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Applicability of the Structural Rietveld Refinement to Estimate CuZn Ferrite Seebeck Constant.

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ABSTRACT

The series of spinel ferrite substance with chemical composition $Cu_{(1-x)}Zn_xFe_2O_4$ where 0.365 <x<0.45 have been synthesized by co-precipitation method continued with investigation of yield structural and Seebeck behavior. Base on using of X-Ray Diffraction - characterization and applying the full fitting of Rietveld refinement method to reveals of lattice parameter and cationic distributions, the fitting of fraction Cu^{2+} ,Zn^{2+},Fe^{2+},and Fe^{3+} contain used to determine entropy and Seebeck coefficient. As the result the series of data and graph can be used to estimate the Seebeck optimum constant base on peak of graph. The optimum value of the Seebeck constant of ferrite is -108 uV/K at entropy value 3.76 [J/mol K] at inversion degree 0.452.

Introduction

Ferrites are usually non-conductive ferrimagnetic compounds derived of iron oxides such as hematite(Fe2O3) or magnetite (Fe3O4).such as iron oxide material has properties as a semiconductor material. [1,2]. Physically the ferrite material particle size in the order of nano-to micro, so it can be displayed in the form of either liquid known as a ferrofluid [2], thin layers (thin film), powder (powder), granules (granular), and or in solid form (bulky) [3,4,5].

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, [3, 6 , 7], material coating pigments absorbing electromagnetic wave frequency selective, anti rust coating materials [8], as an MRI contrast agent (Magnetic resonance Imaging) [9].

Evident of the fact although the ferrite material is simple can be said to be so widespread and was never resolved. [3].LI Zi-heng discover the properties of semiconductor type-P on Zinc-Ferrite materials, and can be used as a photo cell voltage [10] as photo catalys activity [1] 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 a significant of thermoelectric properties were obtained at Ferrite materials doping of 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 Seebeck Constant of Ferrite Materials.

Generally the voltage different-ΔV a cross of the two ends metal rod due to a temperature different ΔT is called the Seebeck effect [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].In the spinel materials has relationship between degree of inversion and entropy or stability of substance. It is expressed by the following equation 2.

$$S_x = -R\{xLnx + (1-x)Ln(1-x) + xLn(x/2) + (2-x)Ln(1-x/2)\} \quad \ldots 2$$

where R is the perfect gas constant [16] .

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

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

[17]

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 . Thermoelectric properties of materials, mainly it has a Seebeck coefficient

$$S_{sebeck} = -\frac{k}{e}\left[Ln\left\{\frac{\beta.Fe^{3+}|oct}{Fe^{2+}|oct}\right\}\right] \text{[18]} \quad \ldots\ldots 4$$

$Fe3+|_{oct}$ concentration of Fe^{3+} on the side oktahetral, $Fe2+|_{oct}$ concentration of Fe^{2+} on octoktahetral side. k -Boltzman constant = 8.6 x 10^{-5} eV β = 1, then $k/e=8.6x10^{-5}$ Volts

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Experimental technique.

The sample were prepared by co-precipitation method of the metal chloride salt, mainly; $FeCL_2.4H2O$, $FeCL_3.6H_2O$, $CuCl_2.4H2O$, $ZnCl_2$ 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.

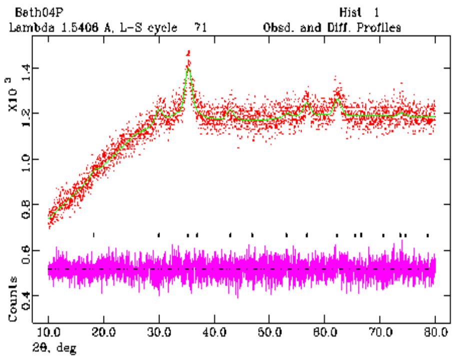
The salt solution is flowed to alkaline solution by peristaltic chemical pump through nozel injector in an adiabatic bath reactor. During the reaction the solution is stirred around speed of 500 rpm.

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.

