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Effect of Zn Substitution on the Thermoelectric Properties of $CuFe_2O_4$

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ABSTRACT

Thermoelectric properties of various composition of Zn substituted CuFe2O4 were studied in this paper. Thermoelectric materials are capable of converting a heat into electrical energy, making them interesting for applications within power generation. The main drawback that limits the areas of thermoelectric application is the expensive materials such as bismuth telluride due to the rare earth content. Hence alternative materials that low cost, easy to reproduce and efficient thermoelectric properties is required to study. The composition of ZnxCu1-xFe2O4 (where x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were prepared through solid state method. The Zn-Cu mixed ferrites were sintered in oxygen atmosphere at 800¬oC. The Zn-Cu ferrites were tests through X-ray diffraction to determine phases with various composition of Zn substitution. The XRD traces show that the Zn-Cu ferrites did not form significant amounts of additional crystalline phases. The Seebeck coefficient were measured by a differential method at room temperature. The Seebeck coefficient was positive for all the compositions showed that the Zn-Cu ferrites behave as p-type semiconductors.

Keywords: Zn-Cu ferrites, Thermoelectric power, Electrical conductivity, Seebeck coefficient;

INTRODUCTION

Current globalization leads to demanding energy consumption without changing global climate. Such drawback is contingent on identifying thermoelectric material which is capable of converting thermal energy into electrical energy and could play an important role in global sustainable energy solution [1]. The direct conversion of temperature differences towards electrical energy (voltage) and vice versa is referred as the phenomenon of thermoelectric [2].

Thermoelectric materials are capable of converting a heat into electrical energy, making them interesting for applications within power generation [3]. Thermoelectric devices have wide applications in infrared sensors, computer chips and satellites due the constraint of movable part and high reliability [4]. One problem that limits the areas of application for thermoelectric devices is the efficiency, which is typically below 10 % for the best thermoelectric materials [5]. Due to the low efficiency, large scale usage has sometimes been believed to be limited to vehicle exhaust heat recovery [6]. Another problem is that many of the best thermoelectric devices are dependent on toxic and expensive materials that are limited in supply [7]. The most common material that used for thermoelectric application is Bismuth Telluride. However, the rarity of bismuth made the material become expensive and toxic for handling [8].

Zinc substituted copper ferrites have been utilized for a long time as high-recurrence apparatuses, for example, radio recurrence loops, transformers centers, bar receiving wires and attractive centers of perused compose sets out toward fast computerized tapes [9,10]. Polycrystalline delicate ferrites are attractive semiconductors, which cannot be reinstated by whatever possible attractive material since ferrites are stable, moderately cheap, effectively produced and have pervasive provisions in the hardware and correspondences businesses because of their intriguing electrical and attractive properties [11,12].

The materials with high thermoelectric efficiency are required large Seebeck coefficient (to obtain a high voltage), high electrical conductivity (to reduce the internal resistance of the material) and low thermal conductivity (to introduce a large temperature difference into both ends of the material) [13]. The Seebeck coefficient also term as thermoelectric power or thermo power effect describes the fact that a temperature gradient drives the diffusion of charged carriers which in turn creates a voltage [14]. In this paper, the effects of Zn substituted on the thermoelectric properties of $CuFe_2O_4$ are studied.

Materials and Methods

The composition of zinc substituted copper

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ferrites with the compositional formula $Zn_xCu_{1-x}Fe_2O_4$ (where x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were prepared through solid state method. The samples were shaped into pellets with 5mm of thickness and 15mm in diameter by using a cold hydraulic press machine at 100MPa. The Zn-Cu mixed ferrites were sintered at 800^{o}C for 4 hours with 10sccm/min (standard cubic centimeter/min) oxygen.

The sintered Zn-Cu mixed ferrites pellets are tested for the thermoelectric analysis, X-ray diffraction, electrical conductivity and gas pycnometer. The chemical composition and crystal structure of the final products were characterized using X-ray diffraction (Bruker D8 Advance X-ray Diffractometer), respectively. The density is analyzed using pycnometer (Micromeritics, AccuPyc II 1340). The Seebeck coefficient were measured by a differential method at room temperature [15]. The thermoelectric power or Seebeck coefficient was calculated using Equation 1.

$$S = \frac{\Delta V}{\Delta T} \qquad (1)$$

Where, ΔV is the thermo e.m.f produced across the sample due to the temperature difference ΔT. The electrical conductivity measurement were carried out based on two probe method using a Keithley's source measure unit (Model SMU 236) based on Ohm's law [16].

