Effect of Hot-Defection on Thermoelectric Properties of $Ca_3Co_4O_9$ Synthesized By Hot Pressing

Anon Angnanon [a,b,*] and Jakrapong Kaewkhao[a,b]

[a]*Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom, 73000, Thailand*
[b]*Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University,Nakhon Pathom, 73000, Thailand*

Received 7 February 2019; Revised 16 August 2019; Accepted 25 December 2019

Abstract

The Calcium Cobalt Oxide ($Ca_3Co_4O_9$) nano powder were synthesized by a Sol-gel method using calcium nitrates ($Ca(NO_3)_2{\cdot}4H_2O$) and cobalt nitrates ($Co(NO_3)_2{\cdot}6H_2O$) raw materials. The nano powder was grinded by mortar for 2 h in air and optimized to achieve highly pure and fully dense pellets by hot pressing method at 900°C for 1 h in Ar atmosphere. The sample was annealed by furnace 900 °C for 12 h in air at after hot pressing. The crystal structure of sample was analyzed by X-ray diffraction technique and compared with literature review data. The electrical resistivity, Seebeck coefficient and power factor of the sample were measured and evaluated by ZEM3 at room temperature to 600 °C. It was found that the crystal structure $Ca_3Co_4O_9$ shows monoclinic structure correspond with literature data, a = 5.31 Å, b = 4.58 Å, c = 11.16 Å and β = 102.82°. The highest power factor value of $Ca_3Co_4O_9$ is 0.18 mW $m^{-1}K^{-2}$ at 600°C.

KEYWORDS: Oxide thermoelectric materials; nano powder

*Corresponding authors ; E-mail : em.anon1121@gmail.com

Introduction

Calcium Cobalt Oxide ($Ca_3Co_4O_9$) nano powders is a material widely used as thermoelectric material. The $Ca_3Co_4O_9$ is oxides as high temperature thermoelectric materials for power generation because of their high thermal stability. Synthesis of highly pure materials of $Ca_3Co_4O_9$ has several methods such as solid state reaction, Sol-gel method, polymerized complex method, spark plasma method and hot pressing method [1 – 5]. Thermoelectric materials were developed efficiency property to high figure of merit (the ZT value), typically evaluated by the dimensionless figure of merit (ZT) given by the following relation: ($ZT = \sigma S^2T/\kappa$), where S, σ, κ and T are Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. From this expression, it is clear that in order to achieve large ZT, a good thermoelectric material must possess high electrical conductivity, large Seebeck coefficient and low thermal conductivity. All these three parameters are interrelated to each other by more fundamental physical parameters [6 – 7]. Power factor ($PF = \sigma S^2$) was study thermoelectric properties in case without thermal properties. $Ca_3Co_4O_9$ phase is stable up to 900 °C and then decomposes to $Ca_3Co_2O_6$, which is stable up to 1026 °C and has potential as a thermoelectric material at high temperature more than 1026 °C [8]

In this work, $Ca_3Co_4O_9$ were synthesized by a sol-gel method and hot pressing using calcium nitrates ($Ca(NO_3)_2{\cdot}4H_2O$) and cobalt nitrates ($Co(NO_3)_2{\cdot}6H_2O$) raw materials. The fully dense pellets by hot pressing method at 900°C for 1 h in Ar atmosphere and the sample was annealed by furnace 900 °C for 12 h in air at after hot pressing that were compered thermoelectric property.

Materials and Methods

The Calcium Cobalt Oxide ($Ca_3Co_4O_9$) nano-powders were synthesized by a Sol-gel method, polymerized complex method based on citrate process, using calcium nitrates ($Ca(NO_3)_2{\cdot}4H_2O$) and cobalt nitrates ($Co(NO_3)_2{\cdot}6H_2O$) as starting materials. The polymerized complex reaction of metal nitrate, citric acid and ethylene glycol. The 7 mol citric acid was dissolved in ethylene glycol 350 ml. The solution was magnetically stirred 40 rpm for 1 h at 200 °C to complete solution.

