

Synthesis of large diameter plat-like $\text{Ca}_3\text{Co}_4\text{O}_9$ particle by molten salt method

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The $\text{Ca}_3\text{Co}_4\text{O}_9$ was synthesized by molten salt method using CoO , CaCO_3 and CaCl_2 as starting materials. The thermal behavior was investigated by directly measuring and comparing the temperatures of the mixture and reference material simultaneously. The obtained compounds were characterized by XRD, SEM and EDS. The results showed that CaCO_3 and CaCl_2 form a molten salt solution at about 628 °C. The highly *c* axis oriented plat-like $\text{Ca}_3\text{Co}_4\text{O}_9$ particles were obtained at 800 °C for 4 hrs and the $\text{Ca}_3\text{Co}_4\text{O}_9$ particles reaches about 300 μm in diameter and 20 μm in thickness. The template formation process dominates the nucleation of $\text{Ca}_3\text{Co}_4\text{O}_9$ and the shape transformation to plat-like shape has happened in the growth of $\text{Ca}_3\text{Co}_4\text{O}_9$ nuclei.

Key words: Molten salt, Nucleation, Growth, $\text{Ca}_3\text{Co}_4\text{O}_9$ plat-like particle.

Introduction

Thermoelectric (TE) energy conversion is an emerging technology for power generation, which economically utilizes waste heat energy thrown away from various industrial factories, transportation system, offices, and homes [1]. Recently, *p*-type layered cobalt oxide $\text{Ca}_3\text{Co}_4\text{O}_9$ has much attracted attention toward the realization of oxide TE devices because of the high TE performance and advantages in terms of thermal stability at high temperatures [2]. In most research, fine grain $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramic shows good thermoelectric performance due to lower thermal conductivity attributed to the strong photo scattering induced by higher grain boundary density [3]. However, by increasing the grain size, the thermoelectric figure-merit (*ZT*) also could be improved for higher electrical conductivity which is caused by lower carrier scattering by grain boundary scattering, in case of the *ZT* of the single $\text{Ca}_3\text{Co}_4\text{O}_9$ crystal with almost no grain boundary achieving to as high as 0.8 [4]. Preparing large $\text{Ca}_3\text{Co}_4\text{O}_9$ particle is an good effective way to increasing the grain size of the sintered ceramic. Meanwhile, preparing large $\text{Ca}_3\text{Co}_4\text{O}_9$ particle is also essential for that the fine $\text{Ca}_3\text{Co}_4\text{O}_9$ particle could be obtained by higher energy milling of those large particles, which is considered as an easy, economic and environmental technology than other methods preparing fine particles, such as sol-gel method,

sol-gel based electrospinning method and hydro-thermal method [5-7]. It's well know that the crystal structure of $\text{Ca}_3\text{Co}_4\text{O}_9$ is composed of a CoO^{2-} layer and a rock-salt-type $\text{Ca}_2\text{CoO}_3^+$ layer, and the hole carrier conduction occurs predominantly in the CoO^{2-} layer [8]. Therefore, plat-like highly *c* axis oriented $\text{Ca}_3\text{Co}_4\text{O}_9$ particle is preferred for fabricating $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics with high *ZT*. So in this work, we aim to preparing large highly *c* axis oriented plate-like $\text{Ca}_3\text{Co}_4\text{O}_9$ particle.

Molten salt synthesis has been established as a useful synthesis technique, in which the molten salts have been used to enhance the rates of the reaction, hence reducing the reaction time and reaction temperature. What's important is that the powder characteristics, such as size and shape, is under of control. It has been used to synthesis plate-like powders of oxides such as $\text{K}_4\text{Nb}_6\text{O}_{17}$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, KNb_2O_6 and MFe_2O_4 (*M* = Zn, Ni, Mn, etc.) and the formation process of those particles is explicitly investigated [9]. Molten salt method for synthesizing $\text{Ca}_2\text{Co}_2\text{O}_5$ has been tried and the temperature dependence of phase composition for resultant particles is discussed, yet the formation process of it is neglected [10]. In our work, the molten salt method is applied to synthesis of $\text{Ca}_3\text{Co}_4\text{O}_9$. The characteristic in size and shape for the $\text{Ca}_3\text{Co}_4\text{O}_9$ is mainly focused on and the process of the formation and growth of $\text{Ca}_3\text{Co}_4\text{O}_9$ in the molten salt is especially discussed.

