International Journal of Engineering and Techniques - Volume 3 Issue 6, Nov - Dec 2017

RESEARCH ARTICLE OPEN ACCESS

Seebeck Constant of Modified CuZnferrite Study

Edie Sasito Sarwodidoyo[1], Rachmad ImbangTritjahjono[2]

1.Department Refrigeration and Airconditiong 2.Department Mechanical engineering.

Politehnick Negeri Bandung. Indonesia

Abstract:

The Spinel ferrite substance with chemical composition $Cu_{(1-x)}Zn_xFe_2O_4$ have been synthesized by co-precipitation method, continued with investigation of yield structural . Using of X-Ray Diffraction – characterization reveals of lattice parameter and voltage of ionic distributions. Measurements are carried out in such circumstances as alternating but irregular voltages The fitting of fraction Cu^{2+} ,Zn^{2+},Fe^{2+},and Fe^{3+} contain used to determine of entropy .The optimum value voltage of ferrite modified is 1.3 V/300K. . From 8 samples tested only two samples that have high electrical properties and two samples have potential toxic properties, namely TP08P. while TP06P is not potential either electrical or poison properties possessed. So the chemical elements belonging to the category are electrical but somewhat toxic in the presence of Cu elements.

Keywords **— Spinel Ferrite, Co-precipitation method, Entropy, Ionic distribution,Electrical and Toxic properties.**

Introduction:

The Electrical measurements are made with attention to the intensity of the changing field at any time. Sometimes it swings positively and swings to negative, like alternating but irregular voltage. This is the case with small intensity measurements.

In the latest development of ferrite materials can be applied both in the field of medical and non-medical, substance thermoelectric generators, material pressure sensor, temperature sensor, humidity sensor, solar cell materials, gas sensor materials CO2, CH2, Nitrogen, Oxygen, [1,2,3] The material coating pigments absorbing electromagnetic wave frequency selective, anti rust coating materials [4], as an MRI contrast agent (Magnetic resonance Imaging) [5].

The ferromagnetic material usually as non-conductive compounds derived of iron oxides such as hematite(Fe2O3) or magnetite (Fe3O4), as iron oxides material have properties as a semiconductor material. [6,7]. Physically the ferrite particle size in the order of nano-to micro, so it can be displayed in the form of ferrofluid [7], thin layers (thin film), powder (powder), granules (granular), and or in solid form

(bulky) [1]

Many scientists are involved in ferrite problems. for example LI Zi-heng [1], discover the properties can be used as cell voltage [10] and as photo catalys activity [6]. In 1997 veingangkar found $Cu_{0.8}Zn_{0.2}Fe_2O_4$ properties that are able to absorb water from the air (hygroscopic) [11]. D Revinder, 2000, found as a thermoelectric properties were obtained at Ferrite with Cu and Zn atoms. Thermoelectric properties due to unstable bond of Fe^{2+} ions and Fe^{3+} ions are located on the side of the octa hedral CuZnFe2O4 spinel crystals [12].A general spinel with an intermediate cation distribution can bewritten in terms of x as follows; $A_{1\ x}B_x[A_xB_{2\ x}]O4$. [13]. The Constant of Seebeck Ferrite Voltage

The voltage different-ΔV a cross of the two ends metal rod due to a temperature different ΔT [14]. It is expressed by the Seebeck equation . $S_{seebeck} = dV/dT$. It is a thermoelectric behavior also. The Ferrite material is one of type semiconductor defect materials has a thermoelectric behavior. The free electrons in the ferrite material as a result of the crystal disorder materials which may be occur in the certain temperature circumstances then behave as a thermoelectric. The material crystals disorder have a relation with entropy value of the substance. Available of Seebeck constant due to crystal disorder have been study since the semicoductor have been studied.The thermoelectric properties of Zn substituted to the Cu-Ferrite at the room temperature has been studied by DR.Ravinder in 2012 [15] .

