Thermoelectric Power Study of CuZn Ferrite in Magnetic Transition Phase as Yield of Flow Injection Synthesis Co-precipitation Reaction.

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***Abstract*— One of using flow injection synthesis of $Cu_{(1-y)}$ Zn_Y $Fe_{2+X}O_4$ is able to estimate the entropy of forming the material, automatically both degree of spinel inversion, magnetic behavior and Seebeck parameter of material can be predicted. Using of Rieltveld refinement of the X-ray de-fraction characterization analysis both the parameter of lattice and oxygen, and cationic distributions can be determined. Furthermore by helping of magnetic characterization measure will be obtained transition magnetic phase of Cu-Zn Ferrite, whether in ferromagnetic or diamagnetic phase. At the phase transition stability disrupted electronic materials, so that behavior can be observed of the thermoelectric behavior materials. All of the parameter able to reveal the $Cu_{(1-x)}$ Zn_x Ferrite Seebeck behavior. Justification of Seebeck estimation could be done by measurement of thermoelectric voltage use of material bulky that is flanked by two silver electrode reveal that inversion x-0.88, 0.9 give the highest Seebeck behavior. A series of spinel inversions dgree as x = 0.379, x = 0.515 and x=0.57 , only the value of x = 0.379 which shows the potential thermoelectric properties. Test of magnetic material using permagraph shows that on the degree inversion 0.379 there is a change from ferromagnetic to diamagnetic, indicate it has been exchanged the electron state energy. Entropi, which is the stability of crystalline materials determined, is influenced by include, temperature also give contribution increase Seebeck paremeter material. This study as encourager not only developing of Cu-ferrite materials as semiconductor materials, but also as a thermoelectric power material**

***Index Term*— Thermoelectric power, Degree of spinel inversion, Cationic distribution, Seebeck parameter, Magnetic transition.**

I. INTRODUCTION

The ferrites material have many important applications in modern telecommunication and electronic devices. For this reason, both the engineers and scientists are keenly interested in

determining their characterization [1,2]. Because of low electrical conductivity of ferrite and rare earth ferrite to compare with those of magnetic materials, they play a useful role in many magnetic applications.

The Cu-Zn-Ferrite as Cuprospinel is a practical the ferrite material both are ease to react, observable and controllable its have been widely used in electronic applications [2]. The crystal structure of CuZnFerrite is spinel (Space group Fd3m) in which the lattice of O^{2-} ions forms tetrahedral and octahedral local symmetry that are referred to as A and B sites**,** respectively [2]**.** In the normal spinel structure, divalent ions (Cu2+ in CuFe2O4) only occupy A sites**,** and trivalent ions (Fe3+ in CuFe2O4) only occupy B sites**.** In inverse spinel structure, divalent ions occupy half of B sites, and trivalent ions occupy the rest of B sites and all A sites. Zn-substitution results to a change of cationic in chemical composition and a different distribution of cationic between A and B sites. [3] Consequently the magnetic and electrical properties of spinel ferrites will change with changing cationic. Mainly equation of spinel ferrite is [2];

$$(Me^{II}_{\delta}.Fe^{III}_{1-\delta})_{tetra}[Me^{II}_{1-\delta}.Fe^{III}_{1-\delta}]_{octa}O_4 \text{…….(1).}$$

where Me =(Mg, Co, Mn , Zn, Cu,etc)
δ=1 for normal spinel, i.e. the divalent metal ion occupies the tetrahedral site and the trivalent ion occupies the octahedral site; δ=0 for inverse or distorted spinel and δ=fraction for random distribution.

The result of type beside depends on the stoichiometri portion but also method of preparation, neither variable with the preparation temperature nor type of cationic systems [5]

The 2-3 spinel structure compound having a spinel cationic A: 2 on side and 2 tetrahedral cationic B: 3 on 2 sides of the octahedron, for 4-2 Spinel has a cationic A: 4 and cationic B:2 fcc unit cell, space group Fd3m , cationic at 8a and 16d positions. Anions on the 32e position . Oxide with the composition of A2 + B3 +2 O4 (A2 + is Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn, and B3 + are Al, Ga, In, Ti, V, Cr, Mn, Fe, co, Ni, and Rh). If the hole is filled by A^{2+} tetrahedral is produced normal spinel, otherwise if filled by B3 + will obtain the inverse spinel. [6]

In the low temperature, the exchange of cationic between tetrahedral and octahedral site can occur simple by transfer of electron of Fe^{2+} and Fe^{3+} followed by exchange of both spinel structure and magnetic behavior. [7]

In general, both the metal and the semiconductor have thermoelectric properties. Ratio between thermal conductivity -κ and electrical conductivity -σ of the material remains and does not depend on the kind of material. Which changes with temperature is material Seebeck coefficient-α.