Experiments and Methods

High purely commercial CaCl_2 (Wako Co., 99.5%), CaCO_3 (Wako Co., 99.5%) and CoO (Wako Co.,

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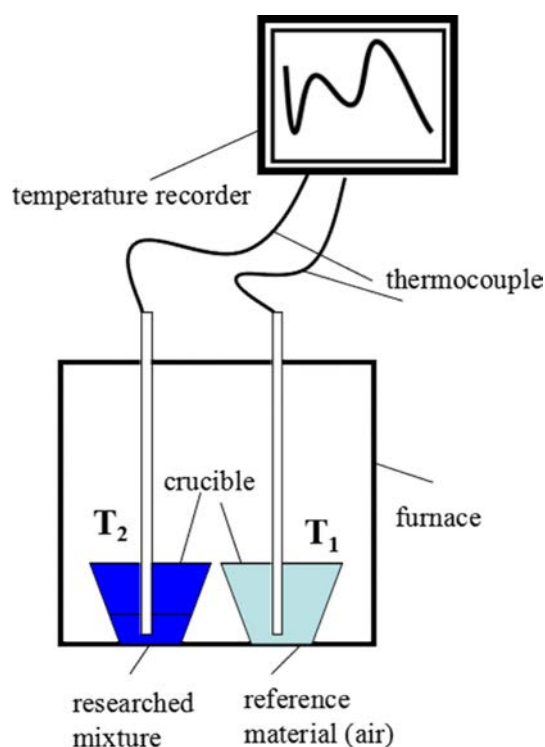


Fig. 1. The diagram of the temperature measurement set-up.

95.5%) as starting materials. They were mixed using acetone as wetting media in an agate mortar for 2 hrs at 200 rpm by a magnetic stirrer in a mole ratio $\text{CaCl}_2 : \text{CaCO}_3 : \text{CoO} = 5 : 3 : 4$. The mixture about 3 g was heated up to 800 °C for 4 hrs in an aluminum crucible by an electric furnace in air, and cooled down to room temperature. The obtained compounds were washed in distilled water repeatedly (at least 5 times) for removing the rest salts. After washing, the compounds were dried at 120 °C for 1 hr.

To detect the thermal behavior of the mixture in the synthesizing process, the temperature of the mixture and the reference material (air) were measured respectively and simultaneously. Fig. 1 shows the diagram of the temperature measurement set-up. In which, T_1 , the reference temperature, and T_2 , the temperature of the mixture. To our knowledge, the absolute value of $d(T_2 - T_1)/dT_1$ reflects the heat generation rate of the researched system.

For characterization of the obtained compounds, the X-ray diffraction (XRD) patterns were obtained using an automated diffraction meter (JDX-3530, JEOL, Japan) with $\text{Cu-K}\alpha_1$ radiation. A scanning electron microscope (JSM-5300, JEOL, Japan) equipped with energy dispersive spectroscopy (EDS) was used to investigate the micro-morphology and element composition of the obtained compounds.