The cationic distribution of the Copper - Zinc Ferrite can be expressed by the following equation 3.

$$(Cu^{2+}_{1-y-x}Zn^{2+}_yFe^{3+}_x)^A[Fe^{3+}_{2-x}Fe^{2+}_x]^BO_4 \ldots \quad 3$$

[16] ………

The Seebeck Coeffisien expressed by equation of

$$V_{seebeck} = -\eta . Ln\left(\frac{\beta . Fe^{3+}}{Fe^{2+}}\right) \quad ....[17] \quad ....4$$

Fe3 + l $_{oct}$ concentration of Fe^{3+} on the side oktahetral, Fe2 + l $_{oct}$ concentration of Fe^{2+} on octoktahetral sideWhere . k -Boltzman constant = 8.6 x 10^{-5} eV

β = 1, then $\eta = k/e = 8.6x10^{-5} Volts$ Where the superscript A as tetrahedral B as octahedral respectively , the Zn Atom portion at the site A will determines the degree of ferrite inversion x .

Many elements are necessary for survival, albeit in small doses. When the supply of essential elements is inadequate it will limit the survival of the organism, but when the supply of that essential element is present excessively, it will give toxic effects. So there is an optimal dose for all these important elements. For example comparing of Cu 2+ with Fe 2+ or Fe 3+. Cu 2+ binds strongly to a nitrogen base, including a histidine chain on the protein side whereas Fe2 + or Fe 3+ does not bind strongly to the nitrogen base. Therefore Cu 2+ is more likely to interfere with protein than iron. At higher levels of iron will be harmful, because iron can catalyze the production of oxygen radicals, because some iron can stimulate bacterial and aggregate growth.[18]

EXPERIMENTAL .

Co-precipitation method is done as follows; ferrite raw material were prepared by of the metal chloride salt, mainly; $ZnCl_2$., $FeCL_2$.4H2O, $FeCL_3.6H_2O$, $CuCl_2$.4H2O,and NaOH. The materials are weighed according to the required stoichiometric ratio and dissolved of salt in distillated water as a mix solution of salt at previously pH values around 2.0, while alkaline pH values around 13.0.

The salt solution is flowed to alkaline solution by peristaltic chemical pump through nozel injector in an adiabatic bath reactor. During the reaction the solution is stirred around speed of 500 rpm.

The yield of precipitate result, proceed by the process of washing, drying in 70^0C crushing of yield to powder around 200 mesh. The mixing ferrite powder of PVA binder was pressed in to 3 mm thick pellets 1.5 cm diameter at pressure of 6 tones. The ferrite is conformed by X-ray diffraction and silver paste is coated on polished pellet to electrical measure.

Pellet pellet is divided into 6 specimens namely; TP04P, TP06P, TP08P, TP085P, TP088P ,TP09P and TP10P.

In Practically the precipitation reaction of magnetite material can be used as a model for ferrite materials.

The magnetite may be formed by reacting a ferric-Fe (III) .aq and a ferro-Fe (II) .aq salt solution in a 2: 1 molar ratio, with an alkaline NaOH, NH4OH solution.

The hydration process of Fe (III) or Fe3 + solution produces Fe $(OH)^{2+}$ and H^+ and Fe $(OH)^{4+}$ in equilibrium with Fe $(OH)^{2+}$ as

$Fe^{3+} + H_2O$ < -- > $Fe(OH)^{2+} + H^+$, $Fe(OH)^{2+}$ + H_2O < --> $Fe(OH)^+_2 + H^+$, $FeOH^{2+}$ <-> $Fe_2(OH)^{4+}_2$
Spartan oxidation of Fe3 + by O2 should be prevented.

The chemical reaction MeFe2O4 with Me as dopants Fe, Cu, and Zn, means Chemical Record CuNn Fe2O4, the reaction basis can be expressed as follows;

a. The general reaction equation of the hydration process.

