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Effects of calcination temperature and time on the Ca₃Co₄O₉ purity when synthesized using starch-assisted sol–gel combustion method

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Abstract: Ca₃Co₄O₉ is a p-type semiconducting material that is well-known for its thermoelectric (TE), magnetic, electronic, and electro-optic properties. In this study, sol–gel autoignition was used to prepare Ca₃Co₄O₉ at different calcination temperatures (773, 873, 973, and 1073 K) and time (4, 6, 8, 10, 12, and 14 h) using starch as a fuel. The phase and microstructure of the prepared Ca₃Co₄O₉ powder were investigated. Thermogravimetry–differential thermal analysis (TGA) confirms that the final weight loss occurred at 1073 K to form Ca₃Co₄O₉ stable powder. The variable-pressure scanning electron microscopy (VP-SEM) images show that the size of powder particles increases from 1.15 to 1.47 μm as calcination time increases from 4 to 12 h, and the size remains almost constant thereafter. A similar pattern is also observed on the increment of the crystallite size and percentage of crystallinity with X-ray diffraction (XRD) analysis. The highest crystallinity is found about 92.9% when the powder was calcinated at 1073 K for 12 and 14 h with 458 and 460 Å crystallite size, respectively. Energy dispersive X-ray spectroscopy (EDS) analysis demonstrates that the calcinated powder has a high intensity of Ca, Co, and O with uniform distribution. High-resolution transmission electron microscopy (HRTEM) images prove that there is no distinct lattice distortion defect on the crystal structure.

Keywords: calcium cobalt oxide; sol–gel; starch; combustion method; crystallite size; crystallinity

1 Introduction

In recent years, utilizing of fossil fuels has shown severe impacts on atmospheric and environmental problems, causing international warming, climate change, greenhouse gas emission, ozone layer depletion, and acid rain. The thermoelectric power generator is one of the promising ways to reduce dependency on fossil fuels to generate energy. Thermoelectric devices can generate electrical energy from waste heat, and they are a highly encouraging solution for waste heat recovery and self-powered systems [1–3]. The oxide-based thermoelectric material can be utilized at high temperature in an oxidizing environment. In addition, these materials are nontoxic and having low processing cost, thermal, and
chemical stability. Therefore, they have been recognized as promising thermoelectric materials [4]. However, despite of these advantages, the disadvantage of thermoelectric oxides is their low efficiency (figure of merit). Therefore, these oxides need to improve their thermoelectric properties to enhance the thermoelectric conversion efficiency.

The misfit of calcium cobalt oxide (Ca$_3$Co$_4$O$_9$) ceramics is eliciting considerable interest for their practical applications in refrigeration devices, recycling of waste heat to electricity, and solar thermoelectric generators [5]. Calcium cobaltite is also extensively studied as a possible thermoelectric oxide material due to its low electrical resistivity and high Seebeck coefficient with low thermal conductivity [6,7]. Therefore, in most thermoelectric applications, doping of Ca$_3$Co$_4$O$_9$ ceramics to increase electric conductivity is indispensable. Many kinds of research have been conducted to evaluate the effects of various doping and co-doping elements on the changes of crystal structure and thermoelectric properties of the material. For instance, in the recent developments, significant enhancement in the thermoelectric performance of Ca$_3$Co$_4$O$_9$ thermoelectric material was reported through combined strontium substitution and hot-pressing process [8]. While in Ref. [9], Na and W dual doping in Ca$_3$Co$_4$O$_9$ system was claimed able to increase figure of merit value more than two times of the undoped sample at 1000 K. The crystal structure of Ca$_3$Co$_4$O$_9$ misfit-layered as shown in Fig. 1 consists of two layers (Ca$_2$CoO$_3$)(CoO$_2$)$_{b_1,b_2}$. The Ca$_2$CoO$_3$ layer is an insulating distorted NaCl type, and the CoO$_2$ layer is an electrically conductive CdI$_2$ type. They stack along the c-axis alternately, with $b_1$ and $b_2$ representing the length of the (Ca$_2$CoO$_3$) and (CoO$_2$) sublattice, respectively, along the b-axis [10,11]. The Ca$_2$CoO$_3$ layer decreases the thermal conductivity due to work as phonon scattering centers, whereas the CoO$_2$ layer serves as electron transport sites due to having an effectively correlated electron system [7].

