การสังเคราะห์และสมบัติเทอร์มออิเล็กทริกสาร Ca$_3$Co$_4$O$_9$ ที่เตรียมโดยวิธีซอลเจลโดยใช้ PVA

Synthesis and Thermoelectric Properties of Ca$_3$Co$_4$O$_9$ Prepared by Sol-gel Method Using PVA

หนึ่งนุช เลิศสงคราม (Neungnuch Lerssongkram)[1]*
สุปรีดิ์ พินิจสุนทร (Supree Pinitsoontorn)[1]
นิตยา แก้วแพรก (Nittaya Keawprak)[2]

บทคัดย่อ

สารเทอร์มออิเล็กทริก Ca$_3$Co$_4$O$_9$ ถูกสังเคราะห์ขึ้นด้วยวิธีซอลเจลโดยใช้สารตั้งต้นประเภทโลหะไนเตรตกับสารโพลีไวนีลแอลกอฮอล์ (PVA) ทำการศึกษาลักษณะทางกายภาพของสารที่สังเคราะห์ขึ้นโดยเทคนิคเทอร์มอกราวิเมทริก/ดิฟเฟอเรนเซียลเทอร์มัลอะนาลิซิส (TG/DTA), เทคนิคการเลี้ยวเบนของรังสีเอกซ์ (XRD), การวิเคราะห์หาปริมาณธาตุด้วยการวัดระดับการกระจายพลังงานของรังสีเอกซ์ (EDX) และการถ่ายภาพด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) ผลการวิเคราะห์พบว่า สามารถสังเคราะห์เฟสเดี่ยวของพหุผลึก Ca$_3$Co$_4$O$_9$ โดยการเผาแคลไซน์ที่อุณหภูมิ 800 °C เป็นเวลา 4 ชั่วโมง หลังจากนั้นอัดขึ้นรูปด้วยวิธีอัดแกนเดี่ยวด้วยความดัน 440 MPa แล้วเผาซินเตอร์ที่ 890 °C เป็นเวลา 4 ชั่วโมง ผลการศึกษาสมบัติทางเทอร์มออิเล็กทริกช่วงอุณหภูมิห้องถึง 600 °C พบว่า ที่อุณหภูมิ 600 °C มีค่าสภาพต้านทานไฟฟ้า สัมประสิทธิ์ซีเบคและสภาพนำความร้อน เท่ากับ 1.44x10^{-4} Ωm, 172 μVK^{-1} และ 1.46 Wm^{-1}K^{-1} ตามลำดับ ซึ่งทำให้ค่า *ZT* มีค่าสูงสุดเท่ากับ 0.12

Abstract

Thermoelectric Ca$_3$Co$_4$O$_9$ powder was synthesized by a sol-gel method using an aqueous solution containing metal nitrates and polyvinyl alcohol (PVA) as starting materials. The physical properties of the samples were characterized by thermogravimetric/ differential thermal analysis (TG/DTA), x-ray diffraction (XRD), energy dispersive x-ray analysis (EDX) and scanning electron microscopy (SEM). The single phase of Ca$_3$Co$_4$O$_9$ compound was obtained at the calcined temperature of 800 °C for 4 h. The polycrystalline bulk samples were compacted by a uniaxial pressure of 440 MPa and then sintered at 890 °C for 4 h. The thermoelectric properties of the sintered samples were investigated from room temperature to 600 °C. At 600°C the electrical resistivity, the Seebeck

[1]Department of Physics, Faculty of Science, Khon Kaen University, Khon kaen, Thailand
[2]Thailand Institute of Scientific and Technological Research (TISTR), Pathum Thani, Thailand
*Corresponding author, e-mail: nuchi_ta@hotmail.com

coefficient and the thermal conductivity of the sample were 1.44×10^{-4} Ωm, 172 μVK^{-1} and $Wm^{-1}K^{-1}$ respectively, which resulted in the highest ZT of 0.12.

