Research Report Highly-Textured Thermoelectric Oxide Polycrystals Synthesized by the Reactive-Templated Grain Growth (RTGG) Method Hiroshi Itahara, Toshihiko Tani

Abstract

The recovery of energy from waste heat by thermoelectric (TE) power generation has been desired as an effective technology to contribute to the reduction of carbon dioxide emissions. Layered oxides have good potential as materials for TE devices, because they are composed of environmentally benign elements and are chemically stable in a high temperature air atmosphere. Layered cobaltites are p-type materials with strong anisotropy in their TE properties and thus fabrication of textured ceramics is required for practical application of the materials. We have proposed for the reactivetemplated grain growth (RTGG) method, the use of platelike β -Co(OH)₂ particles as reactive templates that provide an edge-sharing CoO_6 octahedra layer similar to the CoO_2 layer in the

crystal structure of layered cobaltites. We prepared ceramic specimens by the in situ reaction between the aligned platelike β -Co(OH)₂ templates and the complementary reactants (oxides or carbonates) for target cobaltite compositions. As a result, the textured ceramics, with a high degree of orientation and improved TE properties, have been prepared as designed for various layered cobaltites. In particular, the value of electrical conductivity (an important factor of TE performance) of the textured [Ca₂CoO₃]_{0.62}[CoO₂] ceramic reached about 60 % of that of a single crystal. It was shown that the RTGG method is a versatile and effective fabrication technique for the synthesis of textured ceramics of the layered cobaltites.

Keywords

Thermoelectric power generation, Seebeck effect, Layered cobaltites, Textured ceramics, Reactive template, Reactive-templated grain growth, β -Co(OH)₂, Platelike particle, Topotaxy

1. Introduction

1.1 Layered cobaltites as potential thermoelectric oxides

The recovery of energy from waste heat by thermoelectric (TE) power generation¹⁻⁵) is expected to be one of the promising technologies in the near future to contribute to the reduction of carbon dioxide emissions. TE power generation is based on the Seebeck effect, which is associated with a voltage generation induced by the carrier concentration distribution along a semiconductor when it is subjected to a temperature difference. Thus, the electric current flows when p-type and ntype semiconductors are connected thermally in parallel and electrically in series. The performance of the TE materials is characterized by the figure of merit (Z), $Z \equiv \sigma S^2 / \kappa$. Therefore, 'good' TE materials should exhibit high values of electrical conductivity (σ) and Seebeck coefficient (S), and low values of thermal conductivity (κ) at the same time.

As potential TE materials, in addition to the intermetallic compounds such as skutterudites and clathrates, layered oxides have recently attracted increasing attention⁶⁻⁹⁾ due to their rather good TE performance and their chemical stability in a high temperature air atmosphere. The oxides have other advantages, such as the ease of their production and handling, the existence of developed manufacturing plants readily available for their production, and the possibility of enhancing their properties based on the diversity of their crystal structures and compositions. Figure 1 shows one candidate group of p-type TE oxides, the TE layered cobaltites, including $Na_x[CoO_2]^{10, 11}$ (denoted as NCO), $[Ca_2CoO_3]_{0.62}[CoO_2]^{12-14}$ (denoted as CCO-3-layer), $[Ca_2(Co_{0.65}Cu_{0.35})_2O_4]_{0.624}[CoO_2]^{15}$ (denoted as CCO-4-layer), and $[Bi_2M_{2-x}O_4]_p[CoO_2]$ (M = Sr,^{16, 17)} or Ca¹⁸; denoted as Bi-layered-cobaltites).

1.2 Processing design of the textured ceramics through the RTGG method

The single crystals of NCO¹⁰⁾ and CCO-3-layer¹³⁾ are reported to show a strong anisotropy in their TE properties due to their layered crystal structure. Because of their similar crystal structures (CoO₂ layer + block layer, Fig. 1), the other cobaltites should also show a strong anisotropy in their TE

properties. Although single crystals exhibit high TE properties,^{19, 20)} it is difficult to synthesize the largesize single crystals that are readily applicable to the devices. Thus, a fabrication method of the textured bulk ceramics would be a key technology for practical application. For this purpose, the textured ceramics of CCO-3-layer were fabricated by the mechanical alignment of platelike single crystals^{21, 22)} and by the magnetic alignment at a field as high as 3T.²³⁾ The textured ceramics exhibited improved TE properties compared to the non-textured ceramics. However, these methods have disadvantages such as the compositional limitations for the synthesis of single crystals and the difficulty generating such a high magnetic field in the industrial scale process.

