Research Report

Thermoelectric Properties of Highly Textured Ca-doped $(ZnO)_mIn_2O_3$ Ceramics

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Caドープ型$(ZnO)_mIn_2O_3$配向セラミックスの熱電特性

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Abstract

Highly textured Ca-doped $(ZnO)_mIn_2O_3$ (*m* is an integer) ceramics were fabricated by the reactive templated grain growth (RTGG) method and their thermoelectric properties were examined. Platelike $ZnSO_4 \cdot 3Zn(OH)_2$ particles were used as reactive templates and mixed with In_2O_3 and $CaCO_3$ powders into a stack of tapes. *In situ* formation and subsequent sintering resulted in textured Ca-doped $(ZnO)_mIn_2O_3$ ceramics. The electrical conductivity of the textured specimen along the *ab*-plane was almost two times larger than that of the textured specimen along the *c*-axis and about 30% larger than that of a nontextured specimen. On the other hand, the Seebeck coefficients of the textured specimen exhibited a small anisotropy. The thermal conductivity of the RTGG specimen along the *ab*-plane was higher than that of the RTGG specimen along the *c*-axis. However, both specimens showed similar values at high temperatures. As a result, the Ca-doped specimen along the *ab*-plane with a composite phase of $(ZnO)_3In_2O_3$ and $(ZnO)_4In_2O_3$ showed a *ZT* value of 0.31 (at 1053 K), compared with 0.23 (at 1053 K) for the nontextured specimen.

Keywords Thermoelectric, Layer-structured, Textured ceramics, Zinc indium oxide, Ca doping

要　旨

反応性テンプレート粒成長法 (RTGG法) を用いてCaドープ型$(ZnO)_mIn_2O_3$配向セラミックスを作製し，その熱電特性を調べた。テンプレートとして$ZnSO_4 \cdot 3Zn(OH)_2$板状粒子を用い，それに補完材料であるIn_2O_3と$CaCO_3$の粉末を混合したテープ成形体を積層後，熱処理により合成及び焼結を行った。その結果，テープ面と垂直方向にc軸が揃った配向セラミックスを得た。c軸に垂直なab面内の電気伝導度はc軸方向に比べて2倍の値を示した。一方，熱起電力の異方性は小さかった。熱伝導度に関しては，低温でab面内の方がc軸方向に比べて大きいが，高温では異方性が小さくなった。結果として，無次元性能指数 (*ZT*) の値は温度1053 Kで0.31を得た。この値は無配向材料の値0.23より高く，現状のn型酸化物バルク材料の中で最も高い値の一つである。

キーワード 熱電材料，層状構造，配向セラミックス，酸化インジウム，カルシウムドーピング

特集

1. Introduction

Texture engineering is a key technology for improving the anisotropic properties of materials. Since the introduction of the reactive templated grain growth (RTGG) method,[1] it has been applied to layered oxide thermoelectric materials such as Na_2CoO_4,[2] $[CaCoO_3]_{0.62}[CoO_2]$,[3] and $(ZnO)_5(In_{0.97}Y_{0.03})_2O_3$.[4] These textured ceramics have been proved to show high thermoelectric performance along the layer than randomly oriented ceramics mainly due to their high electrical conductivity, which is one of the factors in the thermoelectric dimensionless figure of merit defined as

$$ZT = \sigma S^2 T/\kappa, \quad (1)$$

where σ, S, T, and κ are the electrical conductivity, Seebeck coefficient, absolute temperature, and thermal conductivity, respectively.

Layer-structured homologous compounds $(ZnO)_mIn_2O_3$ (m is an integer, Z_mIO) have been extensively studied as candidates for n-type thermoelectric oxide materials.[4-9] Koumoto and coworkers first reported that Z_5IO had a fairly high figure of merit, which was then improved with Y substitution for an In site.[5-6] Further enhancement was achieved by the RTGG method, realizing a ZT value of 0.33 at 1073 K in highly textured ceramics.[7] We recently optimized carrier concentrations and structural factor m with various doping effects for nontextured Z_mIO. The obtained ZT value was 0.23 at 1053 K with nontextured Ca-doped $(ZnO)_nIn_2O_3$ (n = ZnO/In_2O_3, 3< n <4), which was relatively high among n-type oxides.[8] Ca doping effectively decreases thermal conductivity at high temperatures.