Introduction

Thermoelectric generators can convert waste heat produced by many sources such as automotive exhaust, solar radiation, and industrial processes into electricity. Conversely, thermoelectric coolers can be used to make refrigerators and other cooling systems. This energy conversion process produces no waste substance and is environmentally friendly. Generally, the performance of a thermoelectric material is evaluated in terms of the dimensionless figure of merit, $ZT = S^2 T/\rho\kappa$ where, S, ρ, κ, and T are Seebeck coefficient, electrical resistivity, thermal conductivity and absolute temperature, respectively. As a result, a good thermoelectric material should simultaneously exhibit small ρ and κ and large S. For practical application, ZT should be more than 1.0. Shikano and Funahashi (2003) reported that the single crystal $Ca_3Co_4O_9$ have a high thermoelectric figure of merit ZT of nearly 0.87 at 700 °C, which indicates that $Ca_3Co_4O_9$ has a high potential for practical application in thermoelectric power generation at high temperature. However, for single crystal material, the size is too small to make a device, it is difficult to prepare and has high cost for industrial exploitation. One alternative way is to use polycrystalline materials. Typically, $Ca_3Co_4O_9$ powders are synthesized by a solid state reaction (SSR) (Li, S et al., 2001; Mikami et al., 2005; Prevel et al., 2007; Wang et al., 2009), which is a simple method and can be used at a large scale. Although it is very simple, this process presents several serious drawbacks, such as high reaction temperature, large particle sizes, and limited degree of chemical homogeneity.

Recently, a new sol-gel synthesis technique has been developed for the synthesis of high purity crystalline $Ca_3Co_4O_9$ at significantly lower temperature than the SSR method (Katsuyama et al., 2008; Zhang et al., 2006; Song and Nan, 2007; Li, D et al., 2005). In this paper, $Ca_3Co_4O_9$ powder was prepared by the sol-gel method in the presence of a dispersant of polyvinyl alcohol (PVA). PVA has many isolated hydroxyl functional groups, which form complexes with metal cations. Therefore, the PVA helps the homogeneous incorporation of metal ions in its polymer network structure so that precipitation of cations can be prevented (Jiu et al., 2002). In this method, the reactant cations are intimately mixed on the atomic scale, so the rate of the reaction will be increased, leading to lower synthesis temperatures and smaller particles.

Experimental Method

The ceramic powder $Ca_3Co_4O_9$ was prepared using the sol-gel method. Stoichiometric mixtures of $Ca(NO_3)2.4H_2O$ and $Co(NO_3)2.6H_2O$ were thoroughly dissolved in aqueous solution of citric acid. Polyvinyl alcohol (PVA) (Molecular Weight = 75000 $gmol^{-1}$) was dissolved separately in warm distilled water to prepare 5% (wv^{-1}) solution. The two solutions were mixed according to the 1: 1: 0.5 molar ratio of the metal ions

to the vinyl alcohol monomer unit of PVA to citric acid in the starting solution. The solution was stirred at room temperature for 30 min, and then heated to 80 °C with continuous stirring until it began to gel. The gel was dried initially at 120 °C in air and then was burnt by a self-spread process. The obtained powders were calcined at temperatures of 600 °C, 700 °C and 800 °C for 4 h. The calcined powders were pressed into pellets with a diameter of 16 mm by a uniaxial pressure. The pellets were sintered at 890 °C for 4 h.

Phase formation analysis was carried out using thermogravimetric/differential thermal analysis (TG/DTA). The phase identification of the obtained samples was verified by x-ray diffraction (XRD) at room temperature. Energy Dispersive x-ray spectroscopy (EDX) is a micro-analytical technique used to obtain information about elemental composition of the sample. The morphology of the samples was observed by scanning electron microscopy (SEM). The electrical resistivity and the Seebeck coefficient were measured simultaneously using ULVAC ZEM-2 by the standard four-probe dc method in a helium atmosphere. The thermal conductivity (κ), of the samples was calculated from $\kappa = DC_p d$ where, D, C_p and d are the thermal diffusivity, the heat capacity and the density of the sample, respectively. The D and C_p of the sample were measured using the laser flash method by ULVAC TC 7000 in vacuum.

