Research Report

Highly-Textured Thermoelectric Oxide Polycrystals Synthesized by the Reactive-Templated Grain Growth (RTGG) Method

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RTGG法で作製した結晶配向熱電酸化物セラミックス

板原浩，谷俊彦

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 reactive-templated grain growth (RTGG) method, the use of platelike β-$\mathrm{Co(OH)_2}$ particles as reactive templates that provide an edge-sharing $\mathrm{CoO_6}$ octahedra layer similar to the $\mathrm{CoO_2}$ layer in the crystal structure of layered cobaltites. We prepared ceramic specimens by the *in situ* reaction between the aligned platelike β-$\mathrm{Co(OH)_2}$ 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 $\mathrm{[Ca_2CoO_3]_{0.62}[CoO_2]}$ 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-$\mathrm{Co(OH)_2}$, Platelike particle, Topotaxy

要　旨

廃熱からエネルギーを回生する熱電変換発電は，二酸化炭素排出量削減技術として実用化が期待されている。環境負荷物質を含まず，高温大気中で安定な層状酸化物導電体は，熱電素子候補物質の一つである。酸化物としては高いp型熱電性能を示すCo系層状酸化物は，その結晶構造に起因して熱電性能に大きな異方性を示す。このため，実用化には配向セラミックスの作製技術が不可欠である。そこで，β-$\mathrm{Co(OH)_2}$がCo系層状酸化物の結晶構造中の$\mathrm{CoO_2}$層と類似の稜共有$\mathrm{CoO_6}$八面体から構成されていることに着目し，$\mathrm{CoO_2}$層を提供する反応性テンプレートとしてβ-$\mathrm{Co(OH)_2}$を利用するRTGG法を提案してきた。配向させた板状β-$\mathrm{Co(OH)_2}$テンプレート粒子と，目的のCo系層状酸化物の組成にするための反応補完物質（酸化物または炭酸塩）とを反応させることによって高配向度のセラミックスを作製した。その結果，優れた熱電性能を示す各種のCo系層状酸化物熱電体の配向セラミックスが設計通りに作製された。特に，$\mathrm{[Ca_2CoO_3]_{0.62}[CoO_2]}$の配向セラミックスの電気伝導度（熱電性能の重要因子の一つ）は，単結晶の約60%という大きな値に到達した。我々の提案したRTGG法が，Co系層状酸化物熱電体の配向セラミックスの汎用的かつ効果的な作製技術であると示された。

キーワード 熱電変換発電，ゼーベック効果，層状コバルト酸化物，配向セラミックス，反応性テンプレート，反応性テンプレート粒成長(RTGG)法，板状β-$\mathrm{Co(OH)_2}$結晶，トポタキシー

1. Introduction

1. 1 Layered cobaltites as potential thermoelectric oxides

The recovery of energy from waste heat by thermoelectric (TE) power generation[1-5] 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 n-type 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 attention[6-9] 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 Ca[18]; denoted as Bi-layered-cobaltites).

1. 2 Processing design of the textured ceramics through the RTGG method

The single crystals of NCO[10] and CCO-3-layer[13] are reported to show a strong anisotropy in their TE properties due to their layered crystal structure. Because of their similar crystal structures (CoO_2 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 large-size 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 proposed[24-26] 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

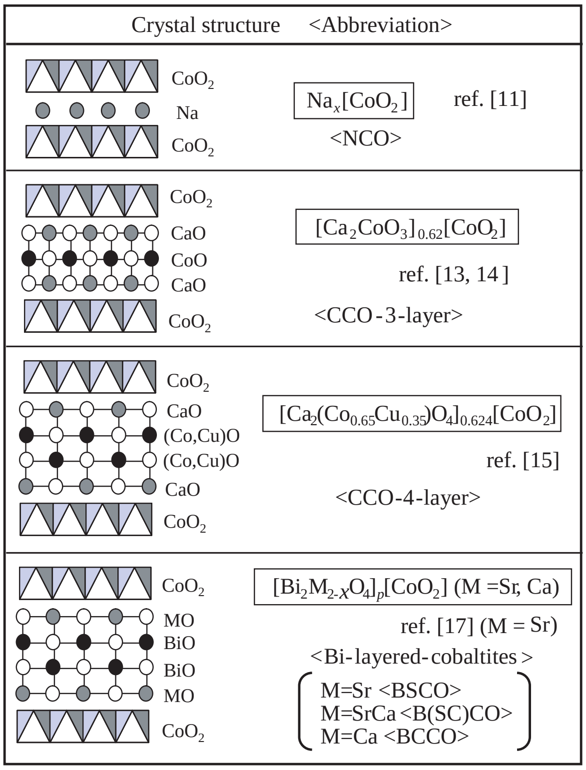

Fig. 1 Schematic representations for crystal structures of the thermoelectric layered cobaltites, and their abbreviations used in this report.