In this paper, we report on Ca-doped $(ZnO)_mIn_2O_3$ ceramics fabricated by the RTGG method. The resulting textured specimens have shown significant improvement in their thermoelectric properties.

2. Experimental procedure

Platelike powder of $ZnSO_4 \cdot 3Zn(OH)_2$ (Hakusui Tech Co., Osaka, Japan) with particle sizes of 2-10 μm and thicknesses of 0.1-0.3 μm was used as the reactive template. The $ZnSO_4 \cdot 3Zn(OH)_2$ platelets, In_2O_3, and $CaCO_3$ (Kojundo Chemical, Saitama, Japan) powders were weighed in specific proportions to have the composition of n = (ZnO)/$(In_{0.975}Ca_{0.025})_2O_3$ (2 < n < 4) where the highest thermoelectric performance was realized in the nontextured ceramics fabricated by the conventional solid-state reaction process.[8] It should be noted that we will use the term "m" to refer to the homologous phase of Z_mIO as distinguished from the n value. They were mixed with a solvent (60% toluene - 40% ethanol, v/v) and binder [poly(vinyl butyral)] in a ball mill for 5 h using zirconia balls. A plasticizer (di-*n*-butyl phthalate) was then added to the slurry and the mixture was milled for another hour. The mixed slurry was tape-casted using a doctor blade to form a sheet with a thickness of about 150 μm, and the obtained sheet was dried in air at room temperature. The sheet was cut, stacked, and pressed at 80 $^{\circ}$C to form a billet with a thickness of about 20 mm. The billet was cut into a rectangular bar perpendicular and parallel to the original sheet plane for use in studying anisotropic transport properties. The specimens were heated at 1073 K for 30 min in flowing air to remove organic substances. After subjecting to cold isostatic pressing at 294 MPa, dewaxed specimens were synthesized at 1150 $^{\circ}$C for 12 h and then sintered at 1300 $^{\circ}$C for 24 h in flowing air (denoted as RTGG specimens). A reference specimen with a random grain orientation was also fabricated by the conventional solid-state sintering methods for comparison (denoted as an REF specimen). The detailed procedure and transport properties of the REF specimen are available elsewhere.[8]

Crystalline phases were determined by X-ray diffraction (XRD, Model RINT-TTR, Rigaku, Tokyo, Japan) analysis with CuKα radiation. The scan was carried out in ranging from 5 to 80° in 2-theta at a scan rate of 4°/min. For each pattern, the peaks were indexed using the card file patterns (JCPDF) of possible reaction products in comparison with the obtained patterns.

The degree of orientation was evaluated in terms of the Lotgering factor, F_L, using the equations described previously.[9] A reflection pole figure of $(00\underline{15})$ was also used to examine the detailed texture. In this measurement, the incident (θ) and diffraction (2θ) angles were maintained constant, and azimuthal (β, 0°< β <360°) scans were carried out around the normal direction (ND), which was perpendicular to the original sheet plane at various polar angles (α, $0^{\circ} < \alpha < 75^{\circ}$). The degree of orientation for the ND, F_{ND}, was calculated using

$$F_{\mathrm{ND}} = \frac{3\langle \cos^2 \alpha \rangle - 1}{2}, \quad \cdots\cdots (2)$$

with

$$\langle \cos^2 \alpha \rangle = \frac{\int_0^{75} \int_0^{360} I_c(\alpha, \beta) \cos^2 \alpha \cdot \sin \alpha \cdot d\beta \cdot d\alpha}{\int_0^{75} \int_0^{360} I_c(\alpha, \beta) \sin \alpha \cdot d\beta \cdot d\alpha}, \quad \cdots\cdots (3)$$

where I_c is the normalized diffraction intensity with the background correction.[10)]

For the RTGG specimens, thermoelectric properties (electrical conductivity, Seebeck coefficient, and thermal conductivity) were examined on rectangular bars parallel (//) and perpendicular (⊥) to the original sheet plane, as compared with the REF specimen. The relative densities of the specimens were determined by Archimedes' method.

