

Effect of the reactive template particle size on the thermoelectric property of $\text{Ca}_3\text{Co}_4\text{O}_9$ oxide with the RTGG and SPS process

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By combining the reactive template grain growth (RTGG) with the spark plasma sintering (SPS) process, a dense and highly textured $\text{Ca}_3\text{Co}_4\text{O}_9$ was produced. The degree of orientation and the thermoelectric property were estimated with various template sizes. The degree of orientation in green tapes was improved by increasing of the particle size due to the particle's interaction and parallelization in the tape casting. The increased alignment also enhanced the texturing of the $\text{Ca}_3\text{Co}_4\text{O}_9$ during the SPS process, therefore, the bulk density and electrical conductivity of $\text{Ca}_3\text{Co}_4\text{O}_9$. The $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics prepared by the RTGG and SPS process possess of the maximum power factor of $5.2 \times 10^{-4} \text{ W/mK}^2$ at 1273°C .

Key word : Spark plasma sintering, Reactive template grain growth, Particle size, $\text{Ca}_3\text{Co}_4\text{O}_9$.

Introduction

$\text{Ca}_3\text{Co}_4\text{O}_9$ oxides have been considered as a candidate for high temperature thermoelectric materials due to their thermal endurance and chemical stability [1]. The thermoelectric properties of $\text{Ca}_3\text{Co}_4\text{O}_9$ oxides are originated from the layered structure of the $\text{Ca}_3\text{Co}_4\text{O}_9$ phase, consisting of alternate stacking of a rock-salt type (Ca_2CoO_3) layer and a CdI_2 -type (CoO_2) layer [2]. Because C-aligned $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics exhibit much higher electrical conductivity due to their anisotropic properties than randomly oriented ceramics, the texturing method of polycrystals has been studied to improve the thermoelectric properties through a reactive templated grain growth (RTGG) technique [3], which uses a mixture of precursor particles with shape anisotropy and equiaxed particles with the composition to form the object material by the reaction with precursor [4, 5]. The RTGG method has been applied by accompanying with the tape casting process to align the anisotropic template to the preferred orientation [6]. The tape casting process is a well-established technique used for the fabrication of ceramic substrates and multilayer structure [7]. Recently, spark plasma sintering (SPS) process was introduced to acquire dense structures of $\text{Ca}_3\text{Co}_4\text{O}_9$ [8]. The SPS process is similar to conventional hot pressing, but heating is also accomplished by spark discharge in voids between the particles. Because of these discharges, the particle surface is activated, and a self-heating phenomenon is

generated, which leads to heat transfer and mass transfer that is completed within an extremely short time [9].

Texturing of the microstructure by RTGG is effective for improving the thermoelectric property of $\text{Ca}_3\text{Co}_4\text{O}_9$ and the densification of anisotropic particles by SPS is also useful. Applications and benefits of the two processes have been reported, respectively [6, 9]. It can be expected that the combined processes of RTGG and SPS could result in better thermoelectric properties. Especially, the characteristics of the particles is an important parameter, which could change the property of the green tape and the final products in the tape casting [10] and also affect the sintering behavior in the SPS process [11]. In the present paper, different sizes of template $\beta\text{-Co(OH)}_2$ were prepared using the precipitation method. The template $\beta\text{-Co(OH)}_2$ particles were aligned and cast with CaCO_3 and other ingredients by a tape casting process. The textured $\text{Ca}_3\text{Co}_4\text{O}_9$ was formed by a reactive grain growth during the calcination and SPS process. The degree of orientation and the thermoelectric properties were measured and the dependency of them on the particle size in $\text{Ca}_3\text{Co}_4\text{O}_9$ is discussed.