Results and Discussion

Fig. 2 shows the diagram of $(T_2 - T_1)$ vs T_1 for the

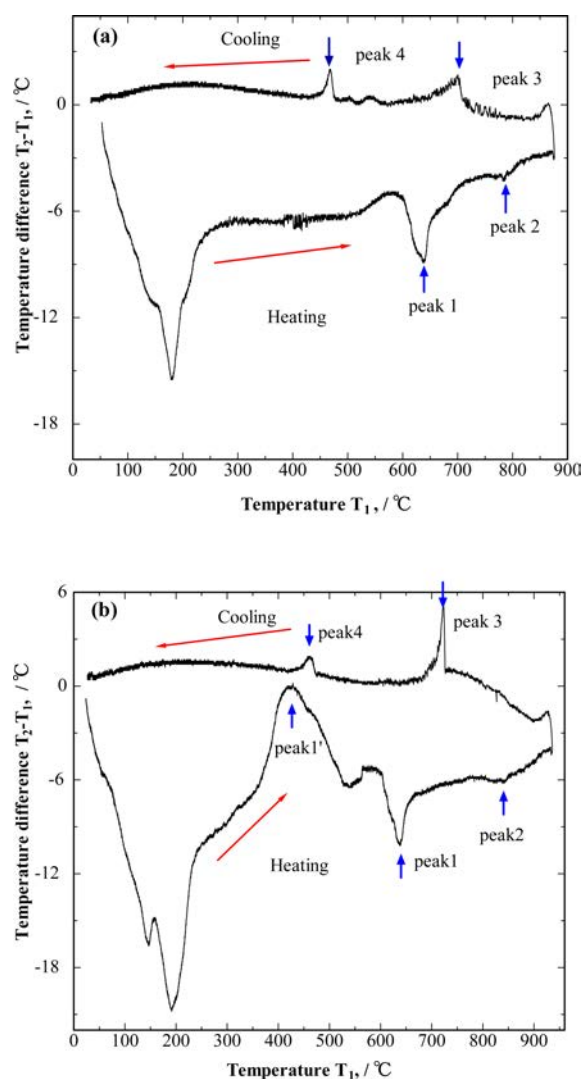


Fig. 2. The temperature difference ($T_2 - T_1$) between mixture (T_2) and reference material (T_1), (a) $\text{CaCl}_2\text{-CaCO}_3$ (5 : 3) system, (b) $\text{CaCl}_2\text{-CaCO}_3\text{-CoO}$ (5 : 3 : 4) system.

binary $\text{CaCl}_2\text{-CaCO}_3$ (5 : 3) system and ternary $\text{CaCl}_2\text{-CaCO}_3\text{-CoO}$ (5 : 3 : 4) system from room temperature to 900 °C with a heating rate 4 °C/min, and cooled down to room temperature. The evaporation of adsorption mass is observed at the temperature range from 120 °C to 200 °C for both systems during the heating process. To $\text{CaCO}_3\text{-CaCl}_2$ system (Fig. 2(a)), at 628 °C, a prominent endothermic peak (peak 1) is observed when heating. It is believed that is attributed to formation of $\text{CaCl}_2\text{-CaCO}_3$ solution, although the composition of the solution is unknown. At 780 °C, another endothermic peak (peak 2) is corresponded to the fusion of the rest of the CaCl_2 . Such a thermal behavior indicates that the CaCO_3 and CaCl_2 easily form an eutectic salt with a low fusion point at about 630 °C [11], hence, enabling the synthesis of the $\text{Ca}_3\text{Co}_4\text{O}_9$ at a lower temperature. During cooling process, there are two exothermic peaks at 710 °C (peak 3) and 475 °C (peak 4) respectively, the former peak corresponded to the solidification of the

Table 1. The temperatures of marked peaks in Fig.2

	peak 1'	peak 1	peak 2	peak 3	Peak 4
CaCl ₂ -CaCO ₃	~	628 °C	780 °C	710 °C	475 °C
CaCl ₂ -CaCO ₃ -CoO	423 °C	627 °C	838 °C	720 °C	489 °C

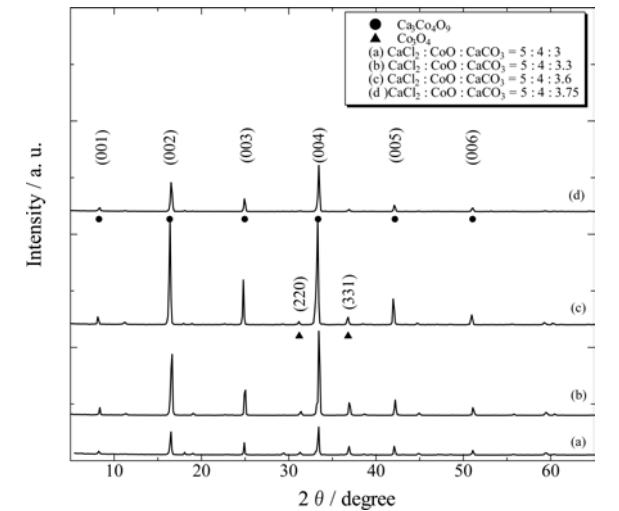


Fig. 3. The XRD patterns of compound particles by increasing the proportion of CaCO₃ in starting mixtures.

CaCl₂, and the latter one correspond to the solidification of CaCl₂-CaCO₃ with a certain composition. To CaCl₂-CaCO₃-CoO system (Fig. 2(b)), besides an obvious exothermic peak corresponded to the oxidation of CoO at about 423 °C, there is a few of difference comparing to CaCO₃-CaCl₂ system, which shows the thermal effect in the synthesis process of the compounds from the starting mixture in molten salt is not evident. Table 1 summarizes the temperatures of the marked peaks in Fig. 2.