Several synthesis methods have been used to produce Ca$_3$Co$_4$O$_9$ powder, including thermal hydro-decomposition [15], pechini [16], polymer solution synthesis [17], and solid-state reaction [18–22]. These processes are operating at high reaction temperatures, long process, and low chemical homogeneity [23]. Apart from powder synthesis, only solid-state reaction technique has reported the effect of calcination procedure, temperature, and time on thermoelectric properties. For instance, Smaczyński et al. [24] studied the influence of the solid-state reaction and calcination at different temperatures and time using the thermogravimetry–differential thermal analysis (TGA) test. The results showed that a stable composition of Ca$_3$Co$_4$O$_9$ powder was obtained at calcination at 1073 K for a higher soaking time between 20 and 30 h. However, some traces of cobalt oxide were still observed in the calcinated powder because of the Ca$_3$Co$_4$O$_9$ nonstoichiometry at room temperature. Bresch et al. [25] investigated the effect of the calcination procedure on the thermoelectric properties of Ca$_3$Co$_4$O$_9$ powder using solid-state reaction technique. According to this study, no systematic study had been done on the thermoelectric properties affected by the calcination procedure. Conversely, the advantages of sol–gel combustion method are simple, easy control of homogeneity and stoichiometry, and

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*Fig. 1* Crystal structure of Ca$_3$Co$_4$O$_9$ [12–14]. Reproduced with permission from Ref. [12], © Elsevier Ltd and Techna Group S.r.l. 2018; Ref. [13], © The Royal Society of Chemistry. 2016; and Ref. [14], © American Chemical Society. 2016.
economical preparation [26,27]. Previous studies showed that synthesized Ca₃Co₄O₉ powder produced by the sol–gel method results in fine-sized particles, as well as regular size distribution, which is significant in improving magnetic, electrical, and optical properties [12,28–31].

In the sol–gel preparation method, ethylene glycol, polyethylene glycol, and nitric acid were used to polymerize the solution, induce nitrate salt decomposition, and facilitate new compound formation [32,33]. On the other hand, citric acid and polyethylene glycol were used to polymerize the solution which produces carbonaceous xerogel and needs to be crushed [3,31,34–36]. Some researchers focused on the preparation of Ca₃Co₄O₉ powder with different calcination conditions by using different preparation techniques. For example, Chen et al. [7] investigated the influence of the precursor calcination temperature on the microstructure properties of Ca₃Co₄O₉ powder. They prepared the calcium cobaltite powder using the sol–gel technique and calcined at various temperatures between 923 and 1073 K. The results showed that the calcination temperature has a significant effect on the microstructure properties. Crystal size increases with the increase in the calcination temperature. However, they did not study the effect of calcination time on the crystallite size.

Most of polymerizing agents used in powder preparation are acid-based which require special care in handling them for preparing ceramic powder. Recent developments show that starch has been increasingly used as a fuel in the sol–gel combustion method [37–43] due to the ease of preparation and environmental friendliness. Apart from that, it only generates CO₂, N₂, and H₂O after ignition [44,45]. Moreover, the use of starch as a fuel is becoming more favorable because its ability to maintain the pH of the gel [46,47] and it generates non-toxic gases during the calcination process.

2 Materials and experiments

Polycrystalline Ca₃Co₄O₉ powder was synthesized using the sol–gel combustion method. Starch (C₆H₁₀O₅)ₙ was used as a combustion fuel and gelling agent. Calcium nitrate tetrahydrate Ca(NO₃)₂·4H₂O (99%) and cobalt nitrate hexahydrate Co(NO₃)₂·6H₂O (99%) were dissolved in distilled water and stirred using a magnetic hot-plate stirrer (IKA-C-MAG HS4, Germany) to obtain a stoichiometric mixture. The starch was mixed with distilled water, and the solution was added gradually into the mixed metal–nitrate solution. The transparent pink solution was heated under constant stirring within 353–373 K to obtain a pink gel. Subsequently, the resultant gel was decomposed using a hot-plate at 673 K for 1 h, and stirred until the gel burned and became a black precursor. TGA of the precursor was carried out using TA instruments Q500 TGA (Leatherhead, UK) from room temperature to 1383 K in the air at a heating rate of 10 °C/min. The precursor was then calcined at different temperatures (773, 873, 973, and 1073 K) and time (4, 6, 8, 10, 12, and 14 h) at a heating rate of 10 °C/min under ambient using Carbolite CWF 12/23 electric furnace. The morphology of Ca₃Co₄O₉ particles was examined using a variable-pressure scanning electron microscope (Model-JEOL JSM-IT300LV) and energy dispersive X-ray spectroscopy (JEOL JSM-IT300LV, Akishima, Japan) for elemental mapping. The crystal structures of calcined Ca₃Co₄O₉ particles powdered at different dwelling times were characterized using a Rigaku (Smartlab) X-ray diffractometer with Cu Kα radiation (λ = 0.154, 18 nm) and 2θ value was between 5° and 60°. The lattice structure of Ca₃Co₄O₉ powder was examined under scanning transmission electron microscopy (STEM) with a JEOL JEM-ARM200F (FEG-STEM/TEM-USA model) at 200 kV with a 0.08 nm resolution, equipped with a Cs-corrector (CEOS GmbH) for the electron probe.