Thus, we have proposed²⁴⁻²⁶⁾ a novel fabrication technique that uses β -Co(OH)₂ platelets as reactive seeds (templates) for a more versatile and effective fabrication method. This technique is based on the reactive-templated grain growth (RTGG) method,^{27, 28)} which is developed by extending the



Fig. 1 Schematic representations for crystal structures of the thermoelectric layered cobaltites, and their abbreviations used in this report.

fabrication strategy of textured Mn-Zn ferrite ceramics²⁹⁾ through a topotactic reaction, and has recently been applied to the textured ceramic production of various functional oxide materials.³⁰⁻³⁷⁾ Figure 2 represents the basic concept of this technique. For the reactive templates, we focused on β -Co(OH)₂ (Fig. 2(a)), which is composed of a CoO₂ layer consisting of edgesharing CoO₆ octahedra, a geometry which all the cobaltites have in common in their crystal structures (Fig. 2(b)). We expected that the β -Co(OH)₂ platelets aligned with the developed $\{00l\}$ plane (Fig. 2(c)) would provide a crystallographic template for the layered cobaltites and that the orientation would be maintained when the complementary elements (e. g., Ca for the CCO-3-layer) are supplied for the target compositions. Here we report the synthesis of textured ceramics as designed for CCO-3-layer,^{24, 25)} CCO-4-layer²⁶⁾ and Bi-layered cobaltites.²⁶⁾

2. Experimental

2. 1 Fabrication of ceramics by the RTGG method²⁴⁻²⁶⁾

Co(OH)₂ powders for use as templates were



Fig. 2 The basic concept in the reactive-templated grain growth (RTGG) method using β -Co(OH)₂ templates: Crystal structures of (a) CdI₂-type β -Co(OH)₂ and (b) CCO-3-layer (one of the layered cobaltites), and (c) schematic representation of the morphology of β -Co(OH)₂ particles suitable for the reactive templates.

prepared by the precipitation method described in previous reports.^{38, 39)} Figure 3 and Table 1 show the schematic representation and the typical preparation conditions, respectively, for the synthesis of textured TE cobaltite ceramics by the RTGG method. The $Co(OH)_2$ powders and complimentary reactants were mixed in a ball mill in an ethanol-toluene solution. Organic binder and plasticizer were added to the mixture and mixed. The mixed slurry was tape-cast and the obtained tape was dried in air at room temperature. The tape (~100 μ m thickness) was cut into an ordered size and ~50 tapes were stacked and pressed to form a single compact. Then the organics in the compact were burned out in air. Finally, the compact was sintered with uniaxial pressing (UPS) in an O_2 atmosphere. Hereafter, we call the sintered ceramics **RTGG-UPS** specimens.

2. 2 Characterizations and thermoelectric property measurements

The crystalline phases of the precipitationprepared powders were determined by X-ray diffraction (XRD) measurements. An oriented particulate monolayer XRD (OPML-XRD) technique⁴⁰⁾ was applied in order to determine the developed plane of the Co(OH)₂ powders. In this technique, the powders were dispersed in a gelatin solution and a drop of the solution was expanded evenly on a flat glass plate. An oriented particulate monolayer membrane was fixed on the glass plate to be analyzed by XRD. In addition, morphology of the particles was observed by a scanning electron microscopy (SEM).

XRD measurements were conducted to determine the crystalline phases and Lotgering's orientation degree⁴¹⁾ (f) of the RTGG-UPS specimens. The f values were calculated using XRD peak intensities (I) by the equation, $f = (P - P_0) / (1 - P_0)$, where $P = \Sigma I (00l) / \Sigma I (hkl)$ and P_0 is P for a randomly oriented powder specimen. The microstructure of the RTGG-UPS specimens was observed by SEM.

A rectangular bar, with the longitudinal direction parallel to the original casting plane, was machined out of the RTGG-UPS specimen. The σ value was measured using a four-probe method. The *S* value was determined by the slope of the relationship between TE voltage generated between both ends of the bar with temperature difference. The κ value was determined through the ac calorimetric method associated with optical pulse heating.⁴²⁾ The *Z* value was calculated from the relationship, $Z \equiv \sigma S^2 / \kappa$.

3. Results and discussion

3.1 Texture development

Figure 4 shows XRD patterns and SEM photographs of the prepared powders.^{38, 39)} The

powders had a platelike shape (~0.5 μ m in diameter with an aspect ratio of ~5, Fig. 4 (a)) developed along the {00*l*} plane (Fig. 4 (b))

Figure 5 shows the XRD pattern and SEM photograph measured for the CCO-3-layer RTGG-UPS specimen. The XRD pattern shows that the specimen exhibited strong diffraction peaks for the $\{00l\}$ plane, and an extremely high *f* value (~1). SEM observation indicated that the $\{00l\}$ plane of



Fig. 3 Schematic representations for the synthesis of the textured ceramics of various thermoelectric layered cobaltites by the reactive-templated grain growth (RTGG) method, and thermoelectric property measurements.