According to above analysis about the thermal behavior for CaCl₂-CaCO₃ and CaCl₂-CaCO₃-CoO, the CaCl₂ and CaCO₃ are completely molten over than 780 °C, therefore, the mixture was heated to 800 °C for 4 hrs. Fig. 3 shows the XRD patterns of obtained compounds. As seen from it, the compounds are composed of Ca₃Co₄O₉ and Co₃O₄, which indicates according to stoichiometry, the CoO is excess. Fig. 3 also shows when increasing the volume fraction of CaCO₃ with the stoichiometry of Ca₃Co₄O₉ in the starting mixture, the phase of Co₃O₄ gradually disappears. Specifically, Table 2 gives the volume fraction of Co₃O₄ in the compounds according to quantitative estimation of phase fractions method [12]. This result shows a

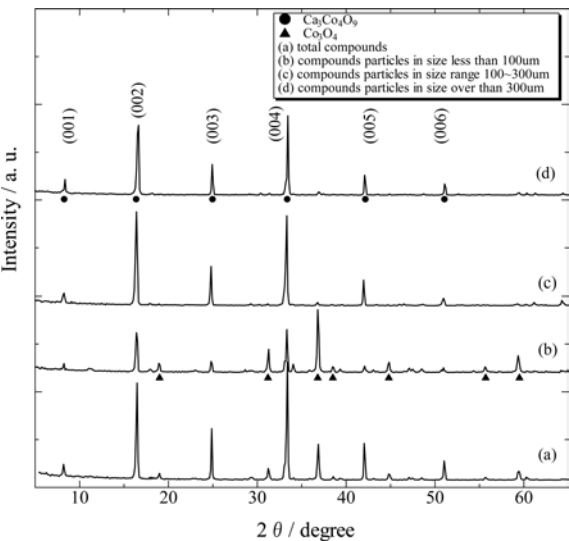


Fig. 4. The XRD patterns of compounds particles after classification by sieving.

difference in preparation for Ca₃Co₄O₉ between molten salt method and solid state method. The lack of the CaCO₃ may arise two aspects: one is the evaporation of CaCO₃ in molten salt and another is the activity of CaCO₃ in molten salt is too low to retained the formation Ca₃Co₄O₉ at later stage, which has been proved in the research about molten carbonates fuel cells in Li₂CO₃-K₂CO₃ molten salts [13]. Moreover, the synthesis time for Ca₃Co₄O₉ in molten salt than solid state method [14] sharply reduces for the generation of liquid phase enhancing the diffusion and reaction. From Fig. 3, what is interesting is that the phase of Ca₃Co₄O₉ is highly *c* axis oriented which will benefit to the enhancement of thermoelectric properties.

Through observation by naked eyes, the obtained compounds with stoichiometry are more inhomogeneous in size. Therefore, they are simply classified into three portions by sieving twice: by the size of the sieve, the compounds particles over than 300 μm, the compounds particles from a range of 100 ~ 300 μm and the compounds particles less than 100 μm. Fig. 4 shows the XRD patterns of these compounds particles in different size. As can be seen, the compounds particles over than 100 μm are almost single phase Ca₃Co₄O₉, of course, the very weak characteristic diffraction peak (331) of Co₃O₄ presents which is attributed to the few Co₃O₄ particles adsorption to the Ca₃Co₄O₉. The compounds particles less than 100 μm are composed of Ca₃Co₄O₉ and Co₃O₄. Table 2 also gives the volume fraction of Co₃O₄ in compounds particles through classification.

Table 2. The volume fraction of Co₃O₄ (%) in compounds particles vs the mole ratio of the starting materials and it through classification by sieving.