After that 3 mol $Ca(NO_3)_2{\cdot}4H_2O$ and 4 mol $Co(NO_3)_2{\cdot}6H_2O$ were added to the solution, it show pink transparent solution and then stirred 40 rpm for 2 h 45 min at 300 °C to produced more and more viscous and bubbly amaranthine resin. The resin was dried to slow self-combustion by heating at 450 °C for 30 min. The powder precursor received was grinded by mortar for 2 h and calcining in static air at 750 °C for 12 h. And then optimized to achieve highly pure and fully dense pellets by hot pressing method at 900 °C for for 1 h in Ar atmosphere on 60 MPa. The sample was annealed by furnace 900 °C for 12 h in air at after hot pressing.

The phase identification of the obtained samples was made by X-ray diffraction on Shimadzu's, XRD-6100, that used Cu radiation target at 40 kV 30 mA and scanning rate of 5° min^{-1} from 10° – 80°. The pellets of composites were cut into standard samples with a dimension of 3 × 3 × 15 mm^3, the Resistivity, Seebeck coefficient and Power factor were measured in the temperature range of 38 – 600 °C by Seebeck Coefficient/ Electric Resistance Measurement System (ZEM-3, ADVANCE RIKO). The microstructure of the powder was examined by scanning electron microscopy on a JEOL, JSM5410LV.

Results and Discussion

The picture of sample was cut into standard samples with a dimension of 3 × 3 × 15 mm^3 for measure resistivity, Seebeck coefficient and power factor shown in Fig. 1.

XRD patterns of the hot pressing at 900 °C 1 h in Ar atmosphere on 60 MPa observed diffraction peaks of the sample matches with $Ca_3Co_4O_9$ phase (JCPDs No.023-0110) and unidentified phase at 61.5° [9 – 11]. Further anealed by furnace 900 °C 12 h in air at after hot pressing presented complete transformation to $Ca_3Co_4O_9$ phase. The $Ca_3Co_4O_9$ phase shows monoclinic structure correspond with literature data, the lattice parameter value for $Ca_3Co_4O_9$ was calculated from X-ray diffraction profiles presented hot pressing sample (a = 5.31 Å, b = 4.58 Å, c = 11.16 Å and β = 102.82°) and the after hot pressing sample (a = 5.33 Å, b = 4.58 Å, c = 11.10 Å and β = 103.55). The after hot pressing sample presented smaller volume of unit cell than hot pressing sample, which corresponds to increase the density that show in Table 2. The relative densities of samples hot pressing and annealed by furnace after hot pressing. We are achieved to preparing bulk samples, the samples are sintered with hot-pressing technique at 900°C for 1 h, which present low relative density above 91.40 – 91.70% of the theoretical density (Table. 2). Fig. 3 shows the SEM observation of $Ca_3Co_4O_9$ particles annealed by furnace after hot pressing [12]. The particles appeared to have strong agglomeration and no specific shape was observed. The average particle size of agglomerated particles was in the range of 2 – 3 μm. The microstructure of sample presents many pores, which in accordance with low relative density.

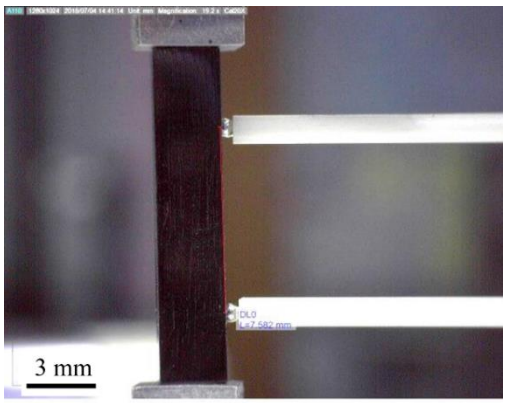

Fig. 1 The sample was cut into standard samples with a dimension of 3 × 3 × 15 mm^3

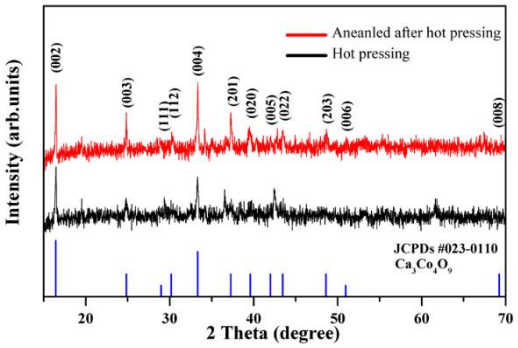

Fig. 2 XRD patterns of samples hot pressing and annealed by furnace after hot pressing.