Table 1 Typical preparation conditions for textured ceramics

5566156		Sintering conditions **		
RTGG-UPS Specimen*	Molar mixing ratio of starting materials	Temperature	Uniaxial Pressure	Time
*		[K]	[MPa]	[ks]
CCO-3-layer	$Co(OH)_2$:CaCO ₃ = 3.92:3.00	1193	9.8	7.2
CCO-4-layer	Co(OH) ₂ :CaCO ₃ :CuO = 4.35:3.00:1.05	1193	19.6	72
BSCO	Co(OH) ₂ :Bi ₂ O ₃ :SrCO ₃ = 2.00:1.00:2.00	1123	9.8	7.2
B(SC)CO	Co(OH) ₂ :Bi ₂ O ₃ :SrCO ₃ :CaCO ₃ = 2.00:1.00:1.00:1.00	1153	9.8	7.2
BCCO	$Co(OH)_2$:Bi ₂ O ₃ :CaCO ₃ = 2.00:1.00:2.00	1173	1.96	7.2

*RTGG: reactive-templated grain growth method, UPS: sintered with uniaxial pressing ** O_2 atmosphere

the grains was along the original casting plane. It was shown that the CCO-4-layer (**Fig. 6** (a)) and Bilayered-cobaltites (Fig. 6 (b)-(d)) ceramics prepared also preferred the $\{00l\}$ plane. Thus, it was proved that the textured ceramics were successfully prepared by the RTGG method for all of the layered cobaltites. It should be emphasized that our method provided textured ceramics of nearly single phase and ordered composition. A typical example is the B(SC)CO ceramic, for which half of the Sr sites of BSCO are substituted by Ca. Because effective doping into the crystal structures enhances TE properties, the RTGG method, which would be applicable to diverse compositions, is a promising technology for the production of various TE oxides.

Additionally, we investigated the formation mechanism of a CCO-3-layer textured ceramic. It was deduced^{24, 25)} that the formation mechanism is based on topotactic conversion, specifically, $\{00l\}\beta$ -Co(OH)₂ \rightarrow $\{111\}$ Co₃O₄ \rightarrow $\{00l\}$ CCO-3-layer. These results were deduced from thermogravimetry, differential thermal analysis, as well as



Fig. 5 (a) XRD pattern measured for a surface parallel to the casting plane, and (b) SEM photograph of a fracture surface perpendicular to the casting plane of RTGG-UPS specimen of CCO-3-layer: RTGG and UPS represent "the reactive-templated grain growth method", and "sintered with uniaxial pressing", respectively.



Fig. 4 (a) SEM photograph, and (b) powder XRD and oriented particulate monolayer (OPML) XRD patterns of precipitationprepared β -Co(OH)₂ platelets.



Fig. 6 SEM photographs of fracture surfaces perpendicular to the casting plane of RTGG-UPS specimens of (a) CCO-4-layer, (b) BSCO [M=Sr], (c) B(SC)CO [M=SrCa] and (d) BCCO [M=Ca]. high-temperature XRD measurement and they indicate that the CCO-3-layer textured ceramic was prepared in the same way as described in the synthetic strategy in Fig. 2. We have also conducted a computational study on the texture development⁴³⁾ using Monte Carlo simulation of grain growth and sintering^{44, 45)} for better processing design of textured ceramics.

3.2 Thermoelectric properties

Figure 7 shows the temperature dependence of σ_{ab} (*ab*: in-plane) of CCO-3-layer specimens. We prepared two kinds of RTGG-UPS specimens; one is a "textured" ceramic (Fig. 5), and the other is a "highly textured" ceramic with enhanced degree of orientation,^{25, 46)} produced by refinement of synthetic conditions. Although these two ceramic specimens had little difference in their *f* values, a more precise texture analysis (rocking curve measurements and evaluation of the orientation distribution) revealed a clear difference in the degree of orientation between



Fig. 7 Temperature dependence of electrical conductivity (σ) for the CCO-3-layer specimens: σ_{ab} (\blacktriangle) and σ_{c} (\blacktriangledown) for "textured" RTGG-UPS specimen, σ^{SSR} for SSR-PLS specimen (\bigcirc), and σ_{ab} for "highly textured" RTGG-UPS specimen (\blacksquare). Here, RTGG, UPS, SSR and PLS represent "the reactive-templated grain growth method", "sintered with uniaxial pressing", "conventional solid-state reaction", and "pressureless sintering", respectively.

