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Dependence of thermoelectric properties on the solid loading of cast tapes in laminated and textured Ca₃Co₄O₉ ceramics

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Textured $Ca_3Co_4O_9$ ceramics were prepared by a reactive templated grain growth process using tape casting process. The effect of the solid loading of the green tape on the thermoelectric properties of the textured $Ca_3Co_4O_9$ was investigated. The findings indicate that the thermoelectric properties of textured ceramics are dependent on the solid loading of cast tapes. The power factor ($S^2\sigma$) for $Ca_3Co_4O_9$ can be optimized by appropriately controlling the solid loading, because the electric conductivity (σ) is susceptible to variations in the bulk density by the solid loading, whereas the Seebeck coefficient (S) is relatively insensitive to this type of variation. The maximum power factor for textured $Ca_3Co_4O_9$ ceramics with a solid loading of 62.2 vol% was 4.52×10^4 W/mK² at a temperature of 1100 K.

Key words: Reactive templated grain growth, Spark plasma sintering, Solid loading, Ca₃Co₄O₉.

Introduction

High temperature thermoelectric oxides with a layered structure typically have comparatively high thermoelectric properties [1]. Because layered structured oxides exhibit anisotropic properties, a textured c-axis aligned ceramic is needed, if thermoelectric performance is to be improved by polycrystal orientation techniques [2]. Reactive templated grain growth (RTGG) method uses a mixture of precursor particles with anisotropic shapes and equiaxed particles with the composition needed to form the desired product in the reaction [3]. The RTGG method is frequently applied by combining it with the tape casting to permit the anistropic template to be aligned to the preferred orientation [4-6]. The tape casting process is a well-established technique used for the fabrication of multilayered, ceramic substrates. This process requires the use of significant amounts of organic compounds. The organic additives, which are a requirement for tape casting, is used to impart strength and flexibility in green tapes during the lamination and cutting process are ultimately eliminated during the sintering process [7]. On the other hand, the compactness of the powder inside the green tape has an effect on the physical properties of the fired material and in particular upon the tape density [8].

The property of anistropic $Ca_3Co_4O_9$ ceramics is strongly influenced by the degree of texturing. And the texture of cast tape and final specimen prepared through RTGG process are expected to change by solid loading, which is inverse proportion to organic amount. However, our understanding of the thermoelectric properties of $Ca_3Co_4O_9$ ceramics as a function of solid loading is currently incomplete. In this report, the influence of solid loading in the cast tape on laminated thermoelectric $Ca_3Co_4O_9$ was examined by varying the ratio used in the solid loading. To increase the density of the structure of the calcined compacts, a spark plasma sintering (SPS) process were applied [9, 10]. The degree of alignment of the prepared samples was characterized by the Lotgering factor (*f*), obtained using X-ray diffraction. Relationship between the solid loading in the cast tape and the thermoelectric properties of RTGG $Ca_3Co_4O_9$ oxide are discussed.

Experimental

Template β -Co(OH)₂ powders were prepared by the precipitation method. Reagent grade CoCl₂ · 6H₂O and NaOH powders were used as raw materials. The raw materials were completely dissolved in distilled water. Solutions of $CoCl_2 \cdot 6H_2O$ and NaOH were prepared at a concentration of 0.1 mol%. The NaOH solution was added to the $CoCl_2 \cdot 6H_2O$ solution at a rate of 5 ml/ min until the mole ratio between the Co^{2^+} and $\mathrm{OH}^{\text{-}}$ in the solution reached 1:2. The resulting solution was allowed to react for 72 h in an atmosphere of nitrogen gas to prevent the oxidation of Co^{2+} . The precipitated β -Co(OH)₂ particles were washed with distilled water and dried at room temperature. The mean particle size of the powdered β -Co(OH)₂ particles was 1.1 μ m. The synthesized β -Co(OH)₂ and CaCO₃ (> 99.9%, Kojundo, Japan) were mixed at a mole ratio of 3:4 in a PE bottle with YSZ ball media for 24 h in a co-solvent