From the result of electrical resistivity and Seebeck coefficient was calculated effective property to evaluate the thermoelectric performance of the materials. The after hot pressing sample has good power factor went compere with hot pressing sample, present power factor value increase with increasing. The highest power factor value of $Ca_3Co_4O_9$ is 0.18 mW $m^{-1}K^{-2}$ at 600 °C in Fig. 6. The sample anealed by furnace after hot pressing shown good

Table 1. Lattice parameters value for $Ca_3Co_4O_9$ from X-ray diffraction profiles.

Samples	Structure	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
Hot pressing	monoclinic	5.31	4.58	11.16	102.82	265.00
After hot pressing	monoclinic	5.33	4.58	11.10	103.55	263.98

Table 2. A list of the bulk density, theoretical density and relative density of samples hot pressing and aneanled by furnace after hot pressing.

Samples	Bulk Density (g cm^{-3})	Theory Density (g cm^{-3})	Relative Density (%)
Hot pressing	2.86	3.13	91.40
After hot pressing	2.89	3.15	91.70

thermoelectric properties when compere with [2] prepared $Co_3Co_4O_9$ by sol-gel method and sintering at 900 °C for 24 h that presented about of electrical resistivity 24.20 mΩ.cm, Seebeck coefficient 205 μV K^{-1} and power factor 0.17 mW m^{-1}K^{-2} at 600 °C.

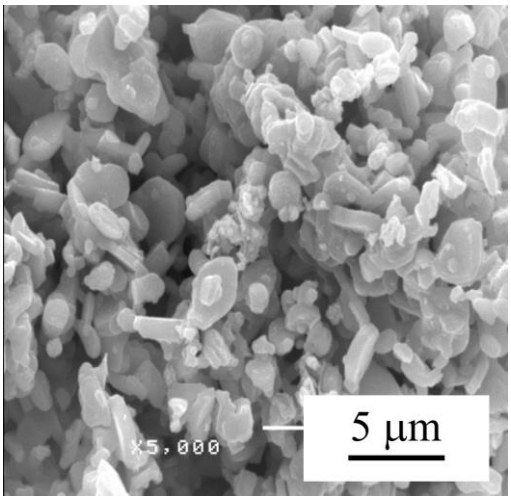

Fig. 3 SEM micrograph of the $Ca_3Co_4O_9$ anealed by furnace after hot pressing.

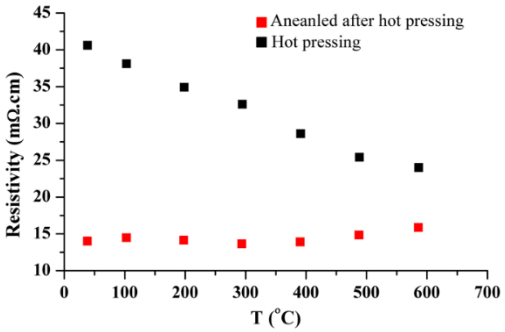

Fig. 4 Temperature dependence of the electrical resistivity of samples hot pressing and annealed by furnace after hot pressing.

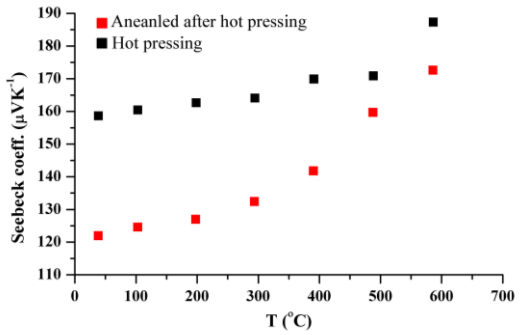

Fig. 5 Temperature dependence of Seebeck coefficient of samples hot pressing and anealed by furnace after hot pressing.