Experimental procedure

$\beta\text{-Co(OH)}_2$ powders were prepared with the precipitation method. Reagent grade $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and NaOH powders were used as raw materials. The raw materials were completely dissolved in distilled water. The solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and NaOH were prepared in concentrations of 0.1, 0.5 and 1 mol%. NaOH solution was added to the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution at a rate of 5 ml/min. until the mole ratio between the Co^{2+} and OH^- in the solution reached 1 : 2. The mixed solution

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was reacted for 24 hours in atmospheric nitrogen gas to prevent the oxidation of Co^{2+} . Precipitated $\beta\text{-Co}(\text{OH})_2$ particles were washed by distilled water and dried at room temperature. Synthesized $\beta\text{-Co}(\text{OH})_2$ and CaCO_3 (> 99.9%, Kojundo, Japan) were mixed by 3 mol : 4 mol in a PE bottle with YSZ ball media for 24 hours in a co-solvent system of methyl ethyl ketone (MEK, 99.5%) and ethanol (ethyl alcohol anhydrous, 99.9%) at a ratio of 69 wt% : 31 wt%. Subsequently, the binder (polyvinyl butyral, Butvar 79; Monsanto, USA) and plasticizer (dibutyl phthalate, Aldrich, USA) were added and then ball-milled for an additional 24 hours. The solid loading of $\beta\text{-Co}(\text{OH})_2$ and CaCO_3 to the total ingredients excluding the solvent was 57.4 vol%. The slurry was cast on a Mylar film at a rate of 30 cm/min. with the doctor blade method after de-airing. The cast slurry was dried in stagnant air for 24 hours. Green tapes were laminated by a warm isostatic press (WIP) process at 80 °C and 350 bar for 30 minutes. Green compacts were calcined to 800 °C in air with at a heating rate of 0.1 °C/min. and held for 4 hours. The calcined samples were sintered by the SPS process at 920 °C and 50 MPa for 10 minutes at a heating rate of 100 °C/min. By the order of the template size, namely 0.4 μm , 0.6 μm and 1.1 μm , the samples through the calcination and SPS processes using green tapes made of synthesized powders were expressed as TS-04, TS-06 and TS-11, respectively. The phase of the precipitated $\beta\text{-Co}(\text{OH})_2$, green tape and $\text{Ca}_3\text{Co}_4\text{O}_9$ specimens were analyzed with X-ray diffraction (D/MAX 2000/PC, Rigaku, Japan) with a $\text{Cu K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$). The Lotgering factor (f) was used to indicate the degree of orientation. The Lotgering factor (f) is a method that calculates the degree of orientation using the intensity shown on the XRD, and it is calculated as $f = (P - P_0) / (1 - P_0)$, where $P = \sum I(00l) / \sum (hkl)$ and P_0 represents a randomly oriented powder specimen. The value of P_0 was calculated using the JCPDS data [12]. The density of the specimen was measured by the Archimedes method. The Microstructure of the precipitated powder, and the $\text{Ca}_3\text{Co}_4\text{O}_9$ specimen were examined with FE-SEM (JSM 6700F, JEOL, Japan). The average diameter of the precipitated particles was characterized by 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 with a thermoelectric property measurement system (Ozawa Science, model RZ2001i, Japan).

Results and discussions

The $\beta\text{-Co}(\text{OH})_2$ template was synthesized with the precipitation method using cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and NaOH solution. Fig. 1 shows the particles of $\beta\text{-Co}(\text{OH})_2$ synthesized with a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and NaOH at concentrations of 0.1, 0.5