3 Results and discussion

The black precursor was obtained after the pink gel heated at 673 K for 1 h. The conversion process of the
gel is represented by Eq. (1). The synthesized black precursor was then studied using TGA, and the results are shown in Fig. 2. It illustrates the weight loss percentage as a function of temperature for the \( \text{Ca}_3\text{Co}_4\text{O}_9 \) sample. The TGA curves show that the \( \text{Ca}_3\text{Co}_4\text{O}_9 \) powder is stable up to 860 K, and no weight loss is observed below this temperature. The maximum weight loss peak occurred at 973 K as a result of \( \text{Ca}_3\text{Co}_4\text{O}_9 \) compound formation, partially (\( \text{CaO} \) and \( \text{Co}_3\text{O}_4 \)) from the decomposition of calcium carbonate into calcium oxide by the release of carbon dioxide (\( \text{CO}_2 \)). The weight loss process is represented by Eq. (2). The final weight loss occurred at 1073 K, where the decomposition residuals of cobalt oxide and calcium oxide formed a stable \( \text{Ca}_3\text{Co}_4\text{O}_9 \) product. Equation (3) explains the weight loss due to \( \text{Ca}_3\text{Co}_4\text{O}_9 \) compounds formed. These results are in agreement with Refs. [45,51,52].

\[
\begin{align*}
[9\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O} + 12\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O} + n(\text{C}_6\text{H}_5\text{O}_5)]_{\text{gel}} & \rightarrow [9\text{CaCO}_3 + 4\text{Co}_3\text{O}_4]_{\text{black precursor}} \\
& + n[\text{N}_2\text{O}_3 + \text{CO}_2 + \text{H}_2\text{O}] \\
\text{CaCO}_3 + \text{Co}_3\text{O}_4 + \text{O}_2 & \rightarrow \text{Ca}_3\text{Co}_4\text{O}_9 \\
& + n[\text{CaO} + \text{Co}_3\text{O}_4] + n[\text{CO}_2 + \text{H}_2\text{O}] \\
9\text{CaO} + 4\text{Co}_3\text{O}_4 & \rightarrow 3\text{Ca}_3\text{Co}_4\text{O}_9 + n[\text{O}_2]
\end{align*}
\] (1)

\[973\text{K}
\]

\[1073\text{K}
\]

Figure 3(a) shows the image of black powder formed after pink gel burnt at 673 K for 1 h. Figures 3(b)–3(e) illustrate the morphology of black powder after being calcined at 773, 873, 973, and 1073 K for 4 h, respectively. As the calcination temperature increases, the size of black powder particles also increases, and the shape of particles becomes more defined at 1073 K.

Figure 4 demonstrates the X-ray diffraction (XRD) results of each calcinated powder. At low calcination temperatures (< 973 K), the \( \text{CaCO}_3 \) and \( \text{Co}_3\text{O}_4 \) phases are dominant while \( \text{Ca}_3\text{Co}_4\text{O}_9 \) phase only appears marginally at 873 K. The amorphous phase of \( \text{Ca}_3\text{Co}_4\text{O}_9 \) formed at 973 K, and single phase of \( \text{Ca}_3\text{Co}_4\text{O}_9 \) only becomes more evident at 1073 K.

Figures 5(a)–5(f) show scanning electron micrographs of the \( \text{Ca}_3\text{Co}_4\text{O}_9 \) powder when calcined at 1073 K at different calcination dwelling time (4, 6, 8, 10, 12, and 14 h), respectively. The images reveal that the
calcination time has an effect on the particle size distribution and morphology of these particles. The calcined Ca$_3$Co$_4$O$_9$ powder demonstrates a fine particle size with plate-like as well as irregular shape morphology. The distribution of particles size is quite homogenous and normally distributed as shown in Figs. 5(g)—5(l) with a mean of 1.15, 1.19, 1.38, 1.39, 1.47, and 1.47 μm for 4, 6, 8, 10, 12, and 14 h calcination time, respectively. The morphology of the powder has changed slightly with increasing the average particle size, and some agglomerations were observed between fine particles. The number of plate-like shaped particles increased with the increase of calcination time, which is due to the grain growth over the soaking time.

Fig. 4 XRD patterns of black powder before calcination and after calcinated for 4 h at 773, 873, 973, and 1073 K.