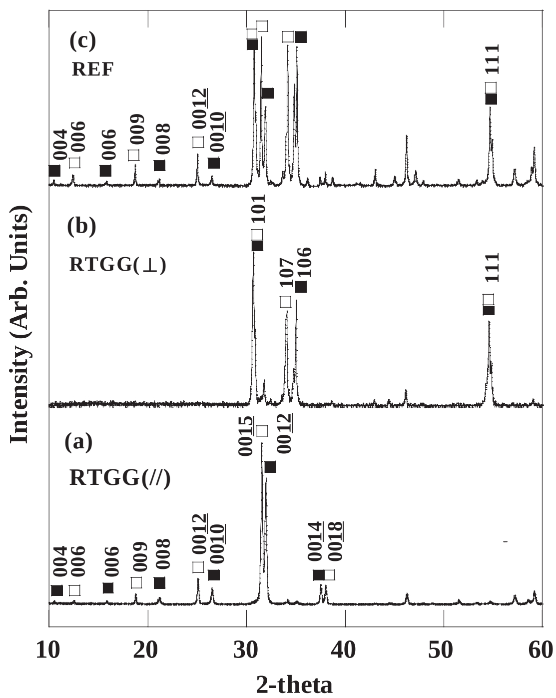

Fig. 1 XRD patterns of Ca-doped RTGG and REF specimens: (a) parallel and (b) perpendicular to sheet plane, compared with (c) pattern for REF specimen. Peaks are indexed as $(ZnO)_3In_2O_3$(□) and $(ZnO)_4In_2O_3$(■) phases.

3. Results and discussion

Figure 1 shows the XRD patterns of the Ca-doped RTGG [parallel (//) and perpendicular (⊥) to the sheet plane] specimens with n = 3 compared with the Ca-doped REF specimen with n = 3.5 that showed the highest figure of merit among the nontextured n-type oxides as previously reported.[8)] The (//) specimen exhibited a high diffraction intensity from {00ℓ} planes but a low diffraction intensity from other crystal planes, while the diffraction lines of the {00ℓ} planes were hardly observed for the (⊥) specimen. The degree of {00ℓ} orientation, F_{L}, calculated by the Lotgering method for the (//) specimen reached 0.94, showing that this specimen obtained by the RTGG method is highly textured. It should be noted that the XRD pattern of the Ca-doped RTGG specimen with n = 3 shows mixed phases of $(ZnO)_3In_2O_3$ and $(ZnO)_4In_2O_3$ and

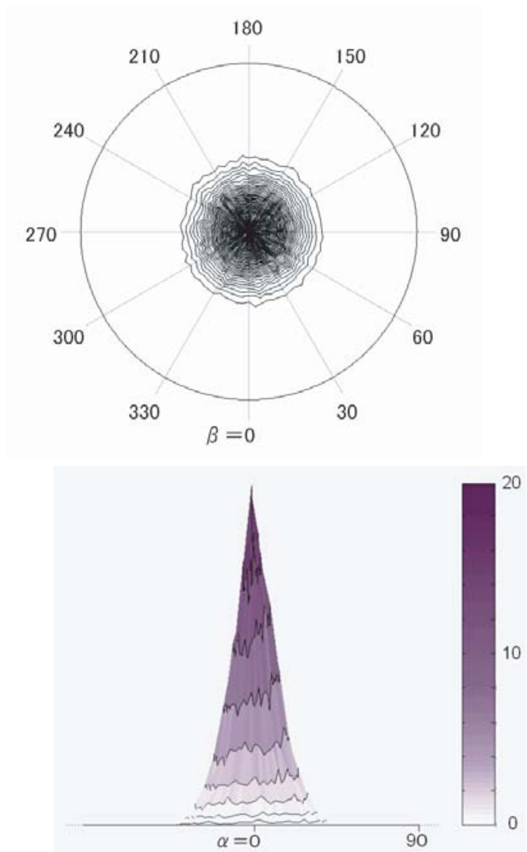

Fig. 2 (00<u>15</u>) pole figure of Ca-doped Z_3IO specimen sintered at 1300 °C. Pole densities are normalized using the average density. The center ($\alpha = 0^{\circ}$) indicates the normal direction, and β is measured from the direction of tape-casting in the RTGG process.

corresponds to the XRD pattern of the nontextured Ca-doped specimen with $n = 3.5$.

