High Temperature Thermoelectric and Optical Properties of Ca$_3$Co$_4$O$_9$ Prepared by Thermal Hydro-Decomposition

Natkrita Prasoetsopha [a], Supree Pinitsoonthorn*[b,c] and Vittaya Amornkitbamrung [b,c,d]

[a] Materials Science and Nanotechnology Program, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand.
[b] Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand.
[d] Integrated Nanotechnology Research Center, Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand.

*Author for correspondence; e-mail: psupree@kku.ac.th

ABSTRACT

The polycrystalline sample of calcium cobalt oxide (Ca$_3$Co$_4$O$_9$) ceramic was prepared by a thermal hydro-decomposition method using the acetate salts as starting materials. The single phase Ca$_3$Co$_4$O$_9$ powder was obtained at the calcined temperature of 1073 K which was confirmed by XRD. The powder exhibited platelet-shape with a particle size of <2 μm. The maximum absorption peak of the powder is 285 nm which showed an indirect band gap of 2 eV using a UV-vis technique. The sintered ceramics showed the Seebeck coefficient of 170 μV/K, the electrical resistivity of 21 mΩ⋅cm and the thermal conductivity of 0.036 W/cm/K at 860 K, which were converted to a figure-of-merit, Z, of 3.7×10$^{-5}$ K$^{-1}$. The density of the ceramic was 3.08 g/cm$^3$ obtained using an Archimedes method which corresponded to a significant amount of 35% pore observed by SEM on the fractured surface.

Keywords: Ca$_3$Co$_4$O$_9$, thermoelectric, UV-vis, thermal hydro-decomposition

1. INTRODUCTION

Thermoelectric (TE) materials have ability to convert waste heat to electricity. Generally, the performance of TE materials are defined in term of a dimensionless figure-of-merit, $ZT = S^2\sigma T/\kappa$ where $Z$ is a figure-of-merit, $T$ an absolute temperature, $S$ a Seebeck coefficient, $\sigma$ an electrical conductivity and $\kappa$ a total thermal conductivity. Bismuth telluride based materials are the state-of-art for both $n$-type and $p$-type TE materials at near room temperature [1-2]. However, they are toxic and rare [3]. Recently, metal oxide ceramic materials have attracted attention for TE materials at high temperature, because they are environmentally friendly, and have high heat...
resistant [4]. One candidate for the oxide materials is Ca$_3$Co$_4$O$_9$, of which the crystal structure consists of two misfit-layered monoclinic subsystems: the rock salt-type Ca$_2$CoO$_3$ layers and CdI$_2$-type CoO$_2$ layers stacking along the c-axis direction [5]. Due to their anisotropy structure, the electrical resistivity along the c-axis is higher than that of the ab-plane. There are many methods for preparing Ca$_3$Co$_4$O$_9$ such as solid-state reaction [6-7], or sol-gel [8-9], which employ high temperature reaction and high cost of production. In this work, Ca$_3$Co$_4$O$_9$ polycrystalline was synthesized by a thermal hydro-decomposition method which is simple and cost effective. Thermoelectric and optical properties of the sample were investigated.

2. MATERIALS AND METHODS

2.1 The Ca$_3$Co$_4$O$_9$ sample was prepared by a thermal hydro-decomposition method. Cobalt acetate (Co(CH$_3$COO)$_2$·4H$_2$O, Aldrich), Calcium acetate (Ca(CH$_3$COO)$_2$·H$_2$O, Poch, 98%) were employed as starting ingredients. In a typical procedure, the acetate salts were dissolved in deionized (DI) water at the ratio of 5:1 (volume/weight) of DI water to the total acetate salts. The mixed solution was stirred with a magnetic stirrer for 10 min at room temperature. After completely dissolved, the mixture solution was heated up to 1073 K and held at that temperature for 4 h in a furnace under normal atmosphere. The obtained product was ground and uniaxially pressed at 440 MPa to form a pellet. Then, the pellet was sintered at 1163 K for 4 h in air.

2.2 The crystal structure of the synthesized Ca$_3$Co$_4$O$_9$ was characterized by X-ray diffraction (XRD) using an X-ray diffractometer with Cu Kα radiation (Phillips, PW3020). The morphology of the sample was analyzed by a scanning electron microscope (SEM) (LEO, 1450VP). The energy gap of Ca$_3$Co$_4$O$_9$ powder was estimated from the absorption spectrum obtained by using ultraviolet-visible spectroscopy (UV-vis) (Shimadzu, UV-160A). The sintered pellet was cut and polished for thermoelectric properties analysis. The resistivity and the Seebeck coefficient were measured by ZEM-2 (Ulvac-Riko) in a temperature range of 325-960 K. The thermal diffusivity and heat capacity were measured using a laser flash technique. The density of the sample was calculated using an Archimedes method.