The α parameter value of semiconductor is usually about ten to several hundreds times parameter α of metal **[7],** therefore many kind of semiconductor materials have been developed as thermoelectric materials.

One of the advantages of co-precipitation synthesis of spinel ferrite material is that it can be used to determine the formation entropy which it means degree of inversion material can be used to estimate the degree of inversion of the spinel crystals of such materials[]and can be used to estimate the electrical properties of materials, such as electrical conductivity and thermoelectric properties of materials.

Spinel crystal structure includes a normal spinel and inverse spinel, both have two sites of the lattice tetrahedral and octahedral lattice. Which in reality the two sites lattices do not line up perfectly rigid. Usually the tetrahedral sites are often too small for the metal Ions, so that cause the oxygen ions move slightly. Any Ions connected with the octahedral sites move in such a way as to shrink the size of the octahedral cell by the same amount of the tetrahedral sites expands.

Thermoelectric Behavior. Of The Cuznferrite As Impact Of Magnetic Phase Exchange..

Irregularly of metal ions in spinel crystal shape irregularity causes the crystals are unstable. The higher the number the higher the inverse spinel crystal instability. and Moving of oxygen ions give unstable sub lattice. Relationship between the degree of regularity with Spinel inversion. degree of regularity in terms of thermodynamics is expressed by entropy-S_x.[6]

$$S = -R\{xLnx + (1-x)Ln(1-x) + xLn(x/2) + (2-x)Ln(1-x/2)\}$$
………..2)

x is invertion degree; for largely inverse spinel x→1 the material in inverse spinel phase, for largely normal spinel x→0 the material in normally spinel.

The cation distribution in the two sub-lattices, i.e. (1) a tetrahedral lattice site A formed by four oxygen anions and (2) an octahedral lattice site B formed by six oxygen anions. the molecular formula of that ferrite can be written as equation (1)[8]. For both divalent cationic Zn , Cu and Fe will follow equation 3, such as;

Zn^{2+} more preferences to site tetrahedral
Cu^{2+} and Fe^{2+} more preference to site octahedral

Then cation distribution equation Cu Zn Ferrite is

$$(Zn^{2+}_{y(1-x)}Cu^{2+}_{x}Fe^{3+}_{(1-y)+yx})[Fe^{2+}_{(1-y)(1-x)}Fe^{3+}_{(1-y)-yx}]O_4 \quad ….(3)$$

The Site Preferences of the Ions is determined by;

1. The ionic radii of the specificions
2. The size of the interstices
3. Temperature
4. The orbital preference for specific coordination

The divalent ions are generally larger than the trivalent ions. The octahedral sites are also larger than the tetrahedral therefore, it would be reasonable that the trivalent ions such as F^{3+} would go into the tetrahedral sites and the divalent ions would go into the octahedral.

There is a fundamental relationship between the degree of order-entropy material Seebeck coefficient S with S_{sb} is expressed as, [9]

$$S_{sb} = -\frac{1}{q}\left(\frac{\partial S}{\partial N}\right)_{E,V} \qquad ……….(4)$$

N = the number of particles.
V = Electric potential of particle
E = Energy of particle

As T >>∞ the material forming entropy-S can be written as $k_B Ln(g)$,where g is the electronic degeneracy.

Then $$S_{sb} = -\frac{k_B}{q}\left(\frac{\partial\, Ln(g)}{\partial\,(N)}\right)_{E,V} \qquad ……..(5)$$

Structural Distortions And Thermoelectric Power

The common structural distortion in oxides is a Jahn-Teller distortion. The lifting of the orbital degeneracy is accomplished through the contraction of some bonds to ligands and simultaneous elongation of others. Elongation of bonds leads to greater overlap of electron clouds between cation and bonded oxygen anion and therefore higher energy of the orbital. [9]

The effect of Jahn-Teller distortions is best documented for Cu(II) complexes (with 3 electrons in the e_g level) where the result is that most complexes are found to have elongation along the z-axis.