Results and Discussion

Figure 1. shows the DTA and the TG curves of the dry gel of $Ca_3Co_4O_9$. The high exothermic peak of the sample occurring at 332 °C corresponds to the combustion process. The large volume of gas produced during the reaction promoted the decomposition of residue organics by oxidation and the release of N_xO_y, CO and CO_2 gases (Jiu et al., 2002). At that temperature, TG shows weight loss of up to 14.37 %. The peak at about 395 °C is assigned to the decomposition of the citrate complex to Co_3O_4 and $CaCO_3$. This can be confirmed by the XRD pattern in Figure.2 which was identified to be Co_3O_4 and $CaCO_3$ phases at 600 °C. The endothermic peak at 747 °C may be associated with the decomposition of $CaCO_3$ to CaO and simultaneously the CaO and Co_3O_4 react to form $Ca_3Co_4O_9$ phase (Zhang et al., 2006). The peak at 978 °C may be the temperature of compound decomposition of $Ca_3Co_4O_9$ to $Ca_3Co_2O_6$ (Zhang et al., 2006).
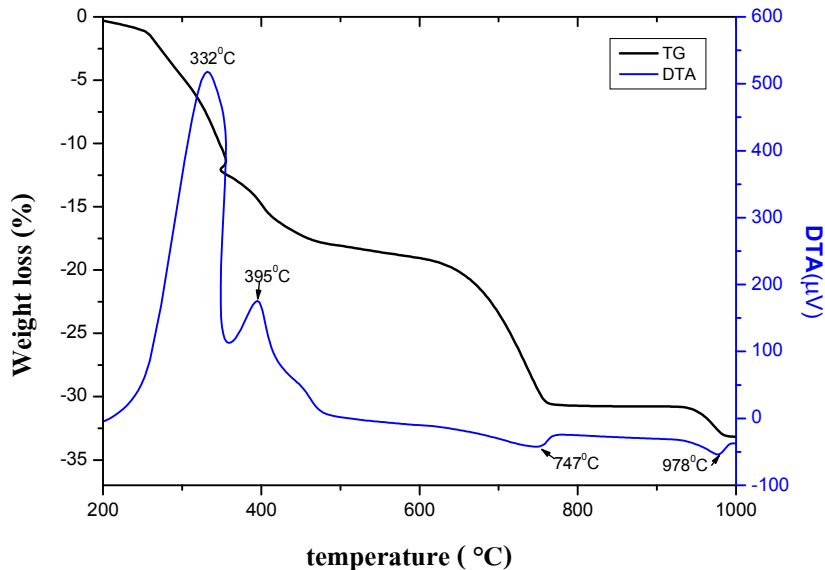
Figure1. TG/DTA curves of the precursor powder

Figure 2. shows the XRD patterns of the powders calcined at temperatures of 600 °C, 700 °C and 800 °C for 4 h. The $CaCO_3$ and Co_3O_4 phases were detected after calcining at 600 °C for 4 h. This may be due to the incomplete reaction. When the temperature increased to 700 °C, $Ca_3Co_4O_9$ compound was found with a small amount of residual $CaCO_3$ and Co_3O_4. The single phase $Ca_3Co_4O_9$ could be obtained at a temperature of 800 °C. All diffraction peaks are identical with the JCPDS card No. 23-0110 for $Ca_3Co_4O_9$. From the results of TG/DTA curves and the XRD patterns, it can be concluded that the synthesis of single phase $Ca_3Co_4O_9$ can be accomplished at 800 °C. Therefore the calcination temperature should be controlled at 800 °C to obtain pure $Ca_3Co_4O_9$ powders.

The lattice parameters of $Ca_3Co_4O_9$ compounds in this study, calculated based on the XRD patterns using a standard least-square refinement method, are shown in Table 1. The $Ca_3Co_4O_9$ crystal structure is a misfit-layered oxide consisting in two monoclinic subsystems, namely Ca_2CoO_3 and CoO_2 layers with identical a, c, and β parameters, but different b parameter where b_1 corresponds to the b-axis length of Ca_2CoO_3 subsystem. The estimated lattice parameters of $Ca_3Co_4O_9$ in this study are consistent with those reported in previous studies (Masset et al., 2000; Song and Nan, 2007).