Figure 2 shows the (00$\underline{15}$) pole figure obtained from the RTGG (//) specimen. The azimuthal angle β was obtained from the direction of the tape casting in the RTGG process. A large peak at the center in the pole figure indicates that the (00$\underline{15}$) plane is preferentially aligned along the ND. The degree of orientation, F_{ND}, reached 0.84. On the other hand, the circularly distributed (00$\underline{15}$) plane implies that there is no distinct texture on the *ab*-plane. These results indicate the feasibility of the present RTGG method by which grain growth follows the morphology of the platelike $ZnSO_4 \cdot 3Zn(OH)_2$ templates via Ostwald ripening, and the tape-casting does not induce any uniaxial distortion.

Figure 3 shows the temperature dependence of the electrical conductivity, σ, for the Ca-doped RTGG [(//) and (⊥)] and REF specimens with $n = 3$ and $n = 3.5$, respectively. The electrical conductivities of the textured specimen exhibited a strong anisotropy: that is, σ(//) was almost twice as large as σ(⊥) in a high temperature region. In addition, σ(//) was about 30 % larger than σ of the REF specimen over the measured temperatures. Note that σ (REF) was not between σ(//) and σ(⊥) in a low temperature region as usually expected for anisotropic crystal systems. The reason for this is that large grains, which are well aligned as a result of the topotactic reaction in the RTGG method, enhance the conductivities in both // and ⊥ directions. For the high-temperature region, σ(⊥) was decreased by the contribution of the interfacial electron phonon scattering in the layered structure. **Figure 4** shows the Seebeck coefficient, *S*, as a function of temperature. The Seebeck coefficient exhibited a small anisotropy, i.e., *S*(//) was ~1.1 × *S*(⊥). This result suggests that the Seebeck coefficient is rather insensitive to the type of microstructure. The thermal conductivities, κ, of three specimens as functions of temperature are shown in **Fig. 5**. The thermal conductivities of all specimens decreased as temperature increased. The specific heat capacity (C_p) increased but the thermal diffusivity (D_T) decreased further, leading to a decrease in thermal conductivity ($\kappa = \rho \cdot C_P \cdot D_T$, ρ being the density) with an increase in temperature. The electrical contribution was calculated using the Wiedeman-Franz law. The electrical part was only about 10 % of the total thermal conductivity and slightly increased at high temperatures. κ(⊥) was lower than κ(//) over the measured temperature, indicating interfacial phonon-phonon scattering that makes the phonon mean free path in κ(⊥) shorter than that in κ(//).

The thermoelectric dimensionless figure of merit was calculated and is shown in **Fig. 6**. The RTGG (//) specimen, in which electrical and thermal fluxes are presumed to be parallel to the preferential

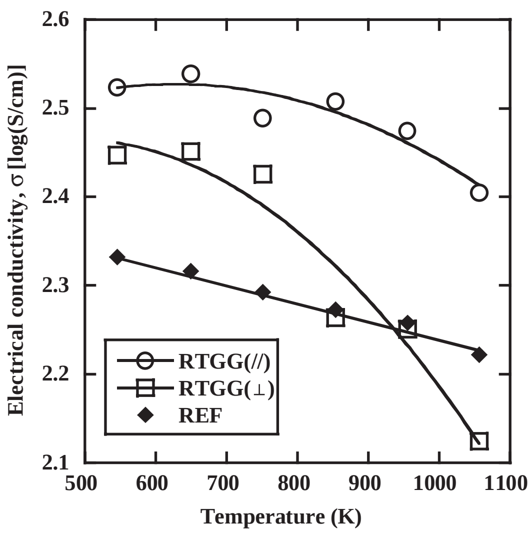

Fig. 3 Temperature dependence of electrical conductivity of Ca-doped textured [(//|) and (⊥)] and REF specimens.

