THE STUDY OF DENSITY, HARDNESS AND POWER FACTOR OF THE $0.9CaFe_2O_4$-$0.1ZnFe_2O_4$ COMPOSITE

Watsayod Ananpreechakorn[a,b,*]

[a] *Bachelor of Education Program in Physics, Faculty of Education, Sakon Nakhon Rajabhat University, Sakon Nakhon, 47000, Thailand.*
[b] *Center of Excellence on Alternative Energy, Research and Development Institution, Sakon Nakhon Rajabhat University, Sakon Nakhon, 47000, Thailand.*

Received 27 December 2016; Revised 22 March 2017; Accepted 5 April 2017

ABSTRACT

The $Ca_{0.9}Zn_{0.1}Fe_2O_4$ specimen were synthesized by solid state reaction method. The calcium carbonate ($CaCO_3$), nano Zinc oxide (ZnO), and Iron (III) oxide (Fe_2O_3) powders were used for raw materials to the study of density, hardness and power factor of the $0.9CaFe_2O_4$ - $0.1ZnFe_2O_4$ composite. The raw materials were mixed by ball milling for 24 h, calcined at 1073 K for 12 h, pressed into pellet sample at 14.88 MPa and sintered at 1173 K for 12 h. It was found that, the substituted sample show crystal structure of orthorhombic, density of 4.49 g/cm^3, relative density of 93.78 % and Vickers hardness of 5.158 GPa. The Seebeck coefficient of sample was increased with density increasing. The electrical resistivity of sample was decreased with increasing temperature. The high density and high vickers hardness effected to high power factor about 1.78 μW/K^{2}m at 473 K.

KEYWORDS: *$Ca_{0.9}Zn_{0.1}Fe_2O_4$; Density; Hardness; Power Factor; Solid state reaction method*

* Corresponding authors; e-mail: watsayod.a@gmail.com

INTRODUCTION

Thermoelectric (TE) material has attracted worldwide attention for the application in electronic cooling, waste heat recovery, aerospace and automobile industries. Good TE materials should have large Seebeck coefficient, low electrical resistivity and low thermal conductivity. The thermoelectric materials could be evaluated by the figure of merit, ZT, which is defined as

$$ZT = \frac{S^2}{\rho\kappa}T \qquad (1)$$

where S is the Seebeck coefficient (V/K), ρ is the electrical resistivity ($\Omega\cdot\mathrm{m}$), κ is the thermal conductivity (W/mK), T is the absolute temperature (K).

Power factor (PF) in order to determine the usefulness of the power factor is calculated by its Seebeck coefficient and its electrical resistivity under a given temperature difference:

$$\mathrm{PF} = \frac{S^2}{\rho} \qquad (2)$$

where S is the Seebeck coefficient, and ρ is the electrical resistivity.

$CaFe_2O_4$ (CFO) is a p-type semiconductor (with band gap ~2.0 eV) composed of earth-abundant elements. Because it is inexpensive and environmentally friendly [1], CFO has been widely investigated for various applications, The CFO crystallization in an orthorhombic structure with lattice constants a=9.238Å, b=10.716Å, and c=3.023Å (the space group is Pnma No.62 [2], JCPDS Card No. 32-0168) is built up of eight-fold coordinated Ca atoms, and distorted FeO_6 octahedra. The electrical conductivity of CFO has low 3-210 S cm^{-1} at 1123-1273 K in air. Z is in the range (12.0–13.9) 10^{-6} K^{-1} [3].

$ZnFe_2O_4$ (ZFO) is a normal spinel with paramagnetic properties at room temperature. The properties of ZFO arise from the occurrence of Zn^{2+} cations occupying tetrahedral sites and Fe^{3+} cations in octahedral sites [4, 5]. ZFO, as a novel narrow band-gap (1.9 eV) semiconductor, has been used as the catalyst in the photocatalytic degradation of pollutants [6 – 8]. Among the spinel metal ferrites, ZFO is promising material due to its low toxicity, high specific surface area, low resistance and fascinating electrochemical behavior.

In this work researcher investigated effect of density and Vickers hardness on power factor of CFO doped nano Zinc oxide (ZnO) prepared by solid state reaction method.