Results and Discussion

Figure 1 show the XRD traces of Zn substituted $CuFe_2O_4$ with different Zn content sintered at 800^{o}C with oxygen. The samples peaks for $Zn_xCu_{1-x}Fe_2O_4$ where x= 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 were identified as the plane reflection for single cubic phase spinel structure of $ZnCuFe_2O_4$. There were no impurity peaks detected. This indicated that the Zn substituted $CuFe_2O_4$ did not had any reaction occur and phase formation with different Zn contents. According to Akhter S. el. al. Akhter powder XRD analysis, who carried out the study on structural and physical properties of $Zn_xCu_{1-x}Fe_2O_4$ where x = 0.0, 0.2, 0.4, 0.6 and 0.8 stated that all the composition shows perfect crystallization with clear diffraction line [17]. The reflection of the X-ray was well defined that expose the development of single-phase cubic spinel structure [18] and noticeable that the characteristic peaks for spinel $ZnCuFe_2O_4$ appear in all samples. The peaks (220), (110), (311), (222), (400), (422), (511) and (440) were related to spinel phase.

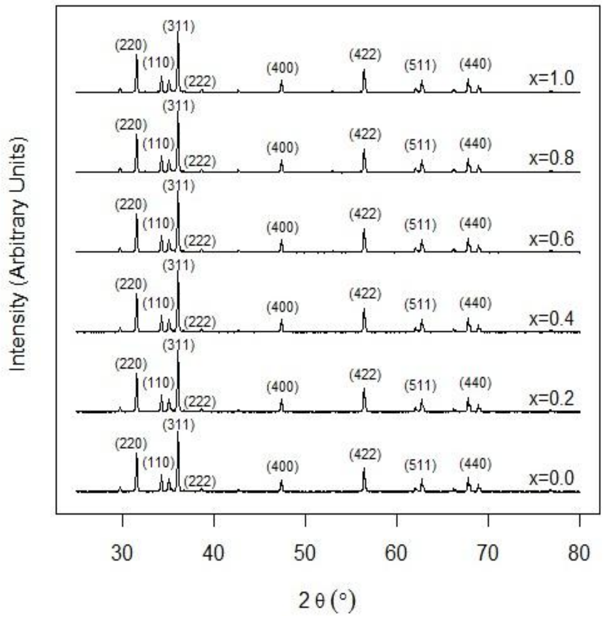

Fig. 1: XRD traces of $Zn_xCu_{1-x}Fe_2O_4$ with different Zn content.

Based on the results shown in Figure 2, the zinc content increased indicated significant change to the density of the $Zn_xCu_{1-x}Fe_2O_4$ bulk pellets. The density of $Zn_xCu_{1-x}Fe_2O_4$ were decreased as the zinc content increased from 0.0 (6.32g/cm^3) to 1.0 (5.62g/cm^3). The reduction of density as the zinc content increased was about 11%. This might due to the Zn substitution that possibly suppress the migration of the boundary and cause deterioration of the sintering properties [19]. Moreover the decrease of the sample density can be relate to the density of Zn^{2+} (7.14 gm/cm^3), which are significantly lower than those of Cu^{2+} (8.96 gm/cm^3) and Fe^{3+} (7.86 gm/cm^3). Hence when low density element substituted in large concentration scale into high density compound, the substituted elements density can be more dominant.

Figure 3 show the Seebeck coefficient $Zn_xCu_{1-x}Fe_2O_4$ increased with increasing the zinc content. The sign of the Seebeck coefficient was positive for all the ferrites and the zinc substituted copper ferrites had been classified as p-type semiconductors. The Seebeck coefficient of $Zn_xCu_{1-x}Fe_2O_4$ increased as the Zn contents increased from 0.0 (21.2 μV/K) to 1.0 (58.2 μV/K). This might due to the Zn substitution to the copper ferrites crystal lattice that reduced the carrier concentration [20]. Since the Seebeck coefficient were related as a function of carrier concentration according to the Jonker and the Pisarenko relations [21] as shown in Equation 2.

$$S = A'Tm_d^*\left(\frac{\pi}{3\eta}\right)^{\frac{2}{3}} \quad (2)$$

Where S is the Seebeck coefficient, η is the carrier concentration, e is the electric charge of the carrier, A' is a constant, T is the absolute temperature, m^*_d is a density of the state (DOS) effective mass at the Fermi level. It was clearly show that the lower carrier concentration value caused a higher value in Seebeck coefficient.