Seebeck can be determined by Koshibae et al. as equation S [9]

$$S_{sb} = -\frac{k_B}{q}Ln\left(\beta\frac{y}{(1-y)}\right) \qquad ……………(6)$$

$$\beta = \frac{g_{(I)}}{g_{(II)}}$$

Where k_B is Boltzmann constant,
q is Fundamental charge
β is Electronic degeneracyparameter.
$g_{(I}$ is Electronic state degeneracy (sites I)
$g_{(II)}$ is Electronic state degeneracy (sites II)
y is Concentration of carrier in Heikes formula

S_{sb} is Seebeck coefficient or thermopower (n and p-type; subscripts n, p) y/(1-y) plays an important role in both the magnitude and the sign of a material‘ thermopower the electronic degeneracy g is calculated as the product of spin-g_{spin} and orbital degeneracy-g_{orbit}, where

$$g = g_{spin} \times g_{orbit} \qquad ……………….(7)$$

The conduction at low temperature is due hopping of the electron between Fe^{3+} and Fe^{2+} as the ionic carrier concentration [9,10] the Seebeck coefficient S_{sb} is

$$S_{sb} = -\frac{k_B}{q}Ln\left(\beta\frac{Fe^{3+}\big|_{oct}}{Fe^{2+}\big|_{oct}}\right) \qquad ……….(8)$$

Equation 8, give interpretation that stability of material phase depend on linier with ratio of the concentrate of tree valent of divalent cationic iron. Increasing the ratio will cause instability of material phase.

2. EXPERIMENTAL TECHNIQUE

The polycrystalline Zinc-substituted Copper ferrites having compositional formula Cu1–xZnxFe2O4 where x stepped 0 ≤ 0.2 ≥ 1, were prepared by the Flow Injection Synthesis technique [9], from pure oxides powders $FeCl_2.4H_2O$, $FeCl_3.6H_2O$, $CuCl_2.4H_2O$, $ZnCl_2$, and precipitator- precursor NaOH.

$$2FeCl_2.4H_2O + 4\ FeCl_3.6H_2O\ + 3xCuCl_2.2H2O + 3(1-x)\ ZnCl_2 + 22\ NaOH \dashrightarrow 3CuxZn(1-x)Fe_3O_4 + 22\ NaCl + (42+6x)\ H2O \quad \ldots\ldots\ldots\ldots 9$$

Table I
Stoichiometri Raw Material of CuZnFerrite.Each salt chlorine solution [gram In 20ml aqDM].Precursor NaOH [gram in 500 ml aqDM].

Sample Code	Cu Cl_2. $4H_2O$	$ZnCl_2$	$FeCl_3$ $6.H_2O$	$FeCl_2$ $.4H_2O$	NaOH
Bath088	9.00 grm	0.49 grm	7.95 grm	21.63 grm	20 grm
Bath 090	9.20 grm	.41 grm	7.95 grm	21.63 grm	20 grm
Bath 1.0	10.22 grm	0	7.95 grm	21.63 grm	20 grm

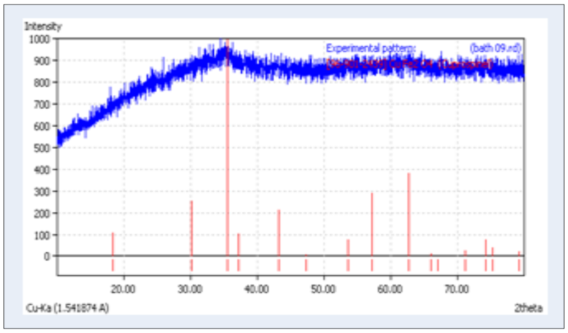


Fig. 3. Identify of x-ray diffraction profile sample Bath-09

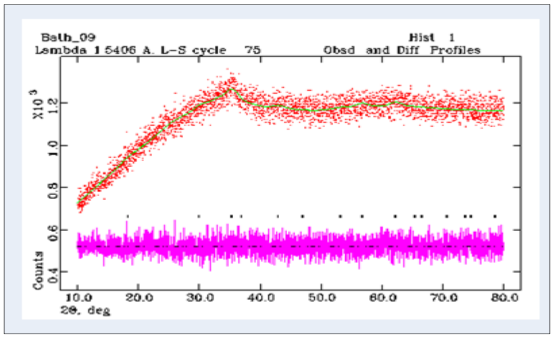
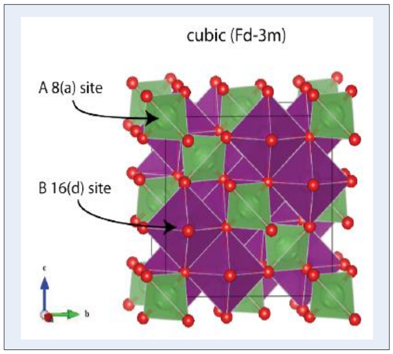