$(1-x)\ Cu^{2+} + xZn^{2+} + 2\ Fe^{3+} + 8OH^- \rightarrow (1-x)\ Cu\ (OH)_2.xZn\ (OH)_2.2Fe\ (OH)_3 \downarrow$

b. Common reaction equations of the ferritization process.

$(1-x)\ Cu\ (OH)_2.xZn\ (OH)_2.2Fe\ (OH)_3\ aq \uparrow t^0$, i Cu (1-x) Znx Fe2O4.nH2O + (4-n) H2O.

Co-precipitation method is done as follows; ferrite raw material. Prior to printing ferrite ingredients first mixed with active acarbon powder with 300 mesh fineness. the ratio of ferrite with carbon 1: 10, then the ferrite mixture of activated carbon dried and pressed 3-5 tons in the form of buttons with a diameter of 1 cm thick 0.5 cm. The division of the sample portion is carried out as follows:
TP04,TP06, TP08,TP085P,TP088,TP09,TP10. Further more electrical measurement process is then performed.

RESULTS

CuZnFerrite provides alternating electric current, when conditioned at low voltages between 2 mVolt to 800 mVolt, with an arbitrary amplitude. So the measurement is conditioned to DC current.

The Spinel structure formula was defined as AB_2O_4. Site A tetrahedral ontain (Cu and Zn) dan site B (Fe) octahedral located at Wyckoff positions, respectively 8(a) dand 16(d) with stoichiometric composition is defined as $[Cu^{2+}_{1-y-x}Zn^{2+}_yFe^{3+}_x]^A[Fe^{3+}_{2-x}Fe^{2+}]$

The pattern of X-ray diffraction (XRD) Rietveld refinement was continuously done until to get goodness factor value close to one. Below the Rieltveld refined for the typical sample $Cu_{(1-x)}Zn_xFe_2O_4$ which the specimen code TP04P,TP08P are shown in Fig.1

Procedures for synthesizing Cu-based NPs (such as ; $CuFe_2O_4$, $Zn_2Fe_2O_4$) generally rely on the same techniques that have been used to prepare other metal NPs. Most methods are either "bottom-up" in which atomic-level precursors are used to synthesize nanosized materials or "top-down" in which a bulk solid is broken down into progressively smaller components.
Besides goodness factor, continues its will obtain the value discrepancy factor -R_{WP} , expected value -R_{exp} , lattice constant-a ,cationic distribution in site A and site B, goodness index χ^2 ,chemical yield formula as listed in the Table

Sample Code	χ^2	Chemical Yield Formula	Cationic Distributions					Lattice constant [^{0}A] a	Cu/Zn
			(A) Tetrahedral			[B] Octahedral			
			Cu^{2+}	Zn^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}		
Zn Group									
TP06	1.09	$Cu_{0.54}Zn_{0.13}Fe_{2.34}O_4$	0.54	0.13	0.36	0.36	1.60	8.4	4.195
TP08	1.07	$Cu_{0.49}Zn_{0.02}Fe_{2.49}O_4$	0.48	0.02	0.45	0.45	1.59	8.39	24.432
TP085	1.12	$Cu_{0.4468}Zn_{0.22}Fe_{2.33}O_4$	0.44	0.22	0.39	0.39	1.55	8.39	2.011
TP088	1.08	$Cu_{0.48}Zn_{0.14}Fe_{2.38}O_4$	0.48	0.14	0.39	0.39	1.59	8.40	3.393
TP09	1.04	$Cu_{0.46}Zn_{0.02}Fe_{2.51}O_4$	0.46	0.02	0.39	0.40	1.72	8.47	21.56
Cu Group									
TP10	1.09	$Cu_{0.42}Fe_{2.57}O_4$	0.43		0.30	0.30	1.96	8.51	
TP04	1.10	$Cu_{0.49}Zn_{0.08}Fe_{2.42}O_4$	0.49	0.08	0.39	0.39	1.65	8.44	5.979