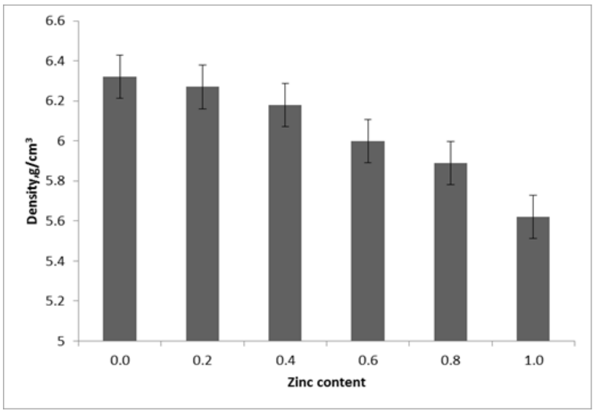

Fig. 2: Density of $Zn_xCu_{1-x}Fe_2O_4$ with different zinc content.

According to the results shown in Figure 4, increasing the Zn content caused a significant decreased in electrical conductivity. This might due to the decrease of carrier concentration caused by the Zn substitution in the copper ferrite crystal lattice [22]. The electrical conductivity of $Zn_xCu_{1-x}Fe_2O_4$ was $0.998x10^{-3}$ S/cm (x=0.0) and decreased to $0.738x10^{-3}$ S/cm, $0.598x10^{-3}$ S/cm, $0.502x10^{-3}$ S/cm, $0.42x10^{-3}$ S/cm, and $0.406x10^{-3}$ S/cm as the Zn content increased to 0.2, 0.4, 0.6, 0.8 and 1.0 respectively. Based to the Jonker and the Pisarenko relations as shown in Equation 3, the electrical conductivity were related as a function of carrier concentration. The electrical conductivity decreased when carrier concentration decreased.

$$\sigma = \eta e \mu \quad (3)$$

Where σ is the electrical conductivity, η is the carrier concentration, e is the electric charge of the carrier and μ is the mobility. Based on Equation 2 and Equation 3, the electrical conductivity (σ) and Seebeck coefficient (S) were both as a function of the carrier concentration (η). It was clearly showed that an increase in Seebeck coefficient caused a decreased in electrical conductivity due to the lower value of carrier concentration.

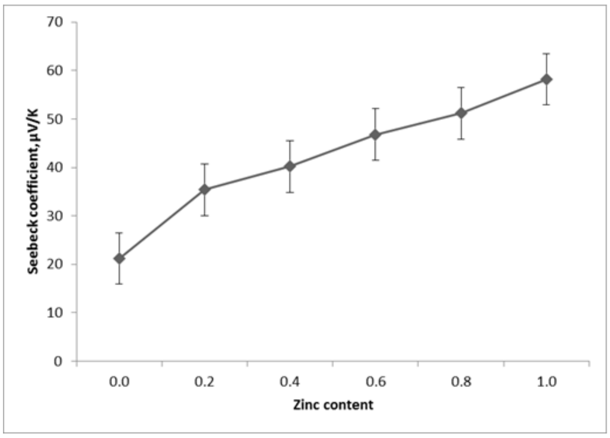

Fig. 3: Seebeck coefficient of $Zn_xCu_{1-x}Fe_2O_4$ with different zinc content.

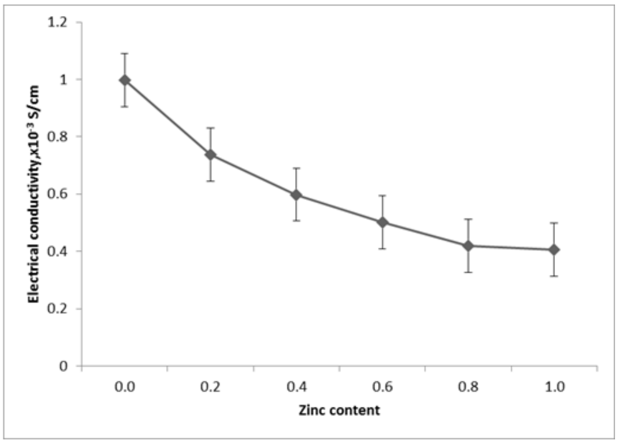

Fig. 4: Electrical conductivity of $Zn_xCu_{1-x}Fe_2O_4$ with different zinc content.

4. Conclusion:

The Zn substituted copper ferrites ($Zn_xCu_{1-x}Fe_2O_4$) with different zinc content (where x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were successfully synthesized by solid state method. The single cubic phase spinel structures of $ZnCuFe_2O_4$ were identified through X-ray diffraction and no impurity were detected. The density of $Zn_xCu_{1-x}Fe_2O_4$ were decreased as the zinc content increased where the higher density was 6.32 g/cm^3 (x=0.0) and lower density was 5.62 g/cm^3 (x=1.0). The Seebeck coefficient and electrical conductivity were shown as a function of carrier concentration based on the Jonker and the Pisarenko relations. The Seebeck coefficient was inversely proportional to the electrical conductivity. The Seebeck coefficient of $Zn_xCu_{1-x}Fe_2O_4$ reached higher value (58.2 µV/K) and lower electrical conductivity (0.406x10^{-3} S/cm) with higher Zn content (x=1.0).