MATERIALS AND METHODS

The $CaCO_3$ (95.0%, powder), ZnO (95.0%, nano powder size 10–30 nm), Fe_2O_3 (95.0%, powder) were used as the starting materials. The compositional formula polycrystalline of zinc substituted calcium ferrite having the $Ca_{0.9}Zn_{0.1}Fe_2O_4$. The Calcium ferrite (CFO) and Zinc oxide (ZnO) were synthesized by the following as equation: $0.9CaCO_3+0.1ZnO+Fe_2O_3 \rightarrow Ca_{0.9}Zn_{0.1}Fe_2O_4+0.9CO_2$. The preparation of $Ca_{0.9}Zn_{0.1}Fe_2O_4$ start from ground in raw materials an agate ball milling tank for 24 h at a speed of 1,430 revolutions per minute (rpm) and calcined at 1073 K for 12 h in air. Then, the calcined powder was pressed into pellet at 14.88 MPa and sintered at 1173 K for 12 h in air.

The X-ray diffraction (XRD) patterns were analyzed in the range of 2θ = 25°–75° using a Shimadzu X-Ray Diffractometer 6100 diffractometer with Cu-Kα radiation. The samples for electrical resistivity and Seebeck coefficient measurements were cut from the pellets in size of 3×3×15 mm^3 at temperature ranges of 343 K to 473 K in air. The thermoelectric properties were measured by 4-point probe and steady-state method. The power factor was calculated from Seebeck coefficient and electrical resistivity.

RESULTS AND DISCUSSION

The XRD patterns of $Ca_{0.9}Zn_{0.1}Fe_2O_4$ as show Fig. 1. The XRD patterns was compared with PDF card number 00-032-0168 and good agreement in the sintered sample with orthorhombic structure. The small secondary phase was found of $ZnFe_2O_4$.

The lattice parameter of all samples are show small change value after substitution as shown in table 1.

The scanning electron microscopy (SEM) of $Ca_{0.9}Zn_{0.1}Fe_2O_4$ show in Fig.2 – 3. It was noticed that, the shape of particles show spherical. The average particle size was found to be in the range of 1–1.5 μm and increase with ZnO doping, the spacing between the particles were expected to become narrower and also there was a decrease in particles size.

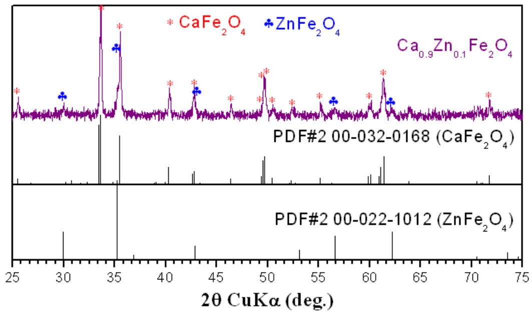

Fig. 1 XRD patter of the $Ca_{0.9}Zn_{0.1}Fe_2O_4$ at 1173 K.

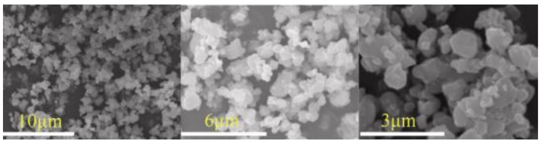

Fig. 2 The microstructure of powder material of $Ca_{0.9}Zn_{0.1}Fe_2O_4$.

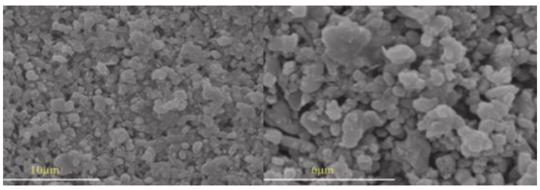

Fig. 3 The microstructure of bulk material of $Ca_{0.9}Zn_{0.1}Fe_2O_4$.

Table 1 Cell parameters for single-phase $Ca_{1-x}Zn_xFe_2O_4$ samples

Sample	a (Å)	b (Å)	c (Å)
$CaFe_2O_4$	9.233	10.689	3.020
$Ca_{0.9}Zn_{0.1}Fe_2O_4$	9.232	10.707	3.015

Table 2 The measured density and the calculated density.