Fig. 10. Refinement of x-ray diffractionprofile sample Bath-09.

Table II
Result of Rielveld Refinement include;
R factor, Chisquared, and Cationic Distribution
of The sample Bath 09.

o.	*Name of Coumpound*	*Phase*	*Ref.*	*Mass Fraction (%wt)*
.	Cuprospinel	$CuZnFe_2O_4$	ICDD- 96-901-2439	> 99.00
space group : F d -3 m (227) Crystal : Cubic lattice Parameter : *a* = 8.470(1) Å, *b* = 8.470(1) Å and *c* = 8.470(1) Å, α=β=γ = 90°, Volume = 607.6(1) $Å^3$ dan ρ density = 5.039 $gr.cm^{-3}$				
R factor	*w*Rp = 3.04 Rp = 2.43	χ^2 (chisquared) = 1.048		
 Fig. 11. Cationic Distribution Sample Bath 0.9				

Based of the stoichiometri,the cationic distribution can be formulated as,

$$[Cu^{2+}_{1-y-x}Zn^{2+}_{y}Fe^{3+}_{x}]^{A}[Fe^{3+}_{2-x}Fe^{2+}_{x}]^{B}O_4$$

Table III
Cationic distribution of Sample Bath0.9

Atom	ite	Cationic Distribution			
		Cu^{2+}	Zn^{2+}	Fe^{2+}	Fe^{3+}
A	(a)	0.463	0.021	-	0.3963
Content		52.60 (at. %)	2.44 (at. %)		44.97 (at. %)
B				0.39	1.7222
Content				8.71 (at. %)	81.29 (at. %)
Composition		0.463	0.021	0.39	2.1185
Empirical Formulation		$Cu_{0.4636}Zn_{0.0215}Fe_{2.5149}O_4$			

Ratio of the Fe^{3+} of Fe^{2+} octahedral cationic of the sample code Bath09 is 4.34.

In the same way can be tabulated cationic distribution of the sample code Bath 088, Bath Bath 0.9 and 1.0 as follows;

Table IV
Cationic Distribution and $Fe^{3+}$of Fe^{2+}ratio
Sample in Magnetic Phase Transition

Sample Code	Empirical of Cationic Distribution	Fe^{3+} of Fe^{2+} ratio
Bath 0.88	$Cu_{0.4798}Zn_{0.1414}Fe_{2.3788}O_4$	4.04
Bath 0.9	$Cu_{0.4636}Zn_{0.0215}Fe_{2.5149}O_4$	4.34
Bath 1.0	$Cu_{0.4292}Fe_{2.5708}O_4$	6.48

The J-H loop hysteresis Identify The magnetic Phase transition Between Sample Bath088 Bath09 and Bath 1.0

Hysteresis loops for each sample Cu-Zn Ferrite were obtained using permagraf instrumentation at room temperature.

Magnetization -J [T] in range -0.1 to 0.1 Tesla, versus magnetic Field –H [kA/m] in range -200 to 2000 kA/m.

At any samples selected in the phase boundary between the ferromagnetic properties of diamagnetic. Samples that are in transition state is sampled with Bath088 code, Bath09 and bath1.0.

Here are the results of the recording instrumentation Permagraf and graphs that show the value of the hysteresis loop between the magnetization J [T] to the external field H [kA / m].