these specimens.^{46, 47)} The values of σ_c (c: out-ofplane), and σ^{SSR} are shown as a comparison in Fig. 7 where the former was measured for the "textured" ceramic, and the latter was measured for the specimen prepared by a conventional solid-state reaction (SSR) followed by pressureless sintering (PLS). It was found that the σ_{ab} value of the "textured" ceramic was more than 5-10 times as large as the σ^{SSR} value over the whole range of measured temperatures. In addition, the "textured" ceramic exhibited a single-crystal-like strong anisotropy, for example, σ_{ab}/σ_c was ~12 at 555 K for the "textured" ceramic while $\sigma_{ab}^{sc}/\sigma_c^{sc}$ was ~17 at 300 K¹³ for the single crystal (SC). Furthermore, the σ_{ab} value of the "highly textured" ceramic reached 2.61×10^4 S/m at 1060 K,^{25, 46)} which is about 60 % of the σ_{ab}^{sc} value. For the other cobaltites also, the σ_{ab} values of the RTGG-UPS specimens were higher than the σ^{SSR} values.²⁶⁾

In the case of *S*, the anisotropy was small,^{24, 25)} consistent with the reference.²¹⁾ On the other hand, κ exhibited a large anisotropy, however, the anisotropy in σ ($\sigma_{ab}/\sigma_c \sim 5.5$ at 1060 K, **Table 2**) exceeded that of κ ($\kappa_{ab}/\kappa_c \sim 3$ at 773 K, Table 2).²⁵⁾ As a result, Z_{ab} was substantially higher than Z_c ($Z_{ab}/Z_c \sim 2.5$ at 1060 K, Table 2 and **Fig. 8**). For the calculation of *Z* values, the κ values were estimated by linear extrapolation of the measured values at temperatures from 373 to 773 K. Furthermore, the "highly textured" ceramic^{25, 46)} reached a fairly large Z_{ab} value of 2.44 × 10⁻⁴ K⁻¹ at 1060 K (Fig. 8).

For further enhancement of the TE properties, we precisely analyzed by the XRD technique, the difference in microstructural properties between "textured" and "highly textured" ceramics, and examined the relationship between "synthetic

Table 2In-plane and out-of-plane thermoelectric
properties measured at 1060 K of 'textured'
CCO-3-layer specimen.

		In-plane	Out-of-plane
Electrical conductivity, σ	$[\times 10^4 \text{S/m}]$	1.54	0.283
Seebeck coefficient, S	[µV/K]	183	153
Thermal conductivity, κ	[W/mK]	3.82*	1.22*
Figure of merit, Z	$[\times 10^{-4} \text{K}^{-1}]$	1.51	0.66

* measured at 773 K.

conditions" and "degree of orientation and TE properties of the textured ceramics".⁴⁶⁾ In addition, we discovered large anisotropy in the magnetic properties of the cobaltites through muon spin rotation and relaxation experiments using the current RTGG-UPS specimens:⁴⁸⁾ in order to elucidate the origin of their high TE properties. We also conducted theoretical calculations of electronic structures⁴⁹⁾ to estimate the anisotropy in TE properties. Through the combination of these investigation technologies, we believe that the RTGG method is effective for the design of highly textured TE oxides and thus we expect the method to be widely used in both the search for the best composition and the production of ceramics applicable to TE devices.

4. Conclusion

Our proposed fabrication technique, the RTGG method, provided textured ceramics as designed for various TE layered cobaltites that commonly have the CoO_2 layer (*i.e.*, CCO-3-layer, CCO-4-layer and Bi-layered-cobaltites). All the prepared ceramic



Fig. 8 Temperature dependence of figure of merit (*Z*) for the CCO-3-layer specimens: Z_{ab} (\blacksquare) for "highly textured" RTGG-UPS specimen, Z_{ab} (\blacktriangle) and Z_c (\blacktriangledown) for "textured" RTGG-UPS specimen: RTGG and UPS represent "the reactive-templated grain growth method", and "sintered with uniaxial pressing", respectively.

specimens exhibited high degree of orientation and enhanced TE properties when compared to the SSR-PLS specimens. For further enhancement of TE properties, it is necessary to conduct effective doping that induces modification in the electronic structure. Therefore, the RTGG method, which would be applicable to compounds of various composition, is expected to be a useful technique for the synthesis of textured ceramics for practical application to TE devices.

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