fabrication strategy of textured Mn-Zn ferrite ceramics[29) 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 CoO_2 layer consisting of edge-sharing CoO_6 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 {00*l*} 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-layer[26) and Bi-layered cobaltites.[26)

2. Experimental

2. 1 Fabrication of ceramics by the RTGG method[24-26)

Co(OH)$_2$ powders for use as templates were 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 μm 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.

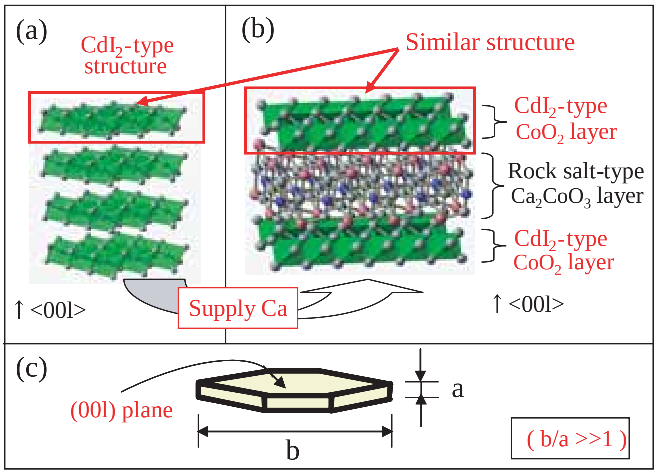

Fig. 2 The basic concept in the reactive-templated grain growth (RTGG) method using β-$Co(OH)_2$ templates: Crystal structures of (a) CdI_2-type β-$Co(OH)_2$ and (b) CCO-3-layer (one of the layered cobaltites), and (c) schematic representation of the morphology of β-$Co(OH)_2$ particles suitable for the reactive templates.

2. 2 Characterizations and thermoelectric property measurements

The crystalline phases of the precipitation-prepared powders were determined by X-ray diffraction (XRD) measurements. An oriented particulate monolayer XRD (OPML-XRD) technique[40) 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 degree[41) (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 μm in diameter with an aspect ratio of ~5, Fig. 4 (a)) developed along the {00l} 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

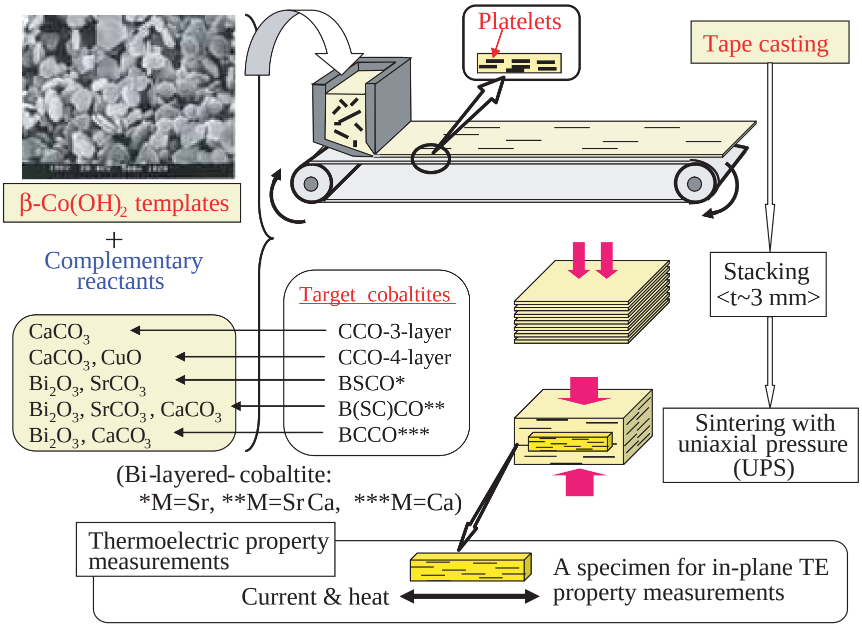

Fig. 3 Schematic representations for the synthesis of the textured ceramics of various thermoelectric layered cobaltites by the reactive-templated grain growth (RTGG) method, and thermoelectric property measurements.