Fig. 5 VP-SEM micrographs of Ca$_3$Co$_4$O$_9$ powder calcined at 1073 K with different calcination time (a) 4, (b) 6, (c) 8, (d) 10, (e) 12, and (f) 14 h and their particle size distribution in (g—l), respectively. Yellow circles indicate plate-like particles.
The effect of calcination time on lattice-parameters was analyzed using XRD patterns on the powder calcined at 1073 K. These XRD patterns are shown in Fig. 6(a). All peaks were indexed according to ICDD PDF card number 00-021-0139. Structural parameters were refined with the superspace group X2/m(0b0)s0 using JANA 2006 software [53]. The refined XRD pattern of 12 h calcination time sample is shown in Fig. 6(b), as an example. Miller indices are also illustrated in Fig. 6(a) and all the peaks determine the transformation of Ca3Co4O9 powder to the monoclinic misfit crystal structure. The lattice parameters were estimated based on the XRD patterns of each powder, as summarized in Table 1. The crystal parameters $a = 4.835$, $b_1 = 4.556$, $b_2 = 2.824$, $c = 10.854$, and $b_1/b_2$ ratio of 1.613 for the 12 h-calcined powder were close to the crystal parameters as reported by Masset et al. [10,54–56]. From XRD data, the analysis of the crystallite size of Ca3Co4O9 nanocrystals was calculated using a modified Scherer equation as follows:

$$D = K\lambda / \beta \cos \theta$$  \hspace{1cm} (4)

where $D$ is the crystallite size (nm), $K$ is a shape factor, which usually takes a value of about 0.9, $\lambda$ is the wavelength of X-ray source for Cu Kα radiation ($\lambda = 0.15418$ nm), $\beta$ is the full width at half-maximum (FWHM) of the observed peak, and $\theta$ is the Bragg diffraction angle ($^\circ$) [38,57–59].

The crystallinities of Ca3Co4O9 powder were calculated from the XRD intensity data by assuming a two-phase structure (crystalline–amorphous) with a line through the minimum intensity to get an arbitrary background to diffraction trail, thus an arbitrary crystalline phase segregating from an amorphous phase [43,44]. The crystallinity $X_{cr}$ was calculated by the following equation:

$$X_{cr} = \frac{A_{cr}}{A_{cr} + A_{am}} \times 100\%$$  \hspace{1cm} (5)

where $A_{cr}$ and $A_{am}$ are the integrated areas of the crystalline and amorphous phases, respectively. Figure 7 illustrates the relationship of the calcination time with the degree of crystallinity and crystallite size of the synthesized Ca3Co4O9. It can be seen that the degree of crystallinity and crystallite size increase with the increasing of calcination time. As the calcination time increases, the crystallinity of Ca3Co4O9 powder improves near to 92.9%, and it becomes less amorphous. The application of TE materials requires pure phase and thermally stable bulk materials [60]. It is noticed that the crystallite size and crystallinity (%) of powder become insensitive after 12 h calcination time.
Table 1  Relevant parameters and reliability factors of Ca$_3$Co$_4$O$_9$ powder from XRD results calcinated at temperature 1073 K with different dwelling time (4, 6, 8, 10, 12, and 14 h)

| Composition Ca$_3$Co$_4$O$_9$ | Dwelling time (h) | 4 | 6 | 8 | 10 | 12 | 14 |
|-----------------------------|------------------|---|---|---|----|----|----|
| **Relevant parameters**     |                  |   |   |   |    |    |    |
| Crystal system              | Monoclinic       |   |   |   |    |    |    |
| Crystallite size (nm)       |                  | 37.8 | 38.1 | 39.3 | 44.0 | 45.8 | 46.0 |
| Theoretical density (g/cm³) |                  | 4.67 | 4.67 | 4.68 | 4.68 | 4.68 | 4.68 |
| Volume (nm³)                |                  | 0.2365 | 0.2364 | 0.2364 | 0.2361 | 0.2365 | 0.2365 |
| **Lattice parameters**      |                  |   |   |   |    |    |    |
| a (nm)                      |                  | 0.4834 | 0.4829 | 0.4834 | 0.4833 | 0.4835 | 0.4836 |
| b$_{Ca_2CoO_3}$ (nm)        |                  | 0.4558 | 0.4554 | 0.4558 | 0.4552 | 0.4556 | 0.4557 |
| b$_{CoO_2}$ (nm)            |                  | 0.2825 | 0.2822 | 0.2824 | 0.2821 | 0.2824 | 0.2824 |
| c (nm)                      |                  | 1.0841 | 1.0857 | 1.0840 | 1.0843 | 1.0854 | 1.0858 |
| α (°)                       |                  | 90 | 90 | 90 | 90 | 90 | 90 |
| β (°)                       |                  | 98.126 | 98.121 | 98.176 | 98.181 | 98.173 | 98.158 |
| γ (°)                       |                  | 90 | 90 | 90 | 90 | 90 | 90 |
| **Reliability factors**     |                  |   |   |   |    |    |    |
| $R_{wp}$ (%)                |                  | 4.68 | 4.38 | 4.23 | 4.20 | 4.18 | 4.16 |
| $R_p$ (%)                   |                  | 4.35 | 4.32 | 4.03 | 3.93 | 3.76 | 3.75 |
| GOF                         |                  | 3.87 | 3.85 | 3.80 | 3.33 | 2.55 | 2.54 |