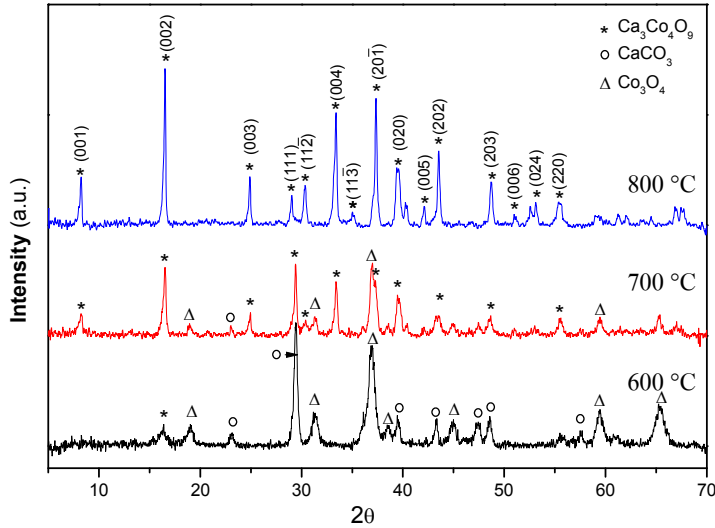**Figure 2.** XRD patterns of the calcined powder at different temperatures

Table 1. Lattice parameters of $Ca_3Co_4O_9$ sintered samples

Samples	Lattice parameter			
	a (nm)	b_1 (nm)	c (nm)	β (deg)
1. Single crystal (Masset et al., 2000)	0.4837	0.4556	1.083	98.06
2. Polycrystalline (present study)	0.4850	0.4568	1.088	98.21
3. Polycrystalline (Song and Nan, 2007)	0.4839	0.4580	1.088	98.26

The SEM micrographs of the specimens are shown in Figure.3. It can be seen that the precursor powder consisted of fine particles and coarse grains (Figure 3 (a)) whereas the calcined powders observed larger grain size with grain size lower than 1 μm (Figure 3 (b)).
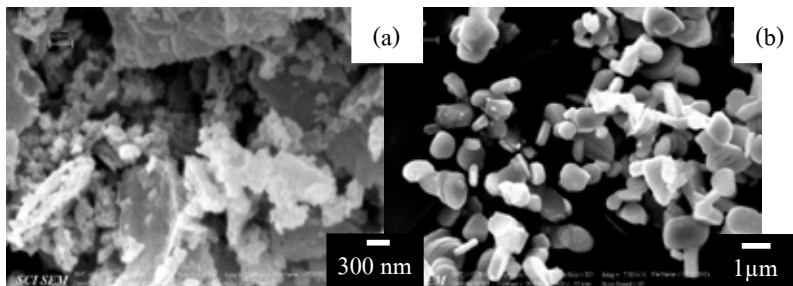

Figure 3. SEM micrographs for (a) precursor powder and (b) calcined powder

The calcined powders were uniaxially pressed with the pressure of 200, 250 and 440 MPa. The SEM micrographs of the pressed surfaces are shown in Figure 4. It can be seen from the figure that pores exist in all samples. However as the packing pressure increased the number of pores was reduced, and thus the sample was denser. It is believed that the thermoelectric properties depend on the density of the samples (Noudem et al., 2009). Thus, the sample compacted at 440 MPa, with the highest density (75.6% of theoretical density (Masset et al., 2000)) was selected for further thermoelectric investigation. Elemental analysis was obtained from EDS and showed that the specimen consisted of Ca, Co and O whose atomic percentage varies locally with an average value of 17.72%, 25.82% and 56.46%, respectively. This corresponds to the approximate molar ratio of Ca: Co: O as 3: 4.3: 9.5.
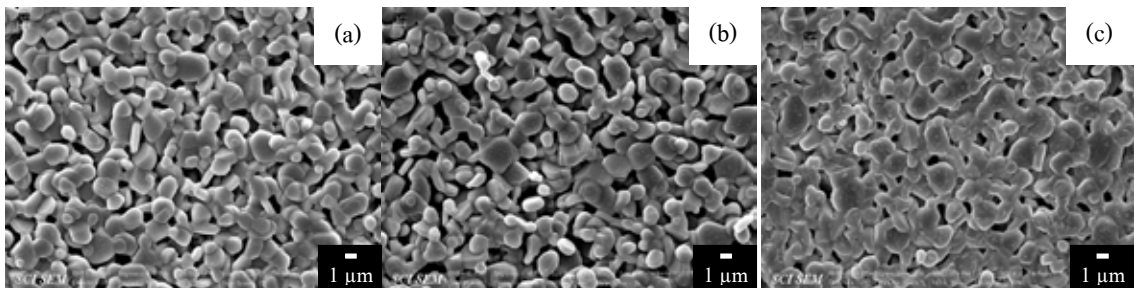