CaCl ₂ : CoO : CaCO ₃				particles through classification by sieving (μm)		
5 : 4 : 3	5 : 4 : 3.3	5 : 4 : 3.6	5 : 4 : 3.75	< 100	100 ~ 300	> 300
32.4	31.3	24.1	7.8	60.1	3.9	3.9

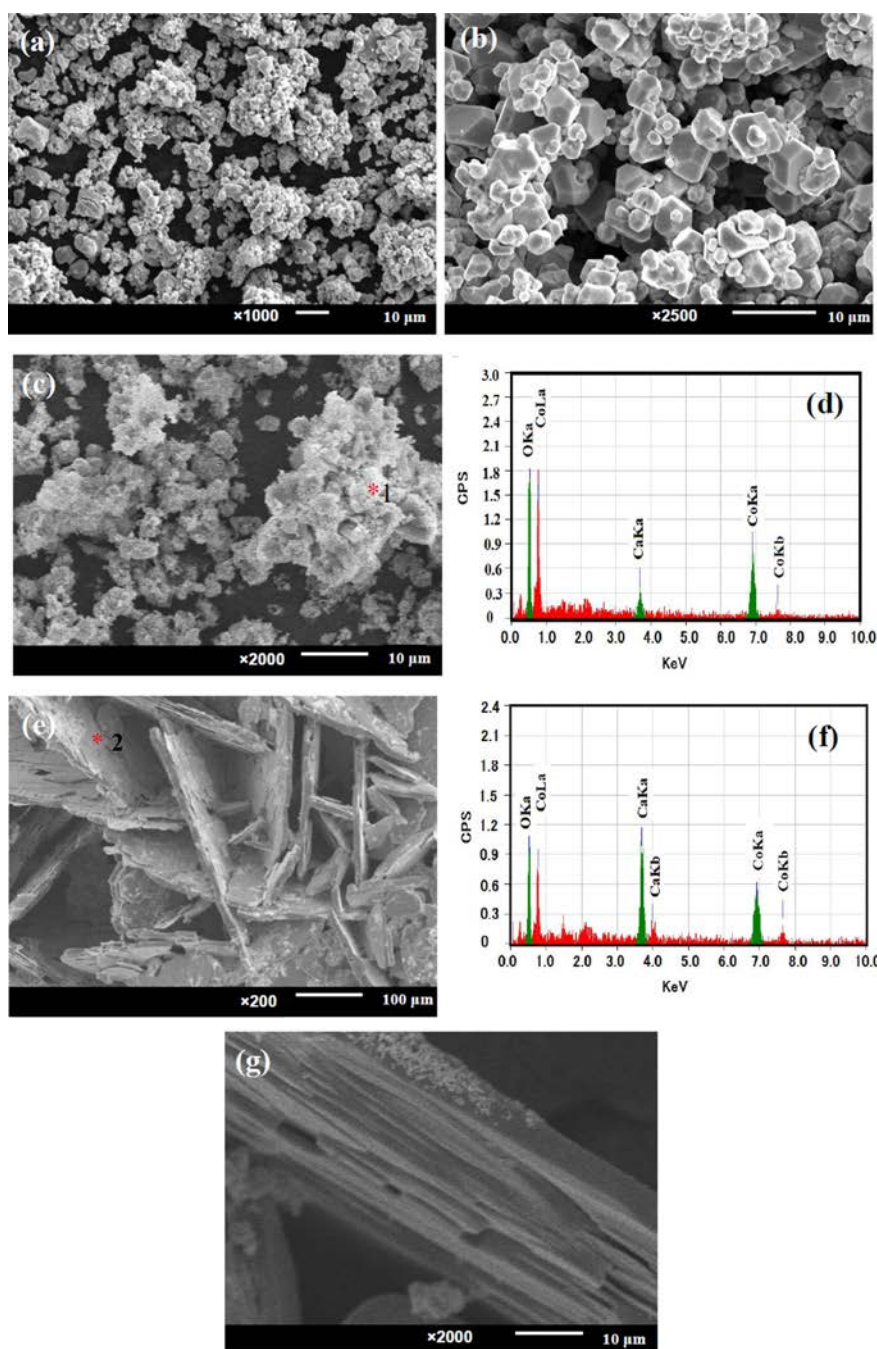


Fig. 5. The morphology and element composition of the materials, (a) the morphology of starting CoO particles, (b) the morphology of Co_3O_4 particles which were obtained by treating CoO in molten CaCl_2 salt at 800°C for 4 hrs, (c) the morphology of obtained compounds in size less than $100\ \mu\text{m}$ by sieving, (d) the element composition (point 1) of the compounds particles in size less than $100\ \mu\text{m}$, (e) the morphology of obtained plat-like $\text{Ca}_3\text{Co}_4\text{O}_9$, (f) the element composition (point 2) of the plat-like $\text{Ca}_3\text{Co}_4\text{O}_9$, (g) the morphology of the plat-like $\text{Ca}_3\text{Co}_4\text{O}_9$ particles in thickness.