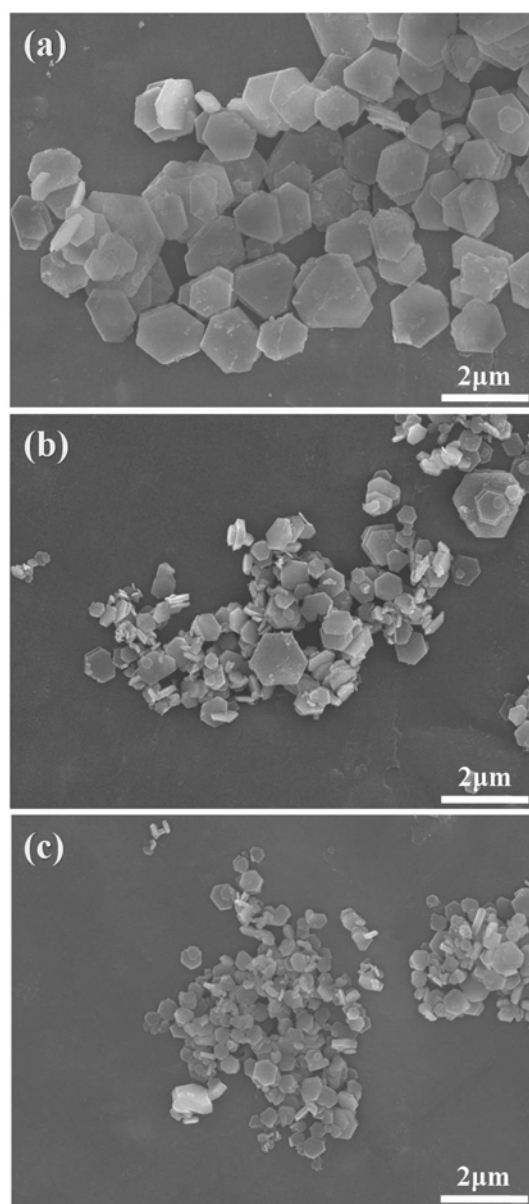


Fig. 1. SEM images of the powders synthesized with the solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and NaOH at the concentrations of (a) 0.1 mol%, (b) 0.5 mol% and (c) 1.0 mol%.

and 1.0 mol%. The grain size of the $\beta\text{-Co}(\text{OH})_2$ powder appeared to be effectively changed by controlling the concentration of Co^{2+} and OH^- . The precipitated particle at a concentration of 0.1 mol% exhibited an average size of 1.1 μm . In addition, increase in the concentration to 0.5 mol% and 1.0 mol% decreased the particle size to 0.6 μm and 0.4 μm , respectively. This can be explained by the following relationship between the degree of supersaturation and the reaction coordination. If the crystal growth rate is dominant over the nucleation rate by a low relative degree of supersaturation in a dilute solution, then large crystals could be precipitated, however, if nucleation proceeds faster than the grain growth by a highly controlled condition, this leads to the small size of the precipitates [13].

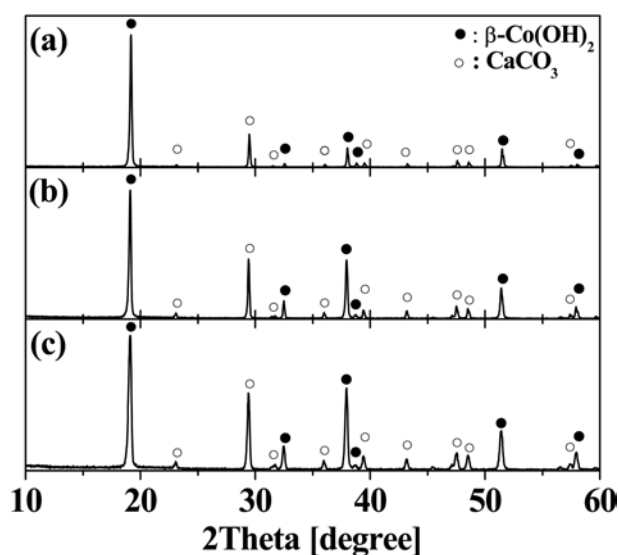


Fig. 2. XRD patterns of the green tapes using the powders synthesized with the solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and NaOH at concentrations of (a) 0.1 mol% (1.1 μm), (b) 0.5 mol% (0.6 μm) and (c) 1.0 mol% (0.4 μm).

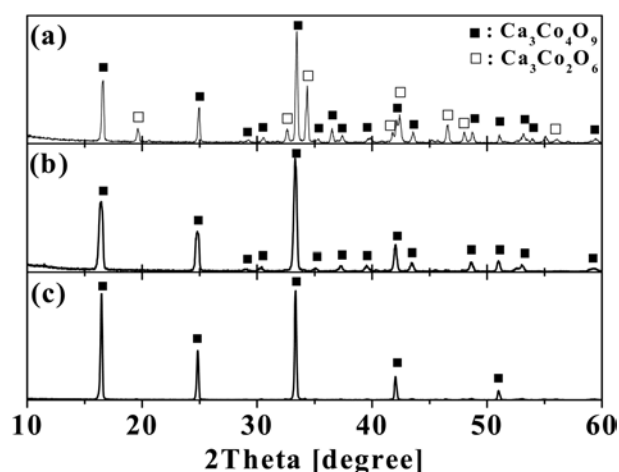


Fig. 3. XRD patterns of specimens prepared by the calcination and SPS process. (a) TS-04 (using green tape with a 0.4 μm template from the 1.0 mol% solution), (b) TS-06 (using green tape with a 0.6 μm template from the 0.5 mol% solution) and (c) TS-11 (using green tape with a 1.1 μm template from the 0.1 mol% solution).