Figure 4. SEM photograph of the sintered samples with operating pressures (a) 200 (b) 250 and (c) 440 MPa

Figure 5 shows the dependence of the electrical resistivity (ρ) on the temperature. It can be seen that the resistivity increased with increasing temperature from room temperature to 100 °C and then slightly decreased from 100 °C to 400 °C. The ρ increased again with temperature in the temperature range of 400-600 °C, which exhibits a metallic conduction behavior.

The temperature dependence of the Seebeck coefficient (S) of the Ca$_3$Co$_4$O$_9$ specimen is also shown in Figure 5. The sign of S is positive over the entire measured temperatures, indicating p-type conduction. The S values increase from 116 to 172 μVK^{-1} with increasing temperature exhibiting metallic conduction behavior which is consistent with the ρ behavior.
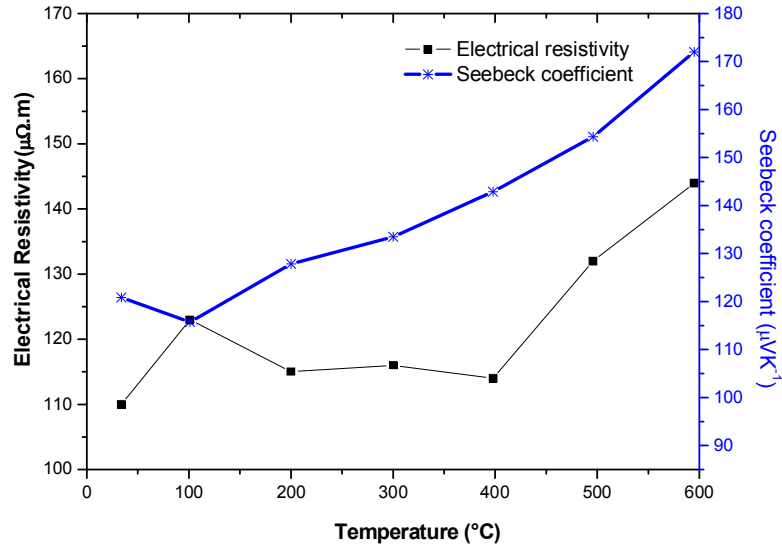
Figure 5. Temperature dependence of Seebeck coefficient and electrical resistivity of the $Ca_3Co_4O_9$

Figure 6 shows the temperature dependence of the thermal conductivity (κ) of sintered $Ca_3Co_4O_9$. The κ was independent of temperature. The κ of polycrystalline $Ca_3Co_4O_9$ in this study is lower than that of the $Ca_3Co_4O_9$ single crystal reported by Shikano and Funahashi (2003). This may be due to boundary scattering by the existence of grain boundaries which can significantly suppress thermal conductivity (Nolas et al., 2001) and a low densification, which can also reduce thermal conductivity in polycrystalline samples (Katsuyama et al., 2008).