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system composed of MEK (methyl ethyl ketone, 99.5%) and Ethanol (ethyl alcohol anhydrous, 99.9%) at a weight percent ratio of 69:31. Subsequently, a binder (polyvinyl butyral, butvar 79, Monsanto, USA) and plasticizer (Dibutyl phthalate, Aldrich, USA) were added and the preparation then ball-milled for an additional 24 h. The solid loading of β -Co(OH)₂ and CaCO₃ to the total ingredients excluding the solvent were varied as follows: (a) 57.4 vol% (b) 62.2 vol%, and (c) 67.5 vol%, respectively. The ratio of binder to plasticizer was fixed at 1:1. The slurry was cast on a Mylar film at a rate of 30 cm/min with a doctor blade after de-airing. The cast slurry was dried in stagnant air for 24 hours. Green tapes were laminated by the warm isostatic pressing (WIP) process at 80 °C and 250 bar for 30 min. Green compacts were calcined to 800 °C in air at a heating rate of 0.1 °C/min and held for 4 h. The calcined samples were sintered by the spark plasma sintering (SPS) process at 920 °C and 50 MPa for 10 min at a heating rate of 100 °C/min. In the present study, the samples produced through the calcination and the SPS processes using the green tapes containing a solid loading of 57.4 vol %, 62.2 vol % and 67.5 vol% are denoted as V1, V2, V3, as the order of the solid loading, respectively. The phase of the precipitated β -Co(OH)₂, green tape, and Ca₃Co₄O₉ specimens were analyzed by X-ray diffraction with Cu Ká radiation source ($\lambda = 1.5406$ Å). The Lotgering factor (f) was used as an indication of the degree of orientation. The Lotgering factor (f) is a method used to calculate the degree of orientation using the intensity shown on the XRD pattern, and is calculated as $f = (P-P_0)/(1-P_0)$, where $P = \Sigma I(00l) / \Sigma(hkl)$ and P_0 represent a randomly oriented powder specimen. The value of P_0 was calculated using JCPDS data [11]. The density of the specimen was measured by the Archimedes method. The packing fraction of the green tape was calculated as $P = D_g \cdot R_a / D_{th}$, where D_g , R_a , and D_{th} represent the green density of the cast tape, the weight fraction of inorganic solid in the green tape, and the theoretical density of the solid, respectively. The green density was obtained using a modified Archimedes method [12]. The microstructure of the precipitated powder, and the Ca₃Co₄O₉ specimen were examined by FE-SEM (JSM 6700F, JEOL, Japan). The average diameter of the precipitated particles was characterized using an image analysis system (Image-Pro Plus V6.2, Media Cybernetics, USA). The electrical conductivity σ and Seebeck coefficient S were measured in a temperature range from 300 °C to 900 °C using a thermoelectric property measurement system (RZ2001i, Ozawa Science, Japan).

Results and discussion

Fig. 1 shows X-ray diffraction patterns of the green tapes, the calcined specimen and the SPS sintered specimen. The X-ray diffraction patterns of the green



Fig. 1. XRD patterns of (a) a green tape with a solid loading of 62.2 vol %, (b) calcined specimen using a green tape with a solid loading of 62.2 vol %, sintered specimens using the green tape with a solid loading of (c) 57.4 vol % (d) 62.2 vol %, and (e) 67.5 vol %, respectively.

tapes (Fig. 1(a)) prepared by the tape casting method using β -Co(OH)₂ and CaCO₃ as the inorganic ingredients were in agreement with the data from standards on β -Co(OH)₂ (JCPDS 30-0443) and CaCO₃ (JCPDS 41-1743). When the green tapes were subsequently dewaxed and calcined, single-phased polycrystalline Ca₃Co₄O₉ was produced by the RTGG process (Fig 1(b)), in which the anisotropic, plate-like form of β -Co(OH)₂ was reacted with isotropic CaCO₃ in a topotactic manner and grown to polycrystalline Ca₃Co₄O₉ [13], diffractions were observed from not only [001] planes, but also other crystal planes, which originated from the growth of Ca₃Co₄O₉ grains into unconstraint interstice formed during the dewaxing of the organic ingredients. After the SPS process for densification, the X-ray diffraction patterns of the sintered specimens with various solid loadings (Fig. $1(c) \sim (e)$) were in agreement with reported data for standard Ca₃Co₄O₉ (JCPDS 21-0139). Diffraction only from the [00l] planes was detected, indicating that the c-axis, which is perpendicular to the sublattice layer, is the preferred orientation [9].