Results

The Results of the Rielvelt refinement by GSAS as shown in Figure 1, shows the residue and a very small calculation error. 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 $[Cu^{2+}_{1-y-x}Zn^{2+}_{y}Fe^{3+}_{x}]^{A}[Fe^{3+}_{2-x}Fe^{2+}$

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 Bath04P,Bath08P are shown in Fig.1



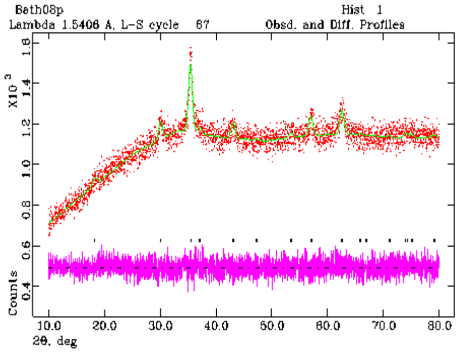


Fig 1. X-Ray diffraction pattern for sample code Bath 04P, Bath 08P.

Besides goodness factor, continues its will obtain the value discrepancy factor -RWP , expected value -Rexp , lattice constant-a ,cationic distribution in site A and site B, goodness index χ2 ,chemical yield formula as listed in the Table 1.

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, Seebeck constant and essential cationic materials, as Table 2 below.

To get an idea of communicative graph then each parameter is shown in the form of a absolute line as in Figure 2 below. From the collection of lines that provide essential information on the lines indicated by the unification of certain nodes.

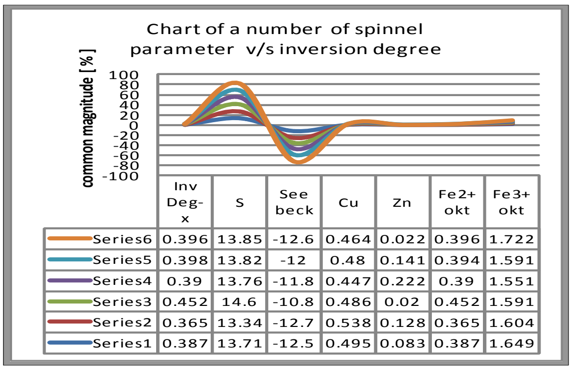


Fig 2. The chart of CuZn Ferrite "$Cu_{(1-x)} Zn_xFe_2O_4$" parameter of inversion.

Table 1. The list value of R_{wp},R_{exp} , χ^2 and chemical formulation.

Specimen Code	R_{wp}	R_{exp}	χ^2	Lattice constant [^{0}A] a	Cationic Distributions (A) Tetrahedral			[B] Octahedral		Chemical Yield Formula
					Cu^{2+}	Zn^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	
Bath04P	3.10	2.47	1.10	8.44	0.49	0.08	0.39	0.39	1.65	$Cu_{0.4951}Zn_{0.0828}Fe_{2.4220}O_4$
Bath06P	3.14	2.52	1.09	8.4	0.54	0.13	0.36	0.36	1.60	$Cu_{0.5382}Zn_{0.1283}Fe_{2.3335}O_4$
Bath08P	3.13	2.5	1.07	8.39	0.48	0.02	0.45	0.45	1.59	$Cu_{0.4862}Zn_{0.0199}Fe_{2.4939}O_4$
Bath085P	3.15	2.51	1.12	8.39	0.44	0.22	0.39	0.39	1.55	$Cu_{0.4468}Zn_{0.2221}Fe_{2.3311}O_4$
Bath088P	3.12	2.49	1.08	8.40	0.48	0.14	0.39	0.39	1.59	$Cu_{0.4798}Zn_{0.1414}Fe_{2.3788}O_4$
Bath-09P	3.04	2.47	1.04	8.47	0.46	0.02	0.39	0.40	1.72	$Cu_{0.4636}Zn_{0.0215}Fe_{2.5149}O_4$
Bath 0 P	3.16	2.52	1.09	8.51	0.43		0.30	0.30	1.96	$Cu_{0.4292}Fe_{2.5708}O_4$

Table 2. The list of top down inversion degree of line series and parameter contain.