Thermal conductivity can be expressed as the sum of the lattice component (κ_l)or phonon and the carrier component (κ_e) as $\kappa=\kappa_e+\kappa_r$. The κ_e is estimated using Wiedemann-Franz's law, $\kappa_e= L\sigma T$ where L is the Lorenz number ($2.45\times10^{-8}V^2K^{-2}$), σ is the electrical conductivity ($\sigma=1/\rho$). The κ_l can be obtained by $\kappa_l=\kappa +\kappa_e$. From calculation, the κ_e value slightly increased with increasing temperature, with the values $0.012 < \kappa_e < 0.105$ $Wm^{-1}K^{-1}$ for all measured temperature range. The contribution of κ_e to total thermal conductivity is quite small, so lattice components predominate in the thermal conductivity. Therefore the behavior of thermal conductivity of $Ca_3Co_4O_9$ was dependent on the lattice component, K_l .
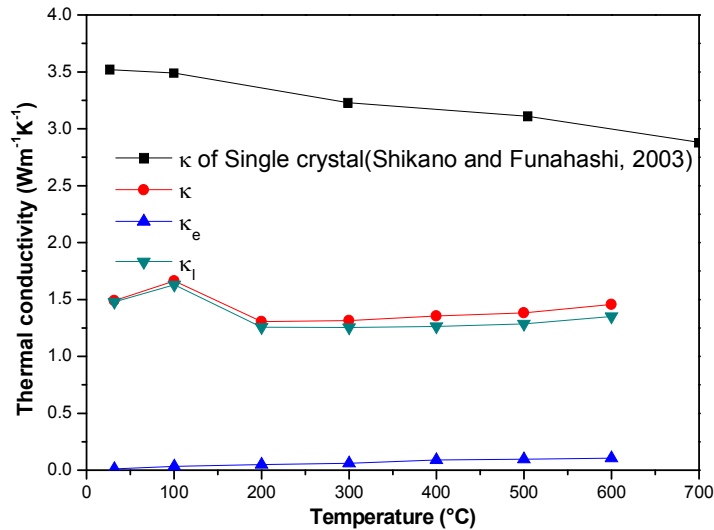
Figure 6. Temperature dependence of thermal conductivity of sintered $Ca_3Co_4O_9$

The temperature dependence of the dimensionless figure of merit, ZT ($ZT = S^2T/\rho\kappa$) was calculated, as shown in Figure 7. The values of ZT increase with increasing temperature. The maximum ZT value of the $Ca_3Co_4O_9$ sample prepared by our PVA sol-gel method, is 0.12 at 600 °C which is comparable to the ZT values of $Ca_3Co_4O_9$ prepared by other methods (Katsuyama et al., 2008; Li,s et al., 2001).

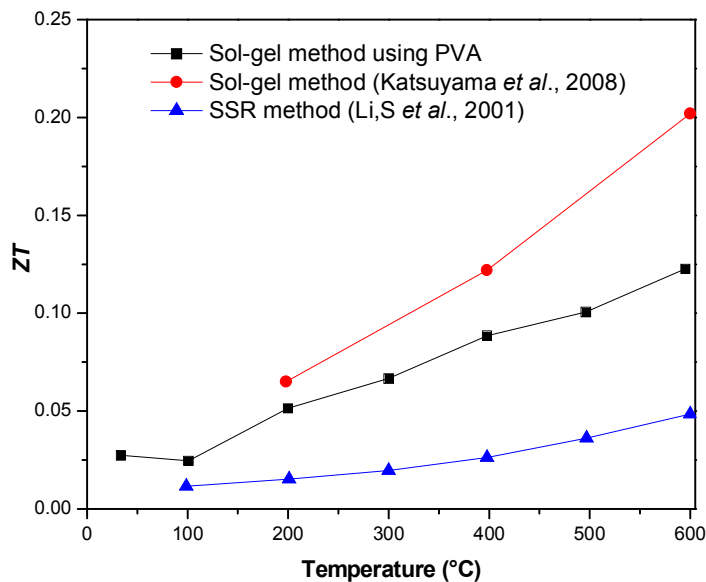**Figure 7.** Temperature dependence of ZT of sintered $Ca_3Co_4O_9$