3. RESULTS AND DISCUSSION

3.1 Figure 1 shows the XRD pattern of the synthesized powder. All diffraction peaks are identified as a single phase of Ca$_3$Co$_4$O$_9$ according to the previous study [5]. Figure 2a illustrates the SEM micrograph of the Ca$_3$Co$_4$O$_9$ powder. It can be seen that the powder exhibits a platelet-shape with the size of <2 μm but the particles are agglomerated. High porosity of the fractured surface ceramic is shown in Figure 2b. The density of bulk ceramic is 3.08 g/cm$^3$, which corresponds to ~65% of the theoretical density [5].
The UV-Vis absorption spectrum of Ca₃Co₄O₉ powder is shown in Figure 3. The powder sample absorbed light in an ultraviolet wavelength which can be implied that electrons were excited and shifted the energy level from the valence band to the conduction band. The maximum absorption peak is about 285 nm (4.35 eV). The absorbance value can be converted to the indirect energy gap ($E_g$) of the sample using equation (1) [10].

$$\alpha h\nu = E_i (h\nu - E_g)^2$$  \hspace{1cm} (1)

where $\alpha$ is an optical absorption coefficient, $hn$ is a phonon energy (eV), $E_i$ is a constant and $E_g$ is an energy gap. The inset in Figure 3 shows the $E_g$ of Ca₃Co₄O₉ (roughly 2.0 eV), which was calculated from the intersection of the slope with the x-axis. This is in agreement with a narrow band of <2 eV obtained from a study using a photoemission spectroscopy technique [11].

3.2 The Seebeck coefficient ($S$) and the resistivity ($\rho$) of Ca₃Co₄O₉ are shown in Figure 4a. The positive values of $S$, indicating $p$-type conduction, increase with increasing temperature. The resistivity decreases with increasing temperature until 660 K, indicating the semiconducting-like behavior. Higher than 660 K, resistivity increased with an increase of temperature, indicating a metallic-like behavior. At 960 K, the $S$ value is 170 $\mu$V/K and the power factor is 1.35 $\mu$Wcm⁻¹K⁻². The thermal conductivity ($\kappa$) and the figure-of-merit ($Z$) are shown in Figure 4b. The thermal conductivity can be expressed by the sum of a lattice contribution ($\kappa_l$) and an electronic component ($\kappa_e$), $\kappa = \kappa_l + \kappa_e$ [2]. The $\kappa_e$ is estimated from Wiedemann-Franz’s law, $\kappa_e = L\sigma T$ where $L$ is the Lorenz number = 2.45×10⁻⁸ V²/K² and $\sigma$ is the electrical conductivity. From calculation, $\kappa_e$ values are not over 3% of the total thermal conductivity which are much lower than that of $\kappa_l$. Thus, the main contribution for the thermal conductivity of Ca₃Co₄O₉ is from the lattice or phonon conductivity. The $Z$ value increased with an increase of temperature and the maximum $Z$ is 3.7×10⁻⁵ K⁻¹ at 860 K.

Figure 2. SEM micrographs of Ca₃Co₄O₉; a) powder calcined at the temperature of 1073 K for 4h and b) the fractured surface of the bulk ceramics.

Figure 3. UV-Visible absorption spectrum of Ca₃Co₄O₉ powder. The insert is $E_g$ of Ca₃Co₄O₉.
4. CONCLUSIONS

Ca$_3$Co$_4$O$_9$ powders, synthesized using a thermal hydro-decomposition method, exhibited platelet-shape with a particle size of <2 μm. The bulk density of the samples was ~65% of the theoretical density. The narrow band gap of the Ca$_3$Co$_4$O$_9$ powder was calculated to be ~2.0 eV. The maximum $S$, $\rho$ were 170 μV/K and 21 mΩ·cm, respectively, at 960 K. The main contribution for the thermal conductivity of Ca$_3$Co$_4$O$_9$ is from the lattice or phonon conductivity. The maximum $Z$ was $3.7 \times 10^{-5}$ K$^{-1}$ at 860 K.

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REFERENCES


Figure 4. Temperature dependence on thermoelectric properties of Ca$_3$Co$_4$O$_9$: a) the Seebeck coefficient and the resistivity and b) the thermal conductivity and the figure-of-merit.