According to above results, it can be concluded that the $\text{Ca}_3\text{Co}_4\text{O}_9$ particles has a distribution in size, which ascribes the formation process of the $\text{Ca}_3\text{Co}_4\text{O}_9$ in molten salt. It is expected that the plate-like $\text{Ca}_3\text{Co}_4\text{O}_9$ particle with much larger diameter can be synthesized by molten salt method, which is helpful to reduce the proportion of grain boundary of $\text{Ca}_3\text{Co}_4\text{O}_9$ compacts, hence increasing the electrical conductivity.

Generally speaking, the compound particles in molten

salt are formed into two stages: the nucleation reaction of the compounds and the growth of the nucleus to particles. There are two processes to depict the nucleation reaction according to solubility of the reactants in molten salt: one is the template formation and another is the dissolution precipitation [15]. It is no doubt at 800°C , the CaCO_3 are completely fused into liquid molten salt according to Fig. 2. To now, there are few data about the solubility of CoO in molten salt. Limited reports

show that the solubility of group VIII metal oxides, such as NiO and FeO in NaCl molten salt is as low as 10^{-7} mol/g [16]. For further investigating the solubility of CoO in CaCl_2 molten salt, the mixture of CoO and CaCl_2 (3 : 5) was also heated up to 900 °C for 4 hours and cooled down to room temperature. After washing and drying, the obtained powders were characterized by XRD and SEM, It is founded that the CoO are completely converted into Co_3O_4 , but the obtained Co_3O_4 powder are similar to the starting CoO powder in shape from Fig. 5(a) and Fig. 5(b), which indicates that it is difficult for CoO dissolving into CaCl_2 . Therefore, it is expected that in molten salt Ca^{2+} and CO_3^{2-} ions diffuse to Co_3O_4 particles surface and then react with the Co_3O_4 template to from situ $\text{Ca}_3\text{Co}_4\text{O}_9$ nuclei. Fig. 5(c) shows the images for the compounds particles in size less than 100 μm , which has the same shape with Co_3O_4 by comparing to Fig. 5(b), however the particles surface is much rough, and the EDS analysis (Fig. 5(d)) shows the Ca^{2+} ions reacted with the Co_3O_4 . It's emphasized that this is not contradicted with the XRD results of the powders less than 100 μm , because these small particles should be the partly reacted Co_3O_4 particles.

When the reactants in molten salt is consumed or the activity of the reactants is too low to ensure the reaction continuing, the nuclei growth to particle starts. The nuclei growth at this stage is caused by Ostwald ripening [17], the final particles shape during this stage by two routs: the reduction of the surface area resulting in nuclei growth and the disappearing of surface with high energy resulting in a change towards the equilibrium [9]. Fig. 5(e) and Fig. 5(g) show the images of obtained compounds particles (after growth) with larger size after classification, and they are all plate-like shape, the dimension reaching about 300 μm in width and 20 μm in thickness. Through comparison of Fig. 5(c) and Fig. 5(e), the transformation of the shape of $\text{Ca}_3\text{Co}_4\text{O}_9$ has happened, which shows the disappearing of the surface with high energy dominating the nuclei growth process. Fig. 5(f) shows the element composition of these compounds particles after nuclei growth process. As we known, the (001) crystal plane of $\text{Ca}_3\text{Co}_4\text{O}_9$ has the lowest surface energy than others plane [18], therefore, obtaining the plat-like highly c axis oriented $\text{Ca}_3\text{Co}_4\text{O}_9$ particles is explainable, which is helpful to achieve high level texture $\text{Ca}_3\text{Co}_4\text{O}_9$ thermoelectric sintering compacts.

Conclusions

The plat-like highly c axis oriented $\text{Ca}_3\text{Co}_4\text{O}_9$ particles are synthesized by the molten salt method. By increasing the volume fraction of CaCO_3 in staring mixture with the stoichiometry, the single phase of $\text{Ca}_3\text{Co}_4\text{O}_9$ can be obtained. The $\text{Ca}_3\text{Co}_4\text{O}_9$ has a particle size distribution and its largest size reaches 300 μm in diameter. The template formation process dominates the nucleation of $\text{Ca}_3\text{Co}_4\text{O}_9$ and the shape transformation to plat-like has happened in the growth of $\text{Ca}_3\text{Co}_4\text{O}_9$ nuclei.

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