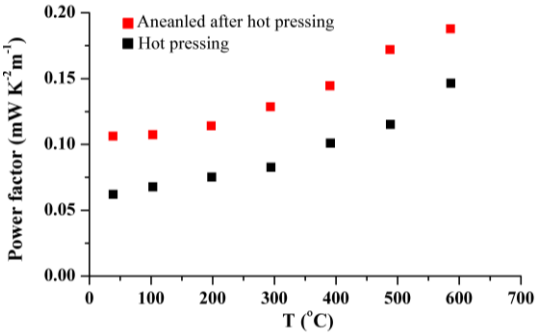

Fig. 6 Temperature dependence of the Power factor of samples hot pressing and anealed by furnace after hot pressing.

Conclusion

The XRD pattern $Ca_3Co_4O_9$ phase (JCPDs No.023-0110) nanopowders were synthesized by a Sol-gel method and hot pressing method at 900 °C for 1 h in Ar atmosphere on 60 MPa that has been successfully after anealed by furnace 900 °C for 12 h in air at after hot pressing.

The strong XRD pattern has affect to the highest power factor value of $Ca_3Co_4O_9$ is 0.18 mW $m^{-1}K^{-2}$ at 600°C when compere with hot pressing sample.

Acknowledgement

This work was financially supported by the Thailand Research Fund (TRF) Research Career Development Grant, RSA (RSA6180070) and Assoc. Prof. Dr. Tosawat Seetawan form Thermoelectric Research Laboratory (TRL), Center of Excellence on Alternative Energy (CEAE), Research and Development Institute, Sakon Nakhon Rajabhat University, Thailand.

References

[1] B. Zheng, Y. Lin, J. Lan, X. Yang, Thermoelectric Properties $Ca_3Co_4O_9$/-Polyaniline Composites J. Mater. Sci. Technol 30 (2014) 423 – 426.

[2] F. Kahraman, M.A. Madre, Sh. Rasekh, C. Salvador, P. Bosque, J.C. Diez, A. Sotelo , M.A. Torres Enhancement of mechanical and thermoelectric properties of $Ca_3Co_4O_9$ by Ag addition Journal of the European Ceramic Society 35 (2015) 3835 – 3841.

[3] N. Puri, R.P. Tandon, A.K. Mahapatro, Fully dense hot pressed calcium cobalt oxide ceramics Ceramics International 44 (2018) 6337 – 6342.

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

[5] Y. Zhang, J. Zhang, Q. Lu, Synthesis of highly textured $Ca_3Co_4O_9$ ceramics by spark plasma sintering Ceramics International 33 (2007) 1305 – 1308.

[6] Z. Shi, J. Xu, J. Zhu, Y. Zhang, T. Gao, M. Qin, G. Dong, F. Gao, H. Sun, Effect of platelet template seeds on microstructure and thermoelectric properties of $Ca_3Co_4O_9$ ceramics Ceramics International 45 (2019) 1977 – 1983.

[7] W. Somkhunthot, N. Pimpabute, A. Vora-ud, T. Seetawan, T. Burinprakhon, Thermoelectricity of p-CCO and n-ZAO thin films, Energy Procedia. 61 (2014) 795 – 798.

[8] L. Dongqing, C. Gang, P. Jian, Y. Xi, X. Hengze, Effect of erbium substitution on thermoelectric properties of complex oxide $Ca_3Co_2O_6$ at high temperatures Journal of rare earths 26 (2008) 168 – 172.

[9] R.K. Gupta, R. Sharma, A.K. Mahapatro, R.P. Tandon, The effect of ZrO_2 dispersion on the thermoelectric power factor of $Ca_3Co_4O_9$ Physica B 483 (2016) 48 – 53.

[10] M. Presečnik, J.D. Boor, S. Bernik, Synthesis of single-phase $Ca_3Co_4O_9$ ceramics and their processing for a microstructure-enhanced thermoelectric performance Ceramics International 42 (2016) 7315 – 7327.

[11] S. Demirel, S. Avci, E. Altin, S. Altin and M.E. Yakinci, Enhanced thermoelectric properties induced by chemical pressure in $Ca_3Co_4O_9$ Ceramics International 40 (2014) 5217 – 5222.

[12] M. Presečnik, S. Bernik, Microstructural and thermoelectric properties of WO_3 ceramics-doped $Ca_3Co_4O_9$ Ceramics International 42 (2016) 16103 – 16108.