Samples ($\bar{x}$)	Weigh in air (g)	Weigh in liquid (g)	Density (g/cm^2)	TD (%)
$CaFe_2O_4$	0.6059	0.446	3.795	79.280
$Ca_{0.9}Zn_{0.1}Fe_2O_4$	0.3753	0.291	4.489	93.778

The density of samples show table 2. The relationship of the vicker hardness and density are summarized in Fig. 4. The $Ca_{0.9}Zn_{0.1}Fe_2O_4$ shows density and vicker hardness higher than un-dope. The density increases with vicker hardness increases.

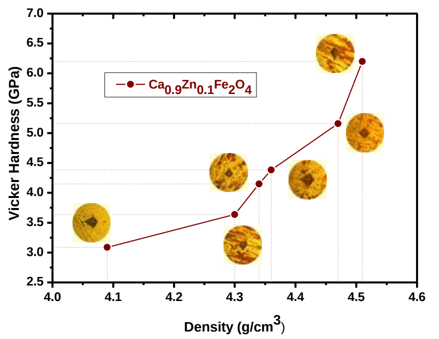

Fig. 4 The graph of density and Vickers hardness.

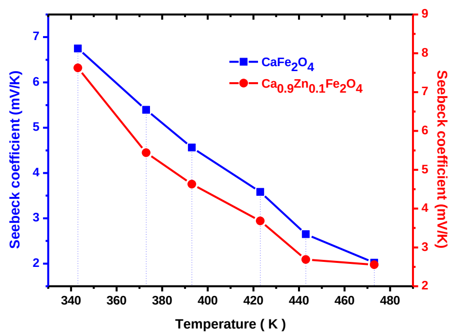

Fig. 5 The graph of Seebeck coefficient as a function of temperature for $Ca_{0.9}Zn_{0.1}Fe_2O_4$.

The temperature dependence of the Seebeck coefficient (S) of $Ca_{0.9}Zn_{0.1}Fe_2O_4$ and sintered at 1173 K as shows in Fig. 5. The Seebeck coefficient values of the samples were p-type semiconductors (which have only positive mobile charges). In addition, S decreased with increasing the operating temperature. The $Ca_{0.9}Zn_{0.1}Fe_2O_4$ showed the best S value of approximately 7.623 mVK^{-1} in the temperature of 343 K.

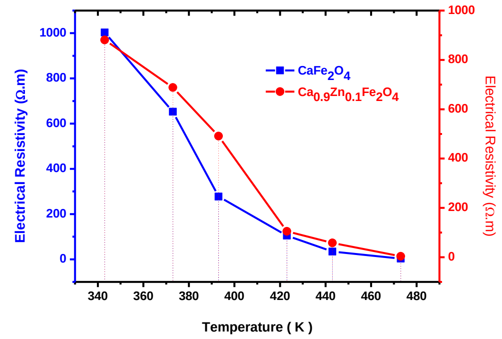

Fig. 6 The graph of Electrical resistivity as a function of temperature for $Ca_{0.9}Zn_{0.1}Fe_2O_4$.

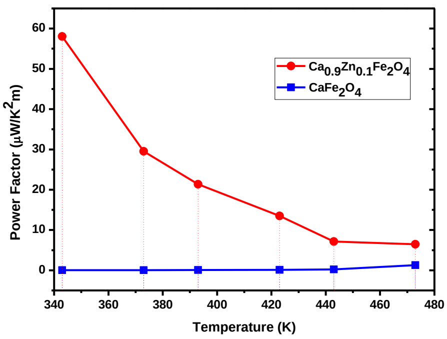

Fig. 7 The relationship of Power factor as a function of temperature for $Ca_{0.9}Zn_{0.1}Fe_2O_4$.

The temperature dependence of the Electrical resistivity (ρ) of $Ca_{0.9}Zn_{0.1}Fe_2O_4$ and sintered at 1173 K as shows in Fig. 6. In addition, ρ decreased with increasing the operating temperature. The $Ca_{0.9}Zn_{0.1}Fe_2O_4$ showed the best ρ value of approximately 3.653 Ωm·cm in the temperature of 473 K.