Based on the XRD results, it can be deduced that the highest purity of Ca$_3$Co$_4$O$_9$ powder is obtained at 1073 K for 12 and 14 h. Considering the energy consumption under these two conditions, 12 h is more favorable since their crystallite size and crystallinity are almost the same. Subsequently, the distribution of the elements on the microstructure of Ca$_3$Co$_4$O$_9$ powder at 1073 K for 12 h was characterized using EDS elemental mapping, and the results are shown in an overlay color image in Fig. 8(a). The measured EDX spectrum of Ca$_3$Co$_4$O$_9$ elements is illustrated in Fig. 8(b) with peaks of Ca, Co, and O, which verify the existence of Ca (24.9 wt%), Co (54.1 wt%), and O (20.7 wt%). Cobalt is homogeneously distributed in the investigated area, as shown in Fig. 8(c) with rose color. Identical distribution of calcium mapping element is represented in a light blue color, as shown in Fig. 8(d). The oxygen content is high and homogeneously distributed too, which referred by green color, as shown in Fig. 8(e). It can be said that from the SEM–EDS mapping, there were formations of an aggregate consisting of Co, Ca, and O. The quantitative of SEM–EDS analysis confirmed that the chemical compositions of the Ca$_3$Co$_4$O$_9$ sample corresponded to the nominal compositions. Furthermore, neither N nor C signals were detected in the EDS spectrum, which means the product is pure and free of any surfactant or impurity.

Figures 9(a)–9(e) show the structure observed for the as-calcined Ca$_3$Co$_4$O$_9$ powder at 1073 K for 12 h. It is noticed that the Ca$_3$Co$_4$O$_9$ particles appear as non-uniform size and shape, as shown in Fig. 9(a). Enlargement view of Ca$_3$Co$_4$O$_9$ particles is illustrated in Fig. 9(b). Darker contrast detected on the particles is attributable to metal-rich cobalt ion aggregates, bound with each other by the calcination process. High-resolution TEM images were obtained from the marked red square area Y in Fig. 9(b). The crystal layered structures of the material with distinct CoO$_2$ and Ca$_2$CoO$_3$ layers are clearly seen without lattice distortion defect. The atomic arrangement of Ca, Co, and O atoms are schematically presented next to high-resolution transmission electron microscopy (HRTEM) image in Fig. 9(d). This image is identical to the description of Ca$_3$Co$_4$O$_9$ crystal structure as described in Fig. 1. The $d$ spacing of planes of Ca$_3$Co$_4$O$_9$ along the $c$ direction is determined using Gatan software which is about 1.08 nm. This result is in agreement with the $d$ spacing counted from the 00l peaks of the $θ$–2$θ$ scan [6,14,18]. The selected area electron diffraction (SAED) patterns of the samples are
Fig. 8  SEM–EDS elemental mapping of Ca₃Co₄O₉ powder calcined at 1073 K for 12 h.

Fig. 9  TEM image of Ca₃Co₄O₉ structure with (a) low-magnification image, (b) enlargement of X-area, (c) enlargement of Y-area, (d) lattice-resolved TEM image and schematic of the atomic arrangement of the layers. (e) shows the SAED patterns recorded from the respective samples.
shown in Fig. 9(e). The samples had particle sizes in the order of several micrometers; therefore, the SAED covers the area, including small grains. The SAED shows diffraction spots of single crystals mixed with a speckled-ring pattern.

4 Conclusions

Ca₃Co₄O₉ is successfully synthesized using starch-assisted sol–gel auto-combustion method. The final powder is obtained through calcination at 1073 K by varying soaking time for 4, 6, 8, 10, 12, and 14 h. All the calcinated powder transforms into a single-phase calcium cobalt oxide with the size ranging from 1.15 to 1.47 µm. Similarly, the purity of calcium cobalt oxide particles increases with the increase of calcination time and becomes saturated after 12 h. TEM images also show no distinct lattice distortion defect observed on the crystal structure. The maximum attainable purity of Ca₃Co₄O₉ is 92.9%, which is a very encouraging result for the thermoelectric material applications. Besides the purity, the performance of thermoelectric material could be further enhanced via doping elements for improving their thermoelectric properties.