Fig. 2 shows the X-ray diffraction patterns of the green tapes prepared by the tape casting process using the precipitated template $\beta\text{-Co(OH)}_2$ and the reactant CaCO_3 . It is found that XRD peaks of the green tapes were in agreement with those of $\beta\text{-Co(OH)}_2$ (JCPDS 30-0443) and CaCO_3 (JCPDS 41-1743). There was no additional peak detected. During the calcination at 800 $^\circ\text{C}$ for 4 hours, a single-phased polycrystalline $\text{Ca}_3\text{Co}_4\text{O}_9$ was produced by the RTGG process, in which anisotropic $\beta\text{-Co(OH)}_2$ in a plate-like form was reacted with isotropic CaCO_3 in a topotactic manner and grown to a polycrystalline $\text{Ca}_3\text{Co}_4\text{O}_9$. Fig. 3 shows the XRD patterns of the specimens sintered by the SPS process using the green tapes. It is seen that the TS-06 and TS-11 specimens contain only $\text{Ca}_3\text{Co}_4\text{O}_9$ phase

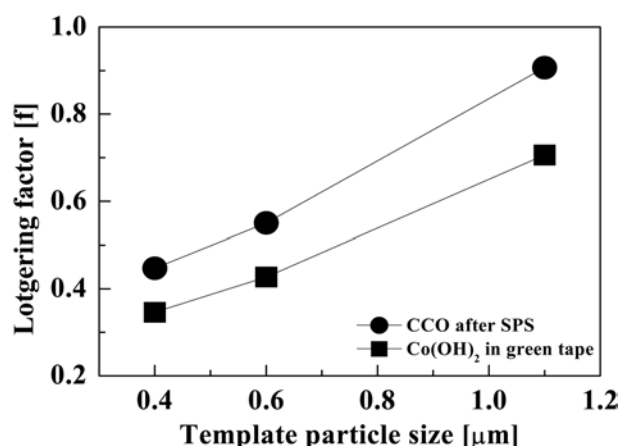


Fig. 4. The Lotgering factor of the green tapes and SPS processed specimens as a function of the template particle size used to synthesize the template particles.

(JCPDS 21-0139) but TS-04 specimen contains also the $\text{Ca}_3\text{Co}_2\text{O}_6$ phase (Fig. 3(a)). The $\text{Ca}_3\text{Co}_2\text{O}_6$ phase is the decomposition phase of $\text{Ca}_3\text{Co}_4\text{O}_9$ [14]. The decomposition reaction in the TS-04 specimen could be due to the small particle size of the template since it takes higher energy under the same operating conditions of the SPS process [15].

Fig. 4 shows the Lotgering factor of the green tapes and specimens after the SPS process. The Lotgering factor calculated for the green tapes shows that the different sizes of particles caused changes in the degree of orientation in the particles in the green tape and specimens prepared by the calcination and SPS process. In the green tape using a 0.4 μm $\beta\text{-Co(OH)}_2$ template, the Lotgering factor was 0.41. Additionally, the Lotgering factor increased to 0.72 as the particle size increased to 1.1 μm . The alignment of the powders was obviously improved by increasing of the particle size. It was caused by the particle interaction in the slurry during the casting process. In highly loaded slurry, the particles interact frequently and move irregularly. The flow quickly aligns the particles due to the particle-particle interactions. The final state depends on the concentration and size of the particles. The interaction between the particles leads to the mutual parallelism of particles [16]. In the TS-04, TS-06, and TS-11 specimens prepared by the SPS process, the degree of orientation increased from 0.45 to 0.91 as the particle size increased from 0.4 μm to 1.1 μm . The degree of orientation increased due to the applied pressure during the SPS [17]. The degree of orientation in TS-04, and TS-06 was increased to about 1 ($\Delta f = 1$), but that of TS-11, in which the particles were almost aligned and thereby the plastic deformation for consolidation could be effective [18], was 2 ($\Delta f = 2$). Enhancement of the orientation by increasing the size of the particles is confirmed in a SEM micrograph of a fractured surface of a $\text{Ca}_3\text{Co}_4\text{O}_9$. As seen in Fig 5, preferred particle orientation was observed in the TS-11