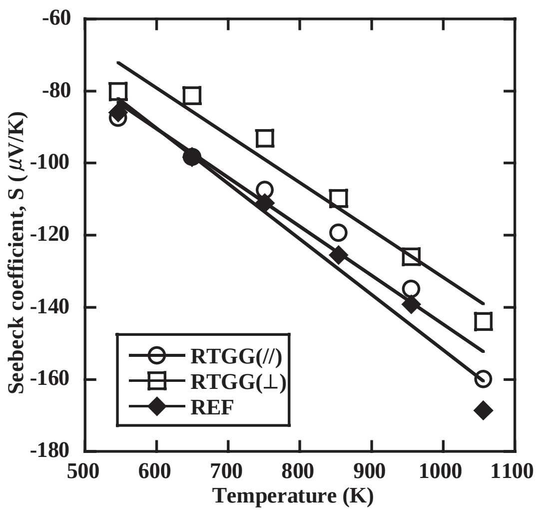

Fig. 4 Temperature dependence of Seebeck coefficient of Ca-doped textured [(//) and (⊥)] and REF specimens.

ab-plane, exhibits higher *ZT* values than the RTGG(⊥) specimen because the anisotropy observed in σ exceeds that of κ. The dimensionless figure of merit of the RTGG(//) specimen increased by about 30% compared with that between the specimens of the REF specimen, mainly due to the difference in electrical conductivity. As a result, the Ca-doped textured specimen with n = 3 shows a *ZT* value of 0.31 at 1053 K.

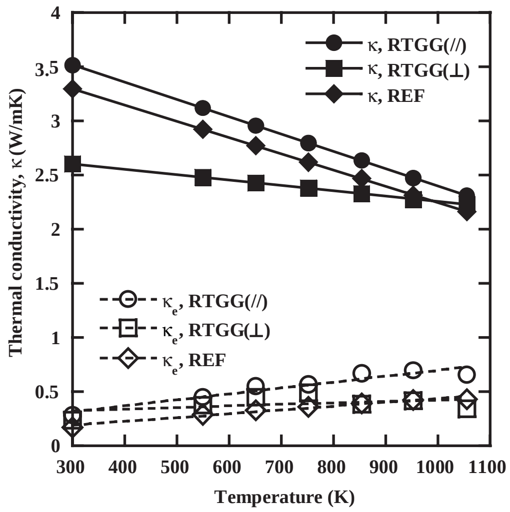

Fig. 5 Temperature dependence of total thermal conductivity (κ) of Ca-doped textured [(//) and (⊥)] and REF specimens. The electronic contribution (κ_e) was calculated using the Weidemann-Franz law.

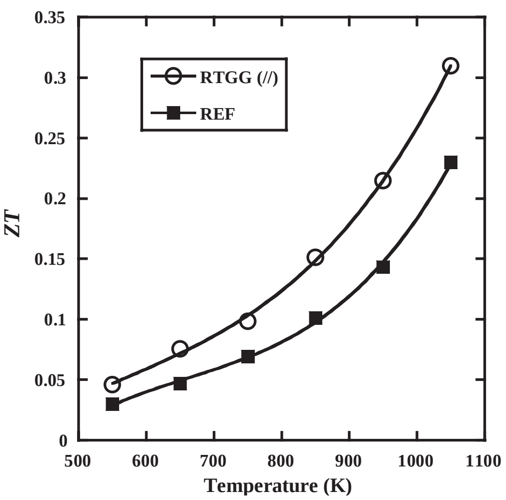

Fig. 6 Temperature dependence of dimensionless figure of merit of Ca-doped textured and REF specimens.

4. Conclusions

Highly textured Ca-doped $(ZnO)_mIn_2O_3$ ceramics were fabricated by the RTGG method using platelike $ZnSO_4 \cdot 3Zn(OH)_2$ particles as reactive templates. The XRD results showed a highly textured composite phase of Z_3IO and Z_4IO for a designed molar ratio of $(ZnO)/(In_{0.975}Ca_{0.025})O_3$ = 3. The textured specimen exhibited a higher in-plane electrical conductivity than the nontextured specimen, leading to a higher figure of merit. The textured Ca-doped specimen showed a *ZT* value of 0.31 (at 1053 K), which is one of the best values in n-type oxides.

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