Table 1. The list value of , χ^2, Cu,Zn,Fe content and chemical formulation

In the table2, there are few Zn and many Cu, as in TP10 P and TP04P. While on TP06P ,TP085P and TP 088 P bit Cu and Zn relatively much. We classify in 2 groups, namely group Zn and Cu group. Group Zn (TP06P,TP 085P and TP088 P), while Cu group are TP10 P and TP04 P.
In the Cu group, the biggest value of Cu / Zn is bath08P which is 24.4 then it is probable that the material is toxic and itchy. Similarly, bath with Cu / Zn 21 is likely to be toxic and itchy, try not to hold the material directly, but use a spoon blend.

Do not to hold the material directly, but use a spoon blend. The data parameters in Table 1 further selected again, to belong the list of parameters that can directly will determine the degree of inversion, material stability,
Fe2 + and Fe3 + content are in table 3, which also illustrates the toxicity and Seebeck coefficients possessed by the sample.
Extreme content in the table is as follows;
Cu / Zn= 24.4 occurred on TP08, and Cu / Zn =21 on TP09,
Cu / Zn= 2.02 occurred on TP085, and Cu / Zn =3.39 on TP088
M= Fe^{3+} / Fe^{2+}=4.3, 4.4 occurred on TP06 and TP0.9
M= Fe^{3+} / Fe^{2+}=3.5 and 3.9 occurred on TP06 and TP0.8

The CuZnFerrite material is further modified by adding a small amount of activated carbon and printed in the form of a 1.5 cm diameter button with a thickness of 3 mm. pressed with a pressure of 5 tons of style. Next is measured electric motion force with digital Sanwa multimeter with the following results;

Figure a sample image of a button that has been measured in Volage

Table 3, $V_{seebeck}$ Voltage Measurement [Volt DC/300K] with Cu/Zn = 2.02

No	Mat.Code	Cu / Zn	Voltage	M	N=LN(M)
1	TP04	5,98	0.503	4,263	1,44997314
2	TP06	4,19	0. 305	4,398	1,48114989
3	TP08	24,43	0.85	3,522	1,25902901
4	TP085	3,88	1,1	3,977	1,38052777
5	TP088	2,02	1,3	4,041	1,39649219
6	TP09P	3,38	0,35	4,346	1,46925588

DISCUSSION.

The CuZnFerrite provides alternating electric current, when conditioned at low voltages between 0.02 mVolt to 800 mVolt, with an arbitrary amplitude. So the measurement is conditioned to DC current.

The ferrite material have parameters may observation object to explore behavior of subtance, but only seven parameters will be observed include ineversion degree parameter as the centre case. The parameters i.e, 1. fraction of both cation irons Fe^{3+} and Fe^{2} in the octahedral site, fraction of divalent metal cations in tetrahedral site i.e Cu^{2+}, and Zn^{2+}, entropi of ferritesubstance , and Seebeckconstant. The sevent parameters sstisfy to estimate of Seebeck constant anf thermoelectric behavior of Cu-Zn Ferrite. Ferrite material which is relatively unstable will have the higher entropy. Given the algebraic entropy is a logarithmic function of the degree of inversion of the degree of entropy will be able to have several peaks exponents modulations.

To ensure that ferite will have a low degree of inversion can be approached by use stoichiometry that divalent metal fraction of the three-valent iros (Me^{2+} / Fe^{3+})> 0.5.

In the Table 3 shows that the degree of inversion is below 0.5 means the use of Fe^{2+} based compounds with the formula (Fe^{2+}+Me^{2+})/ Fe^{3+} =<0.5 will result the inverse spinel with an inversion less than 0.5. If the doping atoms are Cu and Zn it will generate a lot of distortion.

The figure 3, the graph of degree inversion x versus Zn cationic fraction showed linearity ramps due by the radius of Zn^{2+} is greater then other cationic and prove that the degree of inversion of the spinel Cu-ZnFerrite beside be affected by Zn^{2+} but also another cationic such as Cu^{2+} and Fe^{3+}.