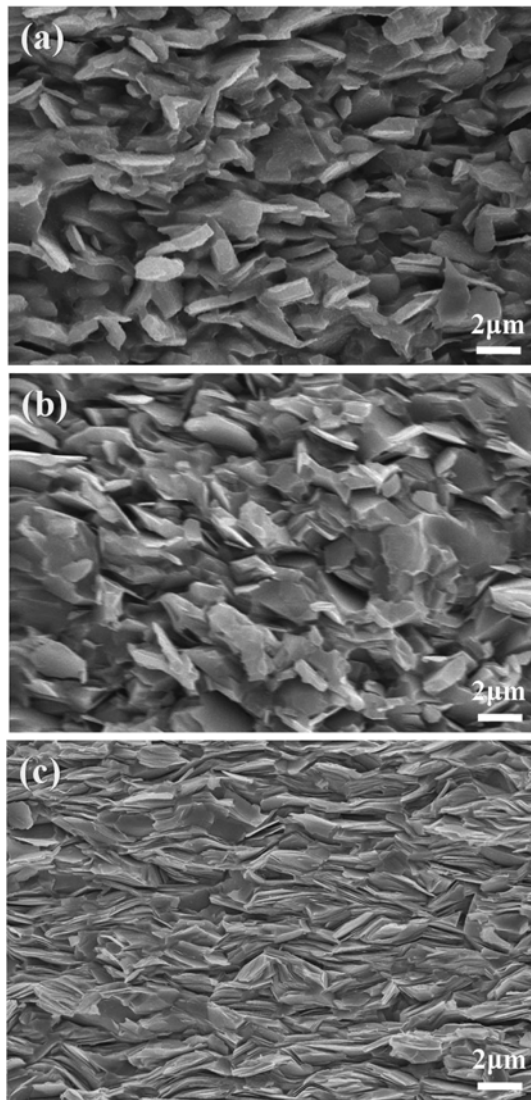


Fig. 5. SEM micrographs of the fractured surfaces of (a) TS-04, (b) TS-06 and (c) TS-11 fabricated by the calcination at 800 °C for 4 hours and the SPS process at 920 °C, and 50 MPa for 10 minutes.

sample compared with the TS-04 and TS-06 samples. The face-to-face contacts of the particles were observed in the sintered compacts but the particle alignment was slightly tilted from the casting direction in TS-11. The relatively random orientation in TS-04 and TS-06 was caused by the reduced interaction between the particles due to the decreased particle size.

Fig. 6 shows the temperature dependence of (a) the electrical conductivity, (b) Seebeck coefficient, and (c) power factors of TS-04, TS-06 and TS-11. The electrical conductivity showed a semiconducting behavior and increased with the temperature. At the same time, the electrical conductivity increased as the template particle size increased. An increase in the conductivity could be anticipated from large particles and their alignment, which reduces the grain boundary and conduction along the *c*-axis [19]. An increase in the conductivity was also attributed to the increase in bulk