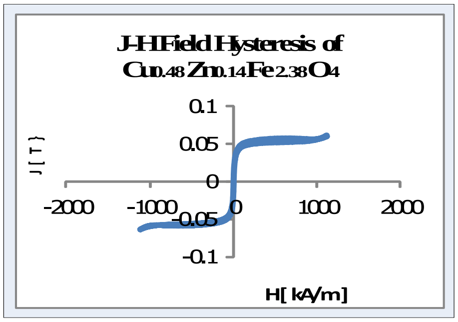


Fig. 12. J-H Loop Hysteresis Sample Bath0.88.($Cu_{0.4798}Zn_{0.1414}Fe_{2.3788}O_4$)

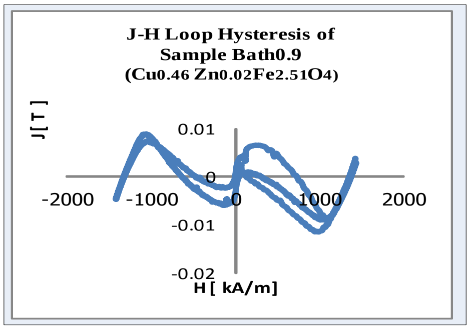


Fig. 13. J-H Loop Hysteresis Sample Bath0.88. ($Cu_{0.46}Zn_{0.02}Fe_{2.51}O_4$)

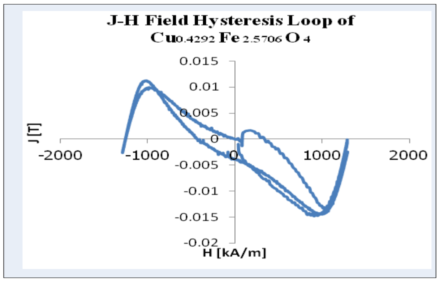


Fig. 14. J-H loop Hysteresis sampleBath1.0. ($Cu_{0.4292}Fe_{2.5708}O_4$)

Indicate that sample Bath0.88 is obtained soft magnetic (ferromagnetic) behavior. While sample Bath0.9 and sample Bath1.0 are obtained have diamagnetic. The entropy of soft magnetic is lower than diamagnetic.

Identify of Thermoelectric Power Behavior of Sample Cu-Zn Ferrite in Phase Transition of Both Sample code Bath088, 090 and 1.0.

Identification of thermoelectric power may be done by direct measuring of voltage or electric potential different between two surfaces of solid material that have different temperature.

The simple measurement techniques are required that can provide heat treatment so that the two surface materials have different temperatures, as well as to measure both the temperature and the electrical voltage between two surface of material.

The necessary equipment as follows; Heat mover thermoelectric cooling or hot gas heater, holder of the sample and sensor, Infra Red thermometers and digital voltmeter.

Fig. 15. Network of the simple measurement instrumentation Of The thermoelectric Power .

On both material surfaces are given by electrical conductive thin film -*Silver conductive paint*, installed both the voltage sensor and thermocouple temperature sensors. The thermocouple sensor have to lay by thin glass to pass on heat but capable as electrical insulators.

Samples compacted in the form of discs 13 mm diameter 3mm thick, both samples surfaces plated by a layer of silver conductive paint as electrode.

Temperature measurement of both surface materials should use the IR thermometer. It works in wireless systems, the results are without disturbance of the Seebeck effect. This is very different from the use of measuring instruments that use a system of thermocouples probe, where the probe signal will be distracted by material seebek voltage.

To avoid sample damage due by excessive heat, the sample is placed between the clamps of ceramic, is left in part to the material surface temperature measurement.

Digital voltmeter should be equipped with buttons holder to hold the voltage number moving.

The voltage measurement results between surface ferrite materials that have been heat-treated are as table follows;

Table V
the case study of voltage measurement and different temperature of two surface cu-znferrite. material..

Sample Bath088 T [K], V[mV}					Sample Bath090 T[K] V[mV]				
T_H	T_C	ΔT	ΔV	S_{sb}	TH	TC	ΔT	ΔV	S_{sb}
305	301	4	8.97	2.24	331	325	6	0.1	0.0003
339	337	2	10	5	320	318	2	0.3	0.00094
355	347	8	13.7	1.71	316	314	2	0.5	0.00158
404	398	4	14.7	3.68	313	310	3	0.1	0.00032
398	396	2.3	15.1	6.57	313	310	3	6.6	0.02109
481	478	3	13.8	4.6	312	310	2	6.7	0.02147
425	419	6	12	2	312	311	1.2	6.3	0.02018
483	478	5	11	2.2	311	307	4	5	0.01608
415	408	7	10.3	1.47	309	307	2	4.7	0.01521
404	397	7	9	1.29	309	307	2.2	6	0.0194
380	370	8	6.8	0.85	308	307	1	5.5	0.01786
354	346	8	5.9	0.74	309	306	2.5	5.6	0.01815
350	344	6	5.5	0.92	307	303	4	5.8	0.01889
332	325	7	5.3	0.76	308	302	6	5.7	0.01851
337	328	9	5.2	0.58	307	304	3	5.9	0.01922
328	320	8	5		307	305	2	3.05	