As shown in Fig. 2, the degree of orientation (*f*) of β -Co(OH)₂ template particles in the green tapes increased linearly from 0.718 to 0.774 when the solid loading was increased from 57.4 vol% to 67.5 vol%. The alignment of the powder in the green tape was improved by increasing the solid loading. This was caused by the interacting and parallelizing of the plate-like β -Co(OH)₂ particles in the slurry by the high concentration of the particles present during the casting process [14]. The degree of orientation was increased as the result of applied pressure during the SPS [15]. After the SPS process, the degree of orientation of the sintered samples was maintained relatively constant around 0.9



Fig. 2. The Lotgering factors for (a) green tapes and (b) specimens after the SPS as a function of the solid loading in cast tape.



Fig. 3. (a) Packing fraction of the green tapes and (b) relative density of specimens after the SPS process as a function of solid loading.

in spite of the changes in solid loading. The discrepancy (Δf) between the degree of orientation in the sintered specimens with various levels of solid loading decreased below 0.018, which was 3 times lower than that $(\Delta f = 0.056)$ in the green tapes. The effectiveness of the solid loading on varying the packing fraction of the green tapes was nearly overwhelmed in the following SPS process, where the structure was compacted by means of an the applied pressure of 50 MPa.

Fig. 3(a) shows the packing fraction of the green tapes, as determined measured by a modified Archimedes method. By increasing the solid loading, the packing fraction of the green tape was increased to above 45% and then became saturated. This can be explained by



Fig. 4. SEM of the fractured surfaces of SPS sintered samples using the green tapes with a solid loading of (a) 57.4 vol% (b) 62.2 vol%, and (c) 67.5 vol%.

Gardner's model, in which the particle separation is decreased and the packing fraction of the particles is increased when the solid loading in the tape is increased, as long as the volume of organics introduced into the slurry is higher than the volume of the particle interstice. Beyond this limit, particle contact occurrs, which induces a constant packing fraction of the green tape [8, 16]. The maximum value for packing fraction was at a solid loading of 62.4 vol%, where the particles were in close contact with one another and the organic compounds facilitated the rearrangement of the particles [17].

As shown in Fig 3(b), the relative density of the sintered sample was increased as the result of the compaction of SPS process and the maximum relative density was 85% at a solid loading of 62.4 vol% where the packing density of the green tape was at a maximum. The bulk density was decreased abruptly by



Fig. 5. Temperature dependence of the (a) electrical conductivity (b) Seebeck coefficient, and (c) power factor of specimens prepared using green tapes with a solid loading of 57.4 vol%, 62.2 vol%, and 67.5 vol%.

the conventional sintering process when the particles were separated by organic materials, was decreased slightly by compensation from the compaction during SPS. However, the maximum relative density of 85% is somewhat lower than reported data obtained using SPS. Further research is clearly needed to optimize the spark plasma sintering process, such as temperature and pressure, to increase the relative density, in addition, to evaluate the effect of solid loading on the properties in such samples. The orientation of the particles and textured structure after the SPS process were confirmed in the micrograph of a fractured surface of Ca₃Co₄O₉ specimen shown in Fig. 4. The plate-like particles were oriented parallel with the casting direction and perpendicular to the pressing direction. The particles were tilted with an acute angle to the casting direction but differences between samples were not obvious in the micrographs.

Fig. 5 shows the temperature dependence of (a) electrical conductivity (b) the Seebeck coefficient and (c) power factors for specimens prepared using green tapes with a solid loading of 57.4 vol%, 62.2 vol%, and 67.5 vol%. The electrical conductivity increased in the order of solid loading as follows: 67.5 vol%, 57.4 vol%, and 62.2 vol%. An enhancement in conductivity could be anticipated from the gain in bulk density, which occurred as the result of the packing and rearrangement of the particles by the lamination process used in preparing the compacts [18] and the SPS process used in the sintering of the calcined specimens. The maximum electrical conductivity and power factor were found for a solid loading of 62.2 vol% in which the relative density was maximum. The positive temperature dependence of the Seebeck coefficient, which was measured along the same direction as the conductivity, indicated that the prepared samples are ptype. The value of the Seebeck coefficient varied slightly with an increase in solid loading, suggesting that the density and microstructure had little influence on the value of the Seebeck coefficient [19]. The Seebeck coefficient of the samples increased with increasing temperature and reached 183 µV/K at 1100 K, approaching that of the single-crystal Ca₃Co₄O₉ along the *ab* palne [20]. Because the electrical conductivity, σ , increased any obvious degradation in the Seebeck coefficient, S, the power factor, $S^2\sigma$, was clearly enhanced. The power factor of all samples increased with increasing temperature and the V2 reached $4.52 \times 10^{-4} \text{ W/mK}^2$ at 1100 K. This value was lower than the reported power factor for aligned Ca₃Co₄O₉ ceramics prepared using the SPS process [21]. The results clearly show that optimization of the solid loading in the slurry was necessary for controlling the packing fraction of the green tape and the relative density of sintered compacts, for which the conductivity and power factor of Ca₃Co₄O₉ ceramics are dependent.