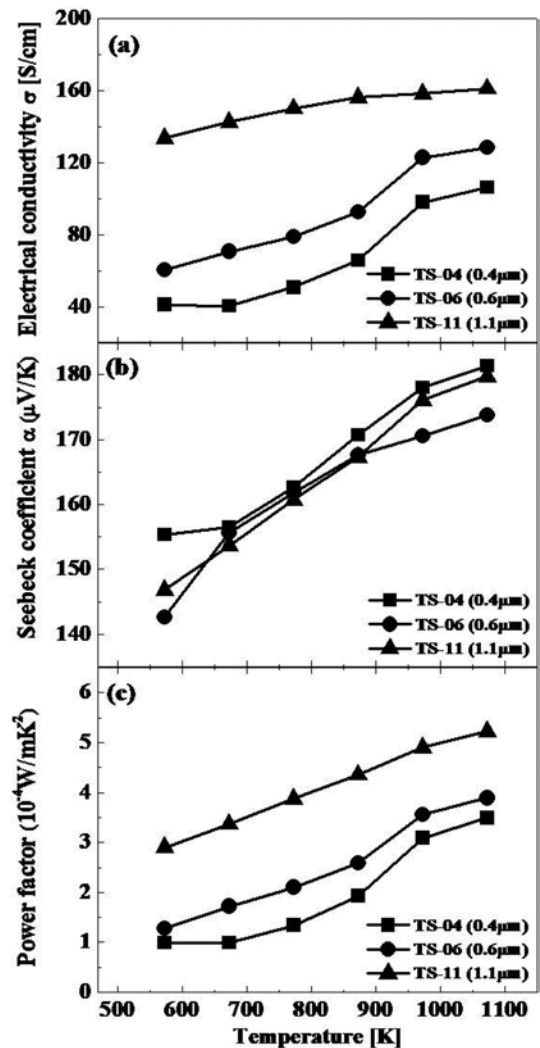


Fig. 6. Temperature dependence of the (a) thermal conductivity (b) the Seebeck coefficient, and (c) power factor for TS-04, TS-06 and TS-11.

Table 1. Mean particle size of the template for tape casting and the density of the specimens after the SPS process.

Sample Notation	Template Size (μm)	Bulk Density (g/cm^3)	Relative Density (%)
TS-04	0.4	4.47	95.6
TS-06	0.6	4.56	97.5
TS-11	1.1	4.64	99.1

density [20], as presented in Table 1. The positive temperature dependence of the Seebeck coefficient, measured along the same direction as the conductivity, indicated that the prepared samples are p-types. The value of the Seebeck coefficient varied slightly when increasing the template size, which indicates that the density and microstructure had little influence on the Seebeck coefficient value [19]. The Seebeck coefficient of the samples increased as the temperature increased and reached 181 $\mu\text{V/K}$ at 1273 °C near to that of a single-crystal of $\text{Ca}_3\text{Co}_4\text{O}_9$ along the *ab*-plane [21].

Since the electrical conductivity σ increased without degradation of the Seebeck coefficient S , the power factor ($S^2\sigma$) was enhanced. The power factor of all the samples increased with the temperature and that of TS-11 reached $5.2 \times 10^{-4} \text{ W/mK}^2$ at 1273°C . This value is estimated to be higher than the power factor reported for aligned $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics prepared using the SPS process [22].

Conclusions

The hexagonal plate-like $\beta\text{-Co(OH)}_2$ templates with various average particle size were synthesized by controlling the concentration of the solutions used in the precipitation method. The influence of the template particle size on the thermoelectric properties of $\text{Ca}_3\text{Co}_4\text{O}_9$ oxide with the RTGG and SPS processes was confirmed. The improvement in the alignment in the green tapes and specimens after the SPS process was obviously improved by increasing the particle size. It was attributed to the increasing particle interaction and orientation in the slurry during tape casting in the RTGG process. Increasing the alignment had the beneficial effect of improving the bulk density, which is a factor that enhanced the conductivity of $\text{Ca}_3\text{Co}_4\text{O}_9$. A dense and highly textured $\text{Ca}_3\text{Co}_4\text{O}_9$ was obtained using a $\beta\text{-Co(OH)}_2$ template with an average diameter of $1.1 \mu\text{m}$, with the power factor reaching $5.2 \times 10^{-4} \text{ W/mK}^2$ at 1273°C . However, smaller templates were not suitable for the process since alignment of the particles did not occur during tape casting and decomposition of $\text{Ca}_3\text{Co}_4\text{O}_9$ occurred in the SPS process. These results suggest that the size of the reactive templates is a decisive factor in the fabrication of $\text{Ca}_3\text{Co}_4\text{O}_9$ oxides when using the RTGG and SPS process.

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