The Power factor (PF) values calculated from the Seebeck coefficient (S) and Electrical resistivity (ρ) of $Ca_{0.9}Zn_{0.1}Fe_2O_4$ sintered at 1173 K show in Fig. 7. The PF values of samples increased with increasing the measurement temperature. In addition, $CaFe_2O_4$ with added

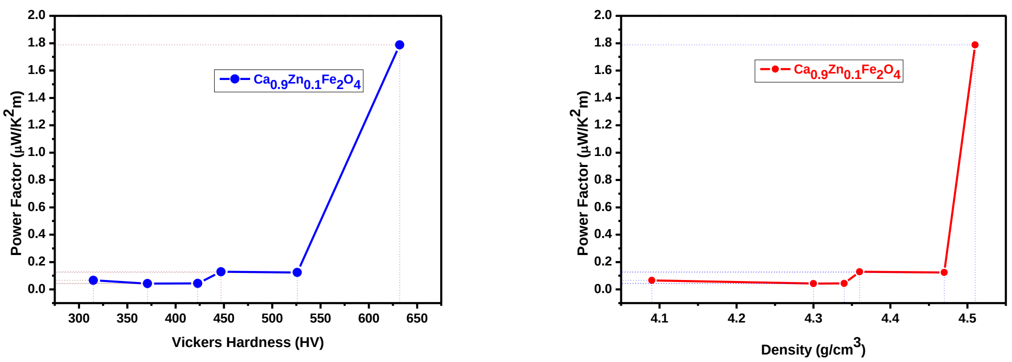

Fig. 8 The relationship of Power factor as a function of vicker hardness and density.

nano ZnO showed a significant improvment of its PF value over that obtained without nano ZnO. Nano ZnO addition at 10 at% led to the maximum increase in PF because of the electrical resistivity. The highest PF was approximately 1.78 μW K^{-2} m at 473 K show in Fig. 8

CONCLUSION

The density and vicker hardness of samples were investigated using the MS Semi-Micro Model and HMV-2, SHIMADZU in Sakon Nakhon Rajabhat University. The density increases with vicker hardness increases. The highest Seebeck coefficient is found to be 7.623 mV/K at 343 K. The $Ca_{0.9}Zn_{0.1}Fe_2O_4$ shows lowest electrical resistivity of 3.653 Ωm·cm at 473 K. The $Ca_{0.9}Zn_{0.1}Fe_2O_4$ shows highest relative density and vickers hardness about 93.78% and 5.16 GPa, respectively. The maximum power factor obtain by $Ca_{0.9}Zn_{0.1}Fe_2O_4$ about 1.787 μW/K^2m at 473 K. The high density and high vickers hardness effected to high power factor.

REFERENCES

[1] R.A. Candeia, M.I.B. Bernardi, E. Longo, I.M.G. Santos, A.G. Souza, Synthesis and characterization of spinel pigment $CaFe_2O_4$ obtained by the polymeric precursor method Mater. Lett. 58 (2004) 569–572.

[2] S. Xiao-ya, W. Li, C. Li-dong, C. Xi-hong, Thermoelectric properties of $M_xMo_6Te_8$(M=Ag, Ca). Trans Nonferrous Met. 19 (2009) 642–645.

[3] W. Ananpreechakorn, T. Seetawan, Thermal Conductivity of Nano ZnO Doped $CaFe_2O_4$, Integr. Ferroelectr. 165 (2015) 53–60

[4] S. Sultana, Rafiuddin, M.Z. Khan, K. Umar, Synthesis and characterization of copper ferrite nanoparticles doped polyaniline, J. Alloys Compd. 535 (2012) 44–49.

[5] S. M. Hoque, Md. S. Hossain, S. Akhter, F. Hyder, Synthesis and characterization of $ZnFe_2O_4$ nanoparticles and its biomedical applications, Mater. Lett. 162 (1) (2016) 60–63.

[6] J. Liu, G. Lu, H. He, H. Tan, T. Xu, K. Xu, Studies on photocatalytic activity of zinc ferrite catalysts synthesized by shock waves, Mater. Res. Bull. 31 (1996) 1049–1056.

[7] M.A. Valenzuela, P. Bosch, J. Jime´ nez-Becerrill, O. Quiroz, A.I. Pa´ ez, Preparation, characterization and photocatalytic activity of ZnO, Fe_2O_3 and $ZnFe_2O_4$, J. Photochem. Photobiol. A : Chemistry. 148 (2002) 177–182.

[8] W.Q. Meng, F. Li, D.G. Evans, X. Duan, Photocatalytic Activity of Highly Porous Zinc Ferrite Prepared from a Zinc-Iron(III)-Sulfate Layered Double Hydroxide Precursor, J. Porous Mater. 11 (2004) 97–105.