Speciment Code	Inv Deg-x	Ferrite Parameter Line 1. S[J/mol K]	Line 2. Seebeck [E-2mV/K]	Line3. Cu^{2+}	Line 4. Zn^{2+}	Line 5. Fe^{2+} oct	Line 6. Fe^{3+} oct
Bath 04P In Line 1	0.387	3.21	-12.47	0.495	0.0828	0.3867	1.6485
Bath 06P Line 2	0.365	3.03	-12.73	0.538	0.1283	0.3647	1.604
Bath 08P Line 3	0.452	3.76	-10.84	0.486	0.0199	0.4516	1.5907
Bath 085P Line 4	0.390	3.24	-11.78	0.446	0.2221	0.39	1.5511
Bath 088 Line 5	0.398	3.27	-11.95	0.479	0.1414	0.3938	1.5912

Note :The line series show the specimen of ferrite parameters data.
Line 1 as inversion degree shows as horizontal axis
Line 2,3,4,5 and 6 respectively as CuZn Ferrite parameter .
series 1 as line of entropy parameter
series 2 as line of Seebeck parameter
series 3 as line of Cu content parameter
series 4 as line of Zn content parameter
series 5 as line of Fe 2+ content parameter
series 6 as line ofFe 3+ content parameter

The dependence of a number of essential parameters to the degree of inversion illustrative sharpened by the absolute graph in Figure 3. Are formed some peaks of the charts which has essential information,

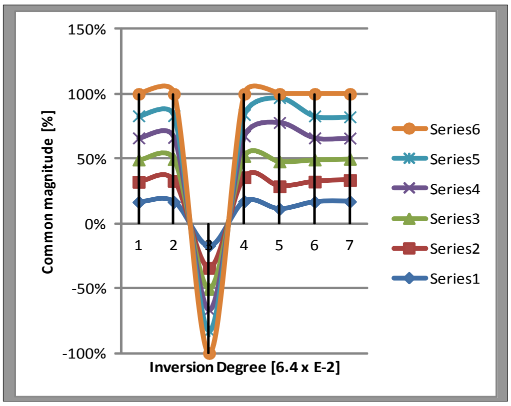


Fig 3.Graph of the dependency of ferrite behavior to the ferrite inversion degree according to fig.2.

The axis of inversion have 6 nodes number, each node as a function of inversion dgree.

Discussion

At the figure 3, there are 6 lines. Each line show of speciment code characteristic, such as example line 6, the speciment code is Bath09.In this node the entropi is 3.29 relatively low.

The ferrite material have lot of parameters may be 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.

As a result the graph of the figure 3 obviously shows that the degree of inversion has a strong role to determining properties of the ferrite material which_in a relatively narrow interval nodes of inversion i.e from 0.35 to 0:45 there are 7-six stables and 4-four unstable state where the stability of state is expressed by the value of entropy- S

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+}.

In the table 3, shows the list of the cationic both di-valences and tree valences include inversion degree a enthalpy and entropy have been estimated by Temkin formula.. For spinnel have degree inversions 0.303 until 0.4516 the entropy value of 2.52 to 3.76

The tetrahedral sites are contained by both cationic of Cu^{2+}, Zn^{2+} and Fe^{2+}. 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 comparative of cationic radius such as; Fe^{2+} > Zn^{2+}>Cu^{2+}>Fe^{3+}.

The Cu2+ cations 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 higer 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+}.

Using the chart at fig.3 shows the node 3 have potential information that ferrite in very unstable state is in line series 3. The entropy ferrite substance value is 3.76 [J/mol K] and the optimum Seebeck constan is -10.84[E-2mV/K]= -108.4 [uV/K] almost the same with result of Dawoud [11] i.e in a hundred around uV/K and behaves as n-type semiconductor.

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.

Summary

1.XRD data analysis use the Rietveld refinement method with the GSAS software 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+}.

2. Using Rieltvelt refinement of the X-Ray diffraction data proceed elaborate 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. The expectation of the Seebeck constant of the CuZnFerrite-"$Cu_{0.486}\,Zn_{0.02}\,Fe_{2.494}\,O_4$" is -108 uV/K at entropy value 3.76 [J/mol K] at inversion degree 0.452.

The ferrite is n-type semiconductor thermoelectric raw material.

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