Conclusions

Homogeneous and single phase $Ca_3Co_4O_9$ compound were successfully synthesized through a simple sol-gel method in the presence of a PVA dispersant. The $Ca_3Co_4O_9$ powders were obtained by calcining the precursor powders at 800 °C for 4 h. The polycrystalline bulk samples were fabricated by a uniaxial pressure of 440 MPa and afterward sintered at 890 °C for 4 h. The thermoelectric properties of the prepared ceramics sample were investigated from room temperature to 600 °C. The electrical resistivity, Seebeck coefficient and thermal conductivity of the sample were measured to be 1.44×10^{-4} m, $172\ \mu VK^{-1}$ and $1.46\ Wm^{-1}K^{-1}$ respectively at 600 °C, which corresponds to a maximum ZT of 0.12.

References

Jiu, J., Ge, Y., Li, X. and Nie, L. 2002. Preparation of Co_3O_4 nanoparticles by a polymer combustion route. **Materials Letter** 54(4): 260-263.

Katsuyama, S., Takiguchi, Y. and Ito, M. 2008. Synthesis of $Ca_3Co_4O_9$ ceramics by polymerized complex and hydrothermal hot-pressing processes and the investigation of its thermoelectric properties. **Master Sci** 43(10): 3553-3559.

Li, D., Qin, X.Y., Gu, Y.J. and Zhang, J. 2005. The effect of Mn substitution on thermoelectric properties of $Ca_3Mn_xCo_{4-x}O_9$ at low temperatures. **Solid State Communications** 134(4): 235–238.

Li, S., Funahashi, R., Yamada, H., Ueno, K. and Sodeoka, S. 2001. Synthesis and thermoelectric properties of the new oxide ceramics $Ca_{3-x}Sr_xCo_4O_{9+\delta}$. **Ceramics International** 27(3): 321-324.

Masset, A.C., Michel, C., Maignan, A., Hervieu, M., Toulemonde, O., Studer, F., and Raveau, B. 2000. Misfit-layered cobaltite with an anisotropic giant magnetoresistance: $Ca_3Co_4O_9$. **Phys. Rev. B**, 62(1), 166 – 175.

Mikami, M., Ando, N. and Funahashi, R. 2005. The effect of Ag addition on electrical properties of the thermoelectric compound $Ca_3Co_4O_9$. **Solid State Chemistry** 178(7): 2186-2190.

Nolas, G.S., Sharp, J and Goldsmid, H.J. 2001. **Thermoelectrics Basic Principles and New Materials Developments.** Berlin Heidelberg: Springer.

Noudem, J.G., Prevel, M., Veres, A., Chateigner, D. and Galy, J. 2009. Thermoelectric $Ca_3Co_4O_9$ ceramics consolidated by Spark Plasma sintering. **Electrocerm** 22(1-3): 91-97.

Prevel, M., Perez, O. and Noudem, J.G. 2007. Bulk textured $Ca_{2.5}(RE)_{0.5}Co_4O_9$ (RE: Pr, Nd, Eu, Dy and Yb) thermoelectric oxides by sinter-forging. **Solid State Sciences** 9(3-4): 231- 235.

Shikano, M. and Funahashi, R. 2003. Electrical and thermal properties of single-crystalline $(Ca_2CoO_3)_{0.7}CoO_2$ with a $Ca_3Co_4O_9$ structure. **Appl. Phys Lett** 82(12): 1851-1853.

Song, Y. and Nan, C.W. 2007. Preparation of $Ca_3Co_4O_9$ by polyacrylamide gel processing and its thermoelectric properties. Sol-Gel. **Sci Technol** 44(2): 139-144.

Wang, Y., Sui, Y., Cheng, J., Wang, X. and Su, W. 2009. Comparison of the high temperature thermoelectric properties for Ag-doped and Ag-added $Ca_3Co_4O_9$. **Journal of Alloys and Compounds** 477(1-2): 817–821.

Zhang, Y.F., Zhang, J.X., Lu, Q.M. and Zhang, Q.Y. 2006. Synthesis and characterization of $Ca_3Co_4O_9$ nanoparticles by citrate sol-gel method. **Materials Letters** 60(20): 2443-2446.