3. ANALYSIS

1.Inthis research Cu-Ferrite, with the sample code Bath1.0 is diamagnetic even by doping zinc atomic until 0.02 mol of 1 mol sample Bath0.9 the material still in diamagnetic. It looks Bath0.88 sample and the sample bath 09 has properties as a phase transition between ferromagnetic and diamagnetic. but it can be predictable that the value of entropy are both likely have a fairly sharp distinction, ferromagnetic entropy lower than diamagnetic.

2. The sample Bath09 content a little of atomic Zinc but still in diamagnetic phase. Little of Zn^{2+} addition as sample Bath088, the magnetic material be changed as soft magnetic or ferromagnetic materials. Its may transition of magnetic phase. The Sample bath10 is diamagnetic material, and in measuring of thermoelectric behavior the material do not result electric voltage both at low and high temperature difference.

3. Measuring of surface temperature and voltage electrode both conducting layer surfaces of material sample were obtained the necessary graph as follow;

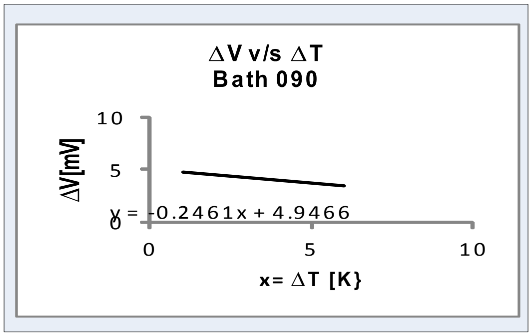


Fig. 16. The linier trend voltage semiconductor electro motive force-emf, of temperature different material surface of Cu-Zn Ferrite.

Thermoelectric power behavior of sample bath 090 is the decreasing temperature different is followed by increasing electrical voltage between low and high temperature surface. In the low temperature and without temperature treatment, the sample bath090 have EMF 4.7 milli volt DC/K. See at the figure 17, EMF of the sample bath088 is 14.47 milli Volt DC/K.

The different temperature surface limite of sample bath090 is 20 K , while sample bath 088 is 15 K. it means that sample bath088 electric source ability better than090, but material toughness sample bath090 better than088.

From the Equation 2,4,8 and the result of XRD Rieltveld refinement to obtain cationic distribution then obtained Molecular Weight-MW, Spinel inversion degree-x obtain the entropi value.

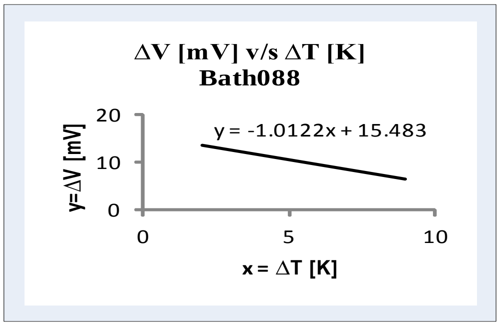


Fig. 17. The linier trend voltage semiconductor -electromotive force-emf, of temperature different Materials surface of Cu-Zn Ferrite.

4. CONCLUSION

The Cu-Zn Ferrite material besides as a semiconductor but in under certain conditions also can be as both thermoelectric materials and magnetic materials.

The Cu-Zn Ferrites will have not Seebeck effect parameter in disturbance magnetic phase especially diamagnetic, thus not only depend on octahedral ferric ratio $(Fe^{3+}/Fe^{2+})_B$ but also value of entropy forming materials as equation 2.

Application of Flow Injection Synthesis to analysis electrical and thermodynamic of material characteristic is very helpful, especially reveal the value of entropy.

Magnetic characterization using permagraf instrumentation help fast reveal stability of material via figure of the J-H loop hysteresis.

Thermoelectric ferrite materials can be either ferromagnetic or diamagnetic. but which has ferromagnetic the potential of thermoelectric is greater.

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