Shows the list of the cationic both di-valences and tree valences include inversion degree a enthalpy and entropy have been estimated by Tem In the table 3kin formula.. Degree inversions for spinnel have 0.3 until 0.45and the entropy value of 2.52 to 3.are contained by both cationic of Cu^{2+}, Zn^{2+} and Fe^{2} ,in the tetrahedral sites The volume of its beside are depends by fraction of tetrahedral ionic site but also fraction of octahedral site contain cationics of Fe^{2+} and Fe^{3+} then the tetrahedral sides volume greater than octahedral. The radius of such as; Fe^{2+} > Zn^{2+}>Cu^{2+}>Fe^{3+} The cations of Cu2+ are in a tetrahedral lattice is not due to a relatively small but the Cu^{2+} cations has a high reactivity to merge with ionic ligand form a tetrahedral structure.

At the same figure 3 see the Cu2+ cationics give an effect significantly to decreas the tetrahedral volume, the tetrahedral size is dominated by Cu^{2+} ion size due to the amount of Cu fraction more than the fraction of the cationic Zn^{2+}. Increasing of the Cu^{2+} contain cause sharp decreasing of the Spinnel volume, indicate tetrahedral volume very sensitive to spinnel CuZnFerrite volume decrase. This decreasing will cause the different energy level. The dependence of both the Seebeck constant entropy and inversion parameters to reviewing requires precise fitting and thoroughly tendentious, a strong trend towards the parameters are not necessarily but it may representative of other parameters. The entropy substance relating to magnetism material is a parameter that can be measured both visually and by instrument.

The CuZnFerrite tend to irregular the entropy tend to higher by existing of Cu^{2+} and Fe^{2+} due increasing of inversion degree. The decreasing of tetrahedral volume due to increasing of Cu^{2+} will give volume unbalance between tetrahedral and octahedral fig. The condition will have an impact include; instability of chemical composition, instability due to the electron migration of $Fe^{2+}$to octahedral site due to exchange of Cu^{2+} to Cu^{1+}.

The fig.2 the line number 6 (orange line) and line number 5 (show three valent irons dominate then all of parameters, it means the cationic of Fe^{3+} and Fe^{2+} especially in the nodes 3 is in unstable state cause the electron migration from unstable cationics to relatively cationic stable, expected cationics Cu and Fe as the cause.

CONCLUCION

1. CuZnFerrite will basically provide alternating power when conditioned at low voltages between 0.02 mVolt to 800 mVolt, with irregular amplitudes.The ferrite is n-type semiconductor thermoelectric raw material.with the Seebeck constant of the CuZnFerrite-"$Cu_{0.486}$ $Zn_{0.02}$ $Fe_{2.494}$ O_4" modified by added Carbon actived is 1.3 Volt DC in 300 K.
2. The study of thermoelectric can identify the existing phases in the CuZnFerrite compounds, which are cationic detailed in the tetrahedral site include Cu^{2+}, Zn^{2+}, and Fe^{2+} , cationic in the octahedral site include Fe^{2+} and Fe^{3+}, by using of practice equation may be done to estimate necessary parameter such as Seebeck constant at the entropy optimum value and cationic dynamic both in the tetrahedral site and in the octahedral site.
3. Cu content is very influential on the Seebeck constant but not linear and CuZnFerrite material modified with Carbonaktive is able to raise the Seebeck voltage considerably.

REFERENCE.