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References

[1] Zakharchuk KV, Tobaldi DM, Xiao XX, et al. Synergistic effects of zirconium- and aluminum co-doping on the thermoelectric performance of zinc oxide. J Eur Ceram Soc 2019, 39: 1222–1229.

[2] Delorme F, Diaz-Chao P, Giovannelli F. Effect of Ca substitution by Fe on the thermoelectric properties of Ca₃Co₄O₉ ceramics. J Electroceram 2018, 40: 107–114.

[3] Cha JS, Choi SM, Kim GH, et al. High-temperature thermoelectric properties of Sm²⁺-doped Ca₃Co₄O₉ fabricated by spark plasma sintering. Ceram Int 2018, 44: 6376–6383.

[4] Seo JW, Kim GH, Choi SM, et al. High-temperature thermoelectric properties of polycrystalline CaMn₁-Nb O₃₋ₓ. Ceram Int 2018, 44: 9204–9214.

[5] Funahashi R, Matsubara I, Ikuta H, et al. An oxide single crystal with high thermoelectric performance in air. Jpn J Appl Phys 2000, 39: L1127–L1129.

[6] Paul B, Schroeder JL, Kerdsoonpanya S, et al. Mechanism of formation of the thermoelectric layered cobaltate Ca₃Co₄O₉ by annealing of CaO-CoO thin films. Adv Electron Mater 2015, 1: 1400022.

[7] Chen S, Song XY, Chen XQ, et al. Effect of precursor calcination temperature on the microstructure and thermoelectric properties of Ca₃Co₄O₉ ceramics. J Sol-Gel Sci Technol 2012, 64: 627–636.

[8] Torres MA, Costa FM, Flahaut D, et al. Significant enhancement of the thermoelectric performance in Ca₃Co₄O₉ thermoelectric materials through combined strontium substitution and hot-processing press. J Eur Ceram Soc 2019, 39: 1186–1192.

[9] Hira U, Han L, Norman K, et al. High-temperature thermoelectric properties of Na- and W-doped Ca₃Co₄O₉ system. RSC Adv 2018, 8: 12211–12221.

[10] Masset AC, Michel C, Maignan A, et al. Misfit-layered cobaltite with an anisotropic giant magnetoresistance: Ca₃Co₄O₉. Phys Rev B 2000, 62: 166.

[11] Miyazaki Y, Onoda M, Oku T, et al. Modulated structure of the thermoelectric compound [Ca₃Co₃O₁₂]₅CoO₂. J Phys Soc Jpn 2002, 71: 491–497.

[12] Króllicka AK, Piersa M, Mirowska A, et al. Effect of sol-gel and solid-state synthesis techniques on structural, morphological and thermoelectric performance of Ca₃Co₄O₉. Ceram Int 2018, 44: 13736–13743.

[13] Xu W, Butt S, Zhu YC, et al. Nanoscale heterogeneity in thermoelectrics: The occurrence of phase separation in Fe-doped Ca₃Co₄O₉. Phys Chem Chem Phys 2016, 18: 14580–14587.

[14] Panchakarla LS, Lajaunie L, Ramasubramaniam A, et al. Nanotubes from oxide-based misfit family: The case of calcium cobalt oxide. ACS Nano 2016, 10: 6248–6256.

[15] Prasoetsopha N, Pinitsoontorn S, Kamwanna T, et al. Thermal hydro-decomposition. J Electron Mater 2014, 43: 2064–2071.

[16] Miyazawa K, Amaral F, Kovalevsky A V, et al. Hybrid microwave processing of Ca₃Co₄O₉ thermoelectrics. Ceram Int 2016, 42: 9482–9487.

[17] Sotelo A, Rasekh S, Madre MA, et al. Solution-based synthesis routes to thermoelectric BiₓCa₃Co₁₋ₓO₉. J Eur Ceram Soc 2011, 31: 1763–1769.

[18] Saini S, Yaddanapudi HS, Tian K, et al. Terbium ion doping in Ca₃Co₄O₉: A step towards high-performance
thermoelectric materials. Sci Rep 2017, 7: 44621.

[19] Paul B, Lu J, Eklund P. Nanostructural tailoring to induce flexibility in thermoelectric Ca$_3$Co$_4$O$_9$ thin films. ACS Appl Mater Interfaces 2017, 9: 25308–25316.

[20] Constantinescu G, Rasekh S, Torres MA, et al. Improvement of thermoelectric properties in Ca$_3$Co$_4$O$_9$ ceramics by Ba doping. J Mater Sci: Mater Electron 2015, 26: 3466–3473.

[21] Diez JC, Torres MA, Rasekh S, et al. Enhancement of Ca$_3$Co$_4$O$_9$ thermoelectric properties by Cr for Co substitution. Ceram Int 2013, 39: 6051–6056.