Table 1 Typical preparation conditions for textured ceramics

RTGG-UPS Specimen*	Molar mixing ratio of starting materials	Sintering conditions **		
		Temperature [K]	Uniaxial Pressure [MPa]	Time [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_2O_3:$SrCO_3$= 2.00:1.00:2.00	1123	9.8	7.2
B(SC)CO	$Co(OH)_2$:Bi_2O_3:$SrCO_3$:$CaCO_3$ = 2.00:1.00:1.00:1.00	1153	9.8	7.2
BCCO	$Co(OH)_2$:Bi_2O_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 Bi-layered-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, $\{00l\}\beta\text{-Co(OH)}_2 \rightarrow \{111\}\text{Co}_3\text{O}_4 \rightarrow \{00l\}$CCO-3-layer. These results were deduced from thermogravimetry, differential thermal analysis, as well as

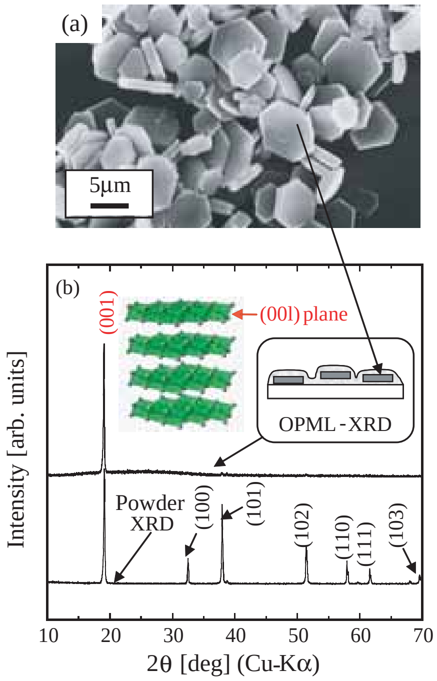

Fig. 4 (a) SEM photograph, and (b) powder XRD and oriented particulate monolayer (OPML) XRD patterns of precipitation-prepared $\beta\text{-Co(OH)}_2$ platelets.

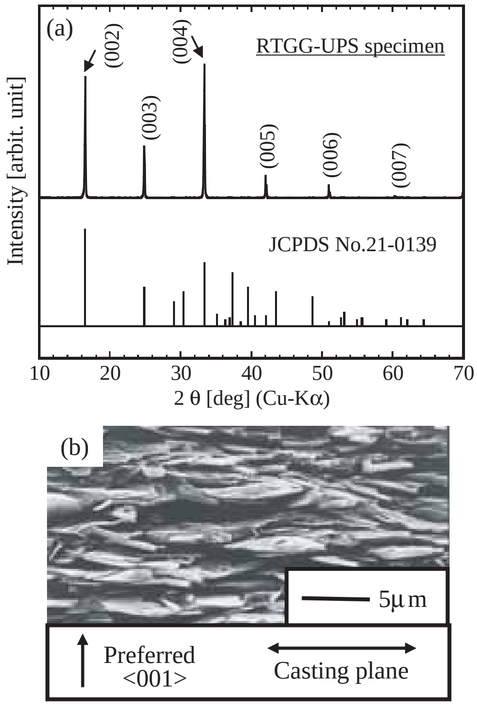

Fig. 5 (a) XRD pattern measured for a surface parallel to the casting plane, and (b) SEM photograph of a fracture surface perpendicular to the casting plane of RTGG-UPS specimen of CCO-3-layer: RTGG and UPS represent "the reactive-templated grain growth method", and "sintered with uniaxial pressing",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

