by RTGG processing, and the p/n bars were connected using noble-metal paste as the high thermoelectric performance planes were aligned parallel to the longitudinal direction. The module exhibited an open-circuit voltage of 1.0 V upon  $\Delta T = 630$  K, which nearly agreed with the value calculated from the  $S$  of the materials. The chemical stability without passivation coating demonstrates suitability to high-temperature thermoelectric applications.

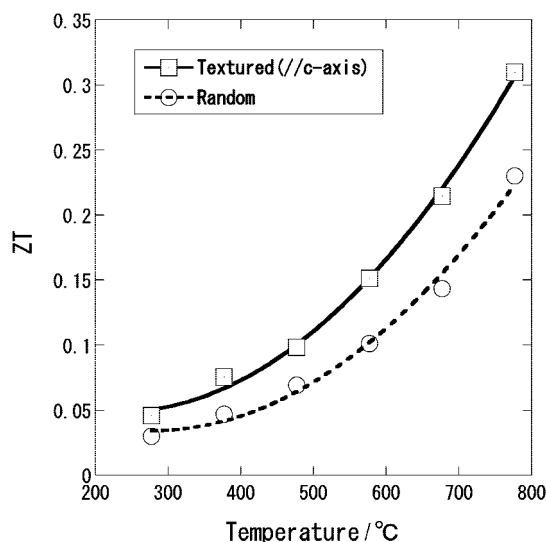


Fig. 13. Temperature dependence of dimensionless figure of merit,  $ZT$ , of Ca-doped textured and randomly oriented  $(\text{ZnO})_m\text{In}_2\text{O}_3$  ceramics ( $m=3$  and  $4$ ).<sup>56)</sup>

### 5. Conclusions

It is shown that the RTGG method is a versatile and effective processing technique for the fabrication of textured ceramics of complex oxides both in (pseudo-)isotropic and anisotropic crystal systems. This method is especially useful for enhancing piezoelectric properties of ceramics with lead-free compositions. The gains in piezoelectric properties are remarkable for bismuth layer structured ferroelectrics because of the strong anisotropy that they acquire when textured by the RTGG process. RTGG has been extended to electrical conductor materials in anisotropic crystal structures. For such systems, the macroscopic carrier transport properties of textured polycrystals strongly depend on their degree of orientation. Further improvement in the processing technique is required to achieve the ultimate texture that will extract the best performance from the polycrystalline form.

The applicability of the RTGG method, however, is dependent on the availability of a suitable template for each target material. The fabrication cost of reactive templates is another issue to be tackled for the application of the proposed process. Furthermore, combining texture engineering with compositional studies is imperative to fabricating ceramics with the best performances.

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