[22] Zhu T, Zhou JM. Effect of Ho doping on the high-temperature thermoelectric properties of Ca$_3$Co$_4$O$_9$-based oxides. Adv Mater Res 2011, 228–229: 947–950.

[23] Vidyasagar K, Gopalakrishnan J, Rao CNR. A convenient route for the synthesis of complex metal oxides employing solid-solution precursors. Inorg Chem 1984, 23: 1206–1210.

[24] Smaczyński P, Sopicka-Lizer M, Kozłowska K, et al. Low temperature synthesis of calcium cobaltites in a solid state reaction. J Electroceram 2007, 18: 255–260.

[25] Bresch S, Mieller B, Selleng C, et al. Influence of the calcination procedure on the thermoelectric properties of calcium cobaltite Ca$_3$Co$_4$O$_9$. J Electroceram 2018, 40: 225–234.

[26] Fey GTK, Cho YD, Prem Kumar T. A TEA-starch combustion method for the synthesis of fine-particulate LiMn$_2$O$_4$. Mater Chem Phys 2004, 87: 275–284.

[27] Xu J, Wei CP, Jia K. Thermoelectric performance of textured Ca$_{3-y}$Yb$_y$Co$_4$O$_9$-$\delta$ ceramics. J Alloys Compd 2010, 500: 227–230.

[28] Katsuyama S, Takiguchi Y, Ito M. Synthesis of Ca$_3$Co$_4$O$_9$ ceramics by polymeric complex and hydrothermal hot-pressing processes and the investigation of its thermoelectric properties. J Mater Sci 2008, 43: 3553–3559.

[29] Zhang YF, Zhang JX, Lu QM, et al. Synthesis and characterization of Ca$_3$Co$_4$O$_9$ nanoparticles by citrate sol–gel method. Mater Lett 2006, 60: 2443–2446.

[30] Presečnik M, de Boor J, Bernik S. Synthesis of single-phase Ca$_3$Co$_4$O$_9$ ceramics and their processing for a microstructure-enhanced thermoelectric performance. Ceram Int 2016, 42: 7315–7327.

[31] Park K, Hakeem DA, Cha JS. Synthesis and structural properties of thermoelectric Ca$_{3-y}$Ag$_y$Co$_4$O$_9$-$\delta$ powders. Dalton Trans 2016, 45: 6990–6997.

[32] Romo-De-la-cruz C, Liang L, Navia SAP, et al. Role of oversized dopant potassium on the nanostructure and thermoelectric performance of calcium cobaltite ceramics. Sustainable Energy Fuels 2018, 2: 876–881.

[33] Kahraman F, Madre MA, Rasekh S, et al. Enhancement of mechanical and thermoelectric properties of Ca$_3$Co$_4$O$_9$ by Ag addition. J Eur Ceram Soc 2015, 35: 3835–3841.

[34] Yang WC, Qian HJ, Gan JY, et al. Effects of Lu and Ni substitution on thermoelectric properties of Ca$_{3-y}$Co$_{4+y}$O$_{9+y}$. J Elec Mater 2016, 45: 4171–4176.

[35] Tang GD, Yang WC, He Y, et al. Enhanced thermoelectric properties of Ca$_{3-y}$Co$_{4+y}$O$_{9+y}$ by Ni, Ce co-doping. Ceram Int 2015, 41: 7115–7118.

[36] Butt S, Xu W, He WQ, et al. Enhancement of thermoelectric performance in Cd-doped Ca$_3$Co$_4$O$_9$ via spin entropy, defect chemistry and phonon scattering. J Mater Chem A 2014, 2: 19479–19487.

[37] Yadav RS, Havlicka J, Hnatko M, et al. Magnetic properties of Co$_{1–x}$Zn$_x$Fe$_2$O$_4$ spinel ferrite nanoparticles synthesized by starch-assisted sol–gel auto-combustion method and its ball milling. J Magn Magn Mater 2015, 378: 190–199.

[38] Singh Yadav R, Havlicka J, Masilko J, et al. Effects of annealing temperature variation on the evolution of structural and magnetic properties of NiFe$_2$O$_4$ nanoparticles synthesized by starch-assisted sol–gel auto-combustion method. J Magn Magn Mater 2015, 394: 439–447.

[39] Motevalian A, Salem S. Effect of glycine-starch mixing ratio on the structural characteristics of MgAl$_2$O$_4$ nano-particles synthesized by sol-gel combustion. Particuology 2016, 24: 108–112.

[40] Dinh TT, Nguyen TQ, Quan GC, et al. Starch-assisted sol–gel synthesis of magnetic CuFe$_2$O$_4$ powder as photo-Fenton catalysts in the presence of oxalic acid. Int J Environ Sci Technol 2017, 14: 2613–2622.