Acknowledgement

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References

1. Zevenhoven, R. and A. Beyene, 2011. The relative contribution of waste heat from power plants to global warming. Energy, 36(6): 3754-3762.
2. Rowe, D.M., 1995. CRC handbook of thermoelectrics. CRC Press.
3. Ammar, Y., S. Joyce, R. Norman, Y. Wang and A.P. Roskilly, 2012. Low grade thermal energy sources and uses from the process industry in the UK. Applied Energy, 89(1): 3-20.
4. Gould, C.A., N.Y.A. Shammas, S. Grainger and I. Taylor, 2011. Thermoelectric cooling of microelectronic circuits and waste heat electrical power generation in a desktop personal computer. Materials Science and Engineering: B, 176(4): 316-325.
5. Tritt, T.M., 2011. Thermoelectric Phenomena, Materials, and Applications. Annual Review of Materials Research, 41(1): 433-448.
6. Aourag, H., B. Khelifa, L. Hamerlaine, H. Belarbi and A. Belaidi, 1990. Conduction band-edge charge densities in II-VI compound semiconductors. Physics Letters A, 145(8-9): 455-460.
7. Nemir, D. and J. Beck, 2010. On the Signi_cance of the Thermoelectric Figure of Merit Z., 39(9): 1897-1901.
8. Cai, Z.K., P. Fan, Z.H. Zheng, P.J. Liu, T.B. Chen, X.M. Cai, J.T. Luo, G.X. Liang and D.P. Zhang, 2013. Thermoelectric properties and micro-structure characteristics of annealed N-type bismuth telluride thin film. Applied Surface Science, 280: 225-228.
9. Tsuchida, K., Y. Tanaka, T. Ifuku, Y. Nakao, T. Matsuda, S. Nagashima, H. Maeda and A. Kato, 1996. Thermoelectric properties of oxide ceramics, 13(5): 478-481.
10. David Emin, 2001. Seebeck Effect. John Wiley & Sons, Inc., Hoboken, NJ, USA.
11. Jadhav, P.A., R.S. Devan, Y.D. Kolekar and B.K. Chougule, 2009. Structural, electrical and magnetic characterizations of Ni-Cu-Zn ferrite synthesized by citrate precursor method. Journal of Physics and Chemistry of Solids, 70(2): 396-400.
12. Arun Majumdar, 2004. Thermoelectricity in Semiconductor Nanostructures. Science, 303(5659): 777-778.
13. Ravinder, D., 2000. Thermoelectric power and electrical conductivity of cadmium substituted manganese ferrites. Materials Letters, 44(3-4): 130-138.
14. Je_rey Snyder, G. and Eric S. Toberer, 2008. Complex thermoelectric materials. Nature Materials, 7(2): 105-114.
15. Ravinder, D., 1999. Thermoelectric power studies of zinc substituted copper ferrites. Journal of Alloys and Compounds, 291(1-2): 208-214.

16. Shaheen, W.M. and M.M. Selim, 2001. Thermal characterization and catalytic properties of the ZnO-Co3O4/Al2O3 system. International Journal of Inorganic Materials, 3(4-5): 417-425.
17. Shahida Akhter, 2011. Synthesis, Structural and Physical Properties of Cu1-xZnxFe2O4 Ferrites. Materials Sciences and Applications, 02(11): 1675-1681.
18. Burdett, J.K., G.D. Price and S.L. Price, 1982. Role of the crystal field theory in determining the structures of spinels. Journal of the American Chemical Society, 104(1): 92-95.
19. Brook, R.J., 1991. Concise Encyclopedia of Advanced Ceramic Materials.
20. Bhan, R. and V. Dhar, 2004. Carrier density approximation for non-parabolic and highly degenerated HgCdTe semiconductors. Semiconductor Science and Technology, 19(3): 413-416.
21. Su, M.Y., C.E. Elsbernd and Thomas, 1990. Jonker "Pear" Analysis of Oxide Superconductors. Journal of the American Ceramic Society, 73(2): 415-419.
22. Wiff, J.P., Y. Kinemuchi, H. Kaga, C. Ito and K. Watari, 2009. Correlations between thermoelectric properties and effective mass caused by lattice distortion in Al-doped ZnO ceramics. Journal of the European Ceramic Society, 29(8): 1413-1418.