[1] Cherkezova.Z, Zeleva, 2011.,Std. of N.siz. Fer.Mat. Prep. by Co-Preci. Met.,In.of Cat. Bulg.Acad.of Sci, Sofia, Bulgaria, Sev. Nati. Conf.on Chemistry

[2] Faraji.M, et al. 2010., Mag. NPs: Synt, Stablz Functz, Chartz, and Appls., J. Iran. Chem. Vol.7, No. 1,March 2010, pp. 1-37, Dept. Chem, Tarbiat Modares Univ. Tehran, Iran

[3] Liu, Yuezhen , Matsuo.M. Dep. of Pol. Sci.and Mat. ,Dalian Univ. of Tech, Dalian116024, Peop. Rep. of China., Mag. Behav.Of Zn-Dop. Fe3o4 N.Part. Est. In Term Of Cryst Domain Size., J. of Phys.Chem,Nov. 30,2011.

[4] Barcena C. et al., Zinc Ferrite N.part As MRI Cont. Agents., First pub. as an Adv.Article 2008DOI.10.1039/b801041,www.rsc.org/chemco.Chem, Cam, UK 21st Jan. 2008.

[5] Latif Abdel, 2012.,Fabrication of Nano-Size Nickle Ferrite for Gas Sensor Applications.,Jour.of.Phys.vol.1No 2 PP 50-53, Research Publ.

[6] Rahman.M et al., Review: Iron Oxide Nano Particles 3,2011, The Cent.Of Adv. Mat. Research,The Chemst.Dept. King Abd Azist, Univ, Jeddah

[7] Kaiser Robert And . Rosensweig. Ronald , avco corporation lowell, mass. For Nat.aeronautics and space admin washington, D.C.,Study of ferromag.iquid, Nasa contr. Report .Washington dc.

[8] Ghazanfar Uzma., 2005.,"Prep and Charct.of Ferrite Materials for Pract.Application", Thesis for Deg. of Doct.PhD"., Univ. of Punjab, Lahore,Pakistan,

[9] Laurent.S. et al.2008., "Magntc Iron Oxide NPs: Synthes, Cedex, France.

[10] Sláma et al., Substitut NiZn Ferrites For Passive Sensor Applications., Jour. of Elect. Engineering, VOL 57. NO 8/S, 2006, 159-162.,

[11] Dawoud H.A.,"Thermoelectric Power of Cu-Zn Ferrites", Phys. Dept, Islamic Univ. of Gaza, Gaza Strip, Palestine, Mat. Sci. and Appl, 2011, 2, 1572-1577 doi:10.4236/msa.2011.211210 Published Online November 2011.

[12] Vaingankar, S.G. Kulkarni* and M.S. Sagare., Humidity Sensing using Soft Ferrites,. Hu, J PHYS. IV FRANCE 7 (1997) Clloque C 1, SupplCment au Journal de Physique 111 de mars 19. Shivaji Univ. Willing. College, Sangli 41 6 415, India

[13]. Attia. S.M, Study of Cation Distribution of Mn-Zn Ferrites., Egypt. J. Solids, Vol. (29), No. (2), (2006) , Phys. & Chem. Dept. Faculty of Edu., Kafr El-Shiekh, Egypt.

[14] Kasap.S.,2001.,Thermoelectric Effect in Mettals: Thermocouples.,An e-Booklet, Dept Elect. Univ.Saskatchewan, Canada.

[15] Manisha C,2009, "Study of the irradiation effect on electrical properties of magnetic oxides",Thesis PhD,Sausahtra Univ.

[16] Gaffoor.Abd,Ravinder,2012.,"HighTempt Thermo lectricPower Studies of Ni-Mg Ferrites", Dept.Physc, Osmania Univ.,Hyderabad, India,W. J.of Cond. Matt. Phys, 2012, 2, 237-240.

[17] Hugh Sr. et al," Simple spinels: crystallographic parameters, cation radii, lattice energies and cation distribution", Dept.Chem. Arizona State Univ. Tempe, Arizona 85287, Amric Mines, Vol. 6E, pages 1E1-I%, 1983.

[18] Sasito edie.,Thermoelectric Power Study of the Formation in Magnetic Transition Phase of Yield of Flow Injection Syntesis Co- Precipitation Reactor.,Faculty of Mathematic and Natural Sciences University of Indonesia, Depok 16424..