[41] Ansari F, Sobbani A, Salavati-Niasari M. Simple sol-gel synthesis and characterization of new CoTiO$_3$/CoFe$_2$O$_4$ nanocomposite by using liquid glucose, maltose and starch as fuel, capping and reducing agents. J Colloid Interface Sci 2018, 514: 723–732.

[42] M A M, Sudin I, Mohd Noor A, et al. Investigation on microstructure and electrical properties of Bi doping Ca$_3$Co$_4$O$_9$ nanoparticles synthesized by sol-gel process. Int J Eng Technol 2018, 7: 31.

[43] Ene CD, Patrinoiu G, Munteanu C, et al. Multifunctional ZnO materials prepared by a versatile green carbohydrate-assisted combustion method for environmental remediation applications. Ceram Int 2019, 45: 2295–2302.

[44] Visinescu D, Tisoaga A, Patrinoiu G, et al. Green synthetic strategies of oxide materials: Polysaccharide-assisted synthesis. Rev Roum Chim 2010, 55: 1017–1026.

[45] Agilandeswari K, Ruban Kumar A. Synthesis, characterization, temperature dependent electrical and magnetic properties of Ca$_3$Co$_4$O$_9$ by a starch assisted sol–gel combustion method. J Magn Magn Mater 2014, 364: 117–124.

[46] Zhang DB, Zhang BP, Ye DS, et al. Enhanced Al/Ni co-doping and power factor in textured ZnO thermoelectric ceramics prepared by hydrothermal synthesis and spark plasma sintering. J Alloys Compd 2016, 656: 784–792.

[47] Han L, van Nong N, Zhang W, et al. Effects of morphology on the thermoelectric properties of Al-doped ZnO. RSC Adv 2014, 4: 12353.

[48] Khorsand Zak A, Abd Majid WH, Mahmoudian MR, et al.

www.springer.com/journal/40145
Starch-stabilized synthesis of ZnO nanopowders at low temperature and optical properties study. *Adv Powder Technol* 2013, **24**: 618–624.

[49] Ahmad K, Wan C, Al-Eshaikh MA, et al. Enhanced thermoelectric performance of Bi$_2$Te$_3$ based graphene nanocomposites. *Appl Surf Sci* 2019, **474**: 2–8.

[50] Zhu HY, Su TC, Li HT, et al. Thermoelectric properties of BiCuSO doped with Pb. *Solid State Commun* 2018, **278**: 1–5.

[51] Yu HB, Wang XP, Li Y. Strong impact of cobalt distribution on the activity for Co$_3$O$_4$/CaCO$_3$ catalyzing N$_2$O decomposition. *Catal Today* 2020, **339**: 274–280.

[52] Qi XL, Fan YY, Zhu DS, et al. Fabrication and characterization of Ca$_3$Co$_4$O$_9$ nanoparticles by sol-gel method. *Rare Met* 2011, **30**: 111–115.

[53] Petříček V, Dušek M, Palatinus L. Crystallographic computing system JANA2006: General features. *Zeitschrift Für Kristallographie-Cryst Mater* 2014, **229**: 345–352.

[54] Lambert S, Leligny H, Grebille D. Three forms of the misfit layered cobaltite [Ca$_2$CoO$_3$][CoO$_2$]$_{1.62}$·A$_4$D structural investigation. *J Solid State Chem* 2001, **160**: 322–331.

[55] Asahi R, Sugiyama J, Tani T. Electronic structure of misfit-layered calcium cobaltite. *Phys Rev B* 2002, **66**: 155103.

[56] Grebille D, Lambert S, Bourée F, et al. Contribution of powder diffraction for structure refinements of aperiodic misfit cobalt oxides. *J Appl Cryst* 2004, **37**: 823–831.

[57] Rahnamaeiy S, Talebi R. Preparation and characterization of the bismuth aluminate nanoparticles via a green approach and its photocatalyst application. *J Mater Sci: Mater Electron* 2016, **27**: 304–309.

[58] Agilandeswari K, Saral AM, Kumar AR. Magnetic, optical, microscopic and electrical behavior of Ca$_2$$_7$Y$_5$Co$_9$O$_{25}$ prepared by a molten flux method. *Mater Sci Semicond Process* 2015, **34**: 205–213.

[59] Rahnamaeiy S, Talebi R. Preparation and characterization of the bismuth aluminate nanoparticles via a green approach and its photocatalyst application. *J Mater Sci: Mater Electron* 2016, **27**: 304–309.

[60] Zhao KP, Duan HZ, Raghuvendra N, et al. Solid-state explosive reaction for nanoporous bulk thermoelectric materials. *Adv Mater* 2017, **29**: 1701148.

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