Conclusions

The influence of the solid loading of the green tape on the thermoelectric properties of $Ca_3Co_4O_9$ oxide was confirmed. The alignment of template particles in the green tapes was improved when solid loading increased. This can be attributed to an increase in particle interactions and orientation in the slurry during the tape casting process. However, this tendency was changed in the packing fraction of the green tapes and the relative density of the sintered compacts because of the rearrangement and the compaction, respectively. The relative density of $Ca_3Co_4O_9$ ceramics reached a maximum at around a solid loading of 62.2 vol%, where the packing fraction was at a maximum. Therefore, optimization of the solid loading clearly had a positive effect on improving bulk density, which results in the formation of Ca₃Co₄O₉ with an enhanced conductivity. The power factor of the textured Ca₃Co₄O₉ prepared using a solid loading of 62.2 vol% reached 4.52×10^{-4} W/mK² at 1100 K. These results suggest that the solid loading of the green tape needs to be optimized to gain a higher packing fraction and relative density in the fabrication of textured Ca₃Co₄O₉ ceramics using the tape casting process.

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Reference

- K. Koumoto, I. Terasaki, and R. Funahashi, Mater. Res. Bull. 31 (2006) 206-10.
- W.-S. Seo, S. Lee, Y. Lee, M.-H. Lee, Y. Masuda and K. Koumoto, J. Electron Microsc. 53 [4] (2004) 397-401.
- 3. Y. Sakuma and T. Kimura, J. of Mat. Sci. 40 [18] (2005) 4811-17.
- S.-H. Hong and G. L. Messing, J. Am. Ceram. Soc. 82 [4] (1999) 867-72.
- 5. T. Tani, S. Isobe, W.-S. Seo and K. Koumoto, J. Mater. Chem. 11 (2001) 2324-28.

- Y. Masuda, D. Nagahama, H. Itahara, T. Tani, W.S. Seo and K. Koumotoa, J. Mater. Chem. 13 (2003) 1094-99.
- 7. R. Moreno, Am. Ceram. Soc. Bull. 71 [11] (1992) 1647-57.
- M. Descamps, G. Rinuet, D. Leger and B. Thieryy, J. Eur. Ceram. Soc. 15 (1995) 357-62.
- 9. Y. Zhang and Q. Lu, Ceram. Int. 33 (2007) 1305-08.
- Y Zhang and J. Zhang, J. Mater. Process. Technol. 208 [1-3] (2008) 70-74.
- 11. F.K. Lotgering, J. Inorg. Nucl. Chem. 9 (1959) 113-23.
- 12. D.J. Shanefield and R.E. Mistler, Am. Ceram. Soc. Bull. 53 [5] (1974) 416-20.
- 13. H. Itahara, C. Xia, J. Sugiyama and T. Tani, J. Mater. Chem. 14 (2004) 61-66.
- H. Watanabe, T. Kimura and T. Yamaguchi, J. Am. Ceram. Soc. 72 [2] (1989) 289-93.
- 15. Z.A. Munir and U. Anselmi-Tamburini, J. Mater. Sci. 41 (2006) 763-77.
- R.A. Gardner and R. W. Nufer, Solid State Technol. 17 [5] (1974) 38-43.
- T. Ueyama and N. Kaneko, in "High Tech Ceramics" Elsevier (1987) 1451-58.
- T. Claassen and N. Calussen, J. Eur. Ceram. Soc. 10 (1992) 263-71.
- M. Mikami, E. Guilmeau, R. Funahashi, K. Chong and D. Chateigner, J. Mater. Res., 20 [9] (2005) 2491-97.
- A.C. Masset, C. Michel, A. Maignan, M. Heriveu, O. Toulemonde, F. Studer and B. Raveau, Phys. Rev. B, B 62 (2000) 166-75.
- 21. Y. Liu, Y. Lin, Z. Shi, C.-W. Nan and Z. Shen, J. Am. Ceram. Soc. 88 [5] (2005) 1337-40.