Fabrication of Textured Ceramics of Thermoelectric Layered Cobaltites

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Key Words: Thermoelectrics, Layered cobaltites, Textured ceramics, Reactive-templated Grain Growth (RTGG)

1. Introduction

The energy recovery from waste heat by thermoelectric (TE) power generation [1] has been attracting attentions as one of the promising technologies for the reduction of CO_2 emissions. Layered cobaltites are the candidate p-type TE materials because they are composed of benign elements and stable in a high temperature air atmosphere. They show anisotropic performance due to their layered crystal structures, thus the production of textured ceramics is essential for the practical application. We propose the fabrication method of textured ceramics of various TE layered cobaltites with enhanced performance. [2-4]

2. Experimental

We fabricated ceramics of $[Ca_2CoO_3]_{0.62}[CoO_2]$ (CCO: rock-salt (RS) type layer + CoO_2 layer [5-6]), $[Ca_2(Cu_{0.65}Co_{0.35})_2O_4]_{0.624}[CoO_2]$ (CCCO: RS type layer + CoO_2 layer [7]) and $[Bi_2M_{2-x}O_4]_p[CoO_2]$ (RS type layer + CoO_2 layer: M = Bi; BSCO [8], M = Ca; BCCO [9]). We applied [2-4] the reactive-templated grain growth (RTGG) method using β-$Co(OH)_2$ (CdI_2-type) platelets as reactive templates that provides an edge-sharing CoO_6 octahedra layer similar to the CoO_2 layer in the crystal structures of the layered cobaltites (see, Fig. 1). We mixed β-$Co(OH)_2$ templates with (001) plane developed [10-11] and complimentary reactants to give the target compositions (*e.g.*, $CaCO_3$ was used to supply Ca for the formation of CCO, see, Fig. 1 and Table 1) with binder in an organic solution. The mixed slurry was tape-cast. The obtained tape was dried, cut into ordered size. About 50 tapes were stacked and pressed to form a single compact. After dewaxing, the compact was sintered with uniaxial pressing in O_2 atmosphere. The details of the procedures are described in the previous reports [2-4].

X-ray diffraction (XRD) measurements were conducted to determine the crystalline phases and Lotgering's orientation degree (f) [12] of the prepared ceramics. The microstructures of the ceramics were observed by a scanning electron microscope (SEM). Electrical conductivity (σ) was measured using a four-probe method.

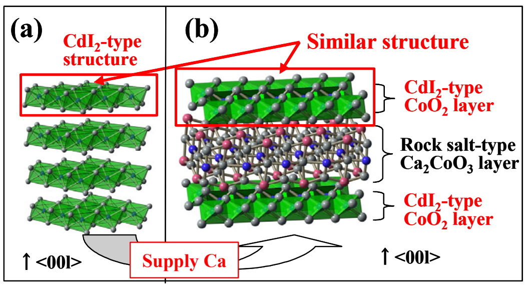

Figure 1. The basic concept of the reactive-templated grain growth (RTGG) using β-$Co(OH)_2$ templates [2-3]; (a) β-$Co(OH)_2$ and (b) $[Ca_2CoO_3]_{0.62}[CoO_2]$ (CCO).

Table 1 Typical preparation conditions

Sample	Molar mixing ratio of starting materials	Sintering conditions* Temp. [K]	Press. [MPa]	Time [ks]
CCO	$Co(OH)_2$:$CaCO_3$ = 3.92:3.00	1193	9.8	7.2
CCCO	$Co(OH)_2$:$CaCO_3$: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
BCCO	$Co(OH)_2$:Bi_2O_3:$CaCO_3$ = 2.00:1.00:2.00	1173	1.96	7.2

* O_2 atmosphere

3. Results and Discussion

RTGG-prepared ceramics for CCO, CCCO, BSCO and BCCO were all found to be highly textured with trace of impurities according to the XRD pattern [2-4] measured for a surface parallel to the casting plane and SEM photographs of fracture surface perpendicular to the casting plane (Fig. 2). It was found [2-4] that the values of σ for these textured ceramics were several times higher than those of non-textured ceramics prepared by the conventional solid-state reaction. It was confirmed [2-3] that RTGG-prepared CCO ceramics showed the single-crystal-like strong anisotropy: $\sigma_{\text{in-plane}}/\sigma_{\text{out-of-plane}}$ was ~ 12 at 555 K for the textured CCO ceramic while $\sigma_{\text{in-plane}}/\sigma_{\text{out-of-plane}}$ was ~ 17 at 300 K for the single crystalline particles [6]. Furthermore, the highest value of σ of textured CCO [2] reached ~ 60 % of that of the single crystalline particles [13] by optimizing the sintering conditions [14].

In addition, we proved [15] that the textured CCO ceramics was formed through the designed scheme shown in Fig.1: A textured CCO ceramic is formed by topotactic conversions via intermediate phases where β-$Co(OH)_2$ template provides the CoO_2 layer of CCO. Finally, it was demonstrated [16] that the TE module using RTGG-prepared p-type CCO and n-type $(ZnO)_mIn_2O_3$ stably generated electric power in a high temperature air atmosphere.

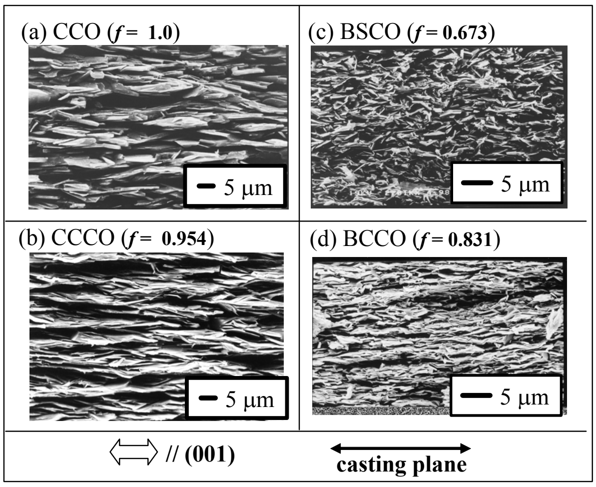

Figure 2. SEM photographs of fracture surface perpendicular to the casting plane. [2-4] The value of f represents Lotgering's orientation degree (f = 1: perfectly textured, f = 0: completely random).

4. Conclusion

RTGG process using β-$Co(OH)_2$ templates as reactive templates was shown to give the textured ceramics of various TE cobaltites with enhanced performance. We expect that the RTGG method would be useful technique for the fabrication process of TE device elements.

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