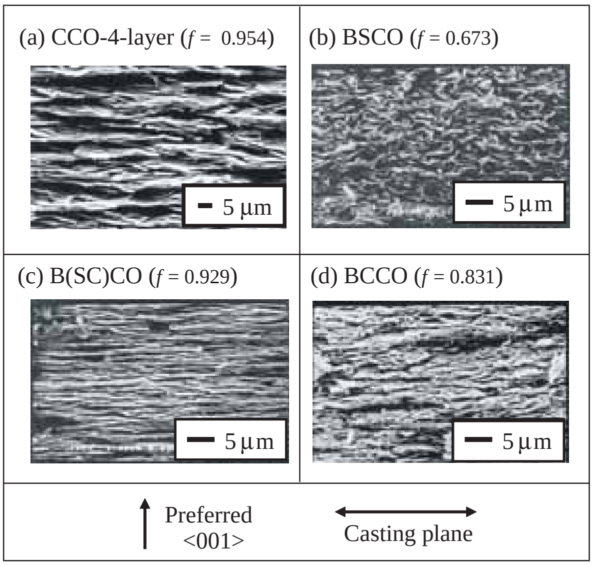

Fig. 6 SEM photographs of fracture surfaces perpendicular to the casting plane of RTGG-UPS specimens of (a) CCO-4-layer, (b) BSCO [M=Sr], (c) B(SC)CO [M=SrCa] and (d) BCCO [M=Ca].

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 sintering44, 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 these specimens.46, 47) The values of σ_c (*c*: out-of-plane), 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)

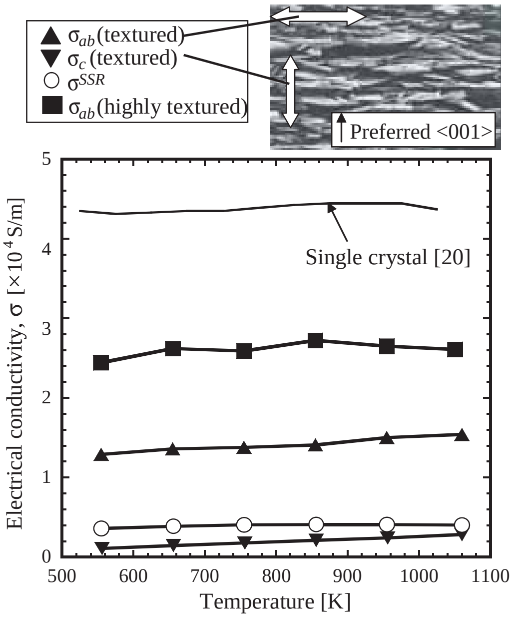

Fig. 7 Temperature dependence of electrical conductivity (σ) for the CCO-3-layer specimens: σ_{ab} (▲) and σ_c (▼) for "textured" RTGG-UPS specimen, σ^{SSR} for SSR-PLS specimen (○), and σ_{ab} for "highly textured" RTGG-UPS specimen (■). Here, RTGG, UPS, SSR and PLS represent "the reactive-templated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

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 (σ_{ab}/σ_c ~5.5 at 1060 K, **Table 2**) exceeded that of κ (κ_{ab}/κ_c ~3 at 773 K, Table 2).25) As a result, Z_{ab} was substantially higher than Z_c (Z_{ab}/Z_c ~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" ceramic25, 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 2 In-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	[× 10⁴ 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*	[× 10⁻⁴K⁻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 structures[49] 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 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.

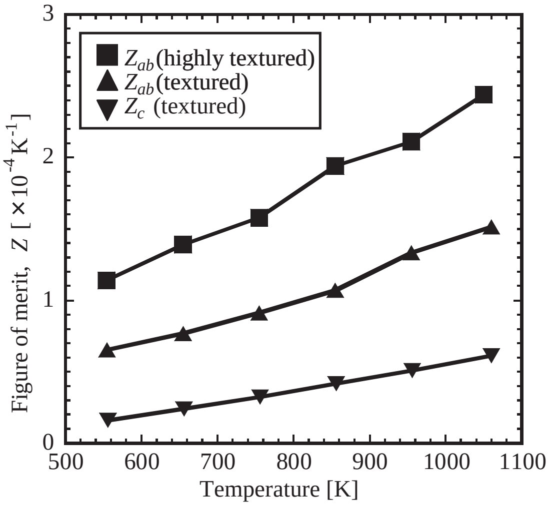

Fig. 8 Temperature dependence of figure of merit (Z) for the CCO-3-layer specimens: Z_{ab} (■) for "highly textured" RTGG-UPS specimen, Z_{ab} (▲) and Z_c (▼) for "textured" RTGG-UPS specimen: RTGG and UPS represent "the reactive-templated grain growth method", and "sintered with uniaxial pressing",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

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