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Development of Cu substituted Ni-Zn nano-ferrites for industrial applications

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ABSTRACT
Cu substituted Nickel-Zincferrite nano-particles with composition$Ni_{0.2}Cu_xZn_{0.8-x}Fe_2O_4$(x=0.0 to 0.8 with step size 0.2) were synthesized using the technique of Citrate-Gel Auto Combustion method at 180 ^{0}C. Sintering of preparedsamples at 500^{o}C for four hours was done and analyzed with XRD. These samples samples were confirmed withspinel structure of single phase.Size of the crystal, density of x-ray, volume and lattice parameterare being computed from XRD data.These nano-particles showUV-Vis absorption band in the wavelength region between200 nm to 800 nm. High temperature thermo electrical Power studies have been carried out starting from room temperature to a temperature well beyond Curie temperature by differential method. Depending on the sign of Seebeck coefficient current nano-ferrites under study are classified as P-type semiconductors. All composition of Ni-Zn-Cu nano-ferrites are useful in Semi condutor industry. Electrical conductivity of Ni-Zn –Cu nano-ferrites have been studied by two probe method.The electrical conduction in these nano-ferrites is explained on the basis of hopping mechanism. The activation energy in the ferrimagnetic region is in general less than that in paramagnetic region.

KEYWORDS: Nano-ferrites; XRD; UV Spectroscopy; Thermo Electric Power; Electrical Conductivity;

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I. INTRODUCTION

The magnetic behavior of materials can be classified into different types given by día, para, ferro, ferric and anti-ferromagnetic materials. Among these ferrites magnetic properties of extraordinary range are exhibited by huge class of oxides. The magnetic lines of force in a ferromagnetic material aredue to the applied magnetic field. In these materialsmagnetic susceptibility is large, positive and decreases with increase in temperature as per Curie-Weiss law.Ferromagnetism is supported by electron spin and the material acts as a powerful magnet. They are widely used in industry and devices like electric motors,generators, transformers, telephone, loudspeakers, magnetic stripe in credit cards. The mainadvantage of ferrites is its compositional variability of very high degree. Nano-particleferrites play significant role in view of their extensive applications. Their physical and chemical properties remarkably differ from their bulk counterparts making them highly potential for different technical applications.Grain boundaries control their transport properties instead of grain itself[1]. Different chemical methods can be used to obtain high level molecular mixing, chemical homogeneity etc. while synthesizing spinel ferrites[2-5]. Synthesis of Nickel-Copper -Zinc ferrites using ceramic, refluxing, combustion, hydrothermal, reverse micelle,co-precipitation, micro emulsion, ball milling and spark plasma sinteringmethods were already reported[6-13].

The present work reports some of the results obtained related to synthesized Ni-Cu-Zn ferrites such as XRD analysis, UV spectroscopy, Temperature dependence of electricalconductivity,Thermo Electric Power andMagnetic properties.

II. EXPERIMENTAL TECHNIQUES

Cu substituted Ni-Zn ferritesof chemical formulation $Ni_{0.2}Cu_xZn_{0.8-x}Fe_2O_4$were synthesized by Citrate-Gel Auto CombustionFigure1.Stiochiometric amounts of metal nitrates ofnickel, copper, ferric and zincof 99% purityare dissolved in distilled water and later mixed with citric acid in 1:1ratio.This mixture after stirring was heated to 80^{o}Cand by adding ammonia the solutions pH value was set to 7 to form a sol. The resulting solution was made to form a viscous gel on stirring and heating between 180^{O}C-200 ^{0}Cto result in ferrite powder. This ferrite powder was grinded using Agate Mortar and calcinated for four hours at 500^{0}C.This powder was mixed with 10%

polyvinyl alcohol (PVA) and pressed to form pellets by applying pressure of 10-ton cm^{-2}. The pellets were finally sintered and coated with silver paste to provide electrical contact.

Bruker D8 X-Ray Diffractometer was used to analyzethe structure and phase nature of the sintered nano-particles. XRD patternsindicated strongest reflection by peak 311for all samples. Debye-Scherrer'sformula was used to calculate the crystalline size from HWFMof reflection peak 311 for all samples[14] while the experimental density was derived from Archimedes principle in xylene media.Reflection and absorption in uv region were given by UV-DRS spectroscopy. During absorption energy is absorbed by the molecules of electron in uv or visible form of light and this electron gets excited to higher orbit [15]. The band gap energy was calculated by using the formula

$E=\frac{\hbar c}{\lambda}$ (or)$E=\frac{1240}{\lambda}$

The seebeckcoefficient (S) is derived using the formula [16]

$$S=\frac{\Delta E}{\Delta T}\ (\mu V/K)(1)$$

where the thermo emf is denoted by ΔE and ΔT denote the differenceof temperaturebetween pellets surfaces.

Activation energies are derived from slopes of plot between temperature and electrical conductivity usingArrhenious relation

$\rho=\rho 0e^{-Eg/kT}(2)$

where Eg is activation energy, k the Boltzmann constant.

Ms and Hc are related through Brown's equation [17]

$Hc=\frac{2K1}{\mu o\ Ms}(3)$

in which Hcis inversely proportional to Msand correlates with our experimental results.

III. RESUITS AND DISCUSSION

3.1.XRD analysis

XRD patterns of the prepared Cu substituted Ni-Zn ferrite sample was displayed in Figure2**.**Thesepatterns confirm single phase cubic spinel structure for (111),(220),(311), (222),(400),(422), (511) and (440) planes which matches with standard pattern JCPDS file number-48-0489.

Table 1. displays lattice parameter, crystallite size, volume andx-ray density of all samples.It is clear from Table1 that the crystallite size rangesbetween14.7 nm to 34.5nm. This decrease in the crystallite size is due to ionic radious of $Cu^{+2}(0.73A^{o})$ being smaller than that of $Zn^{+2}(0.74A^{o})$. Lattice parameters decrease with increased Cu concentration obeying Vegard's law [18]. X-ray density was observed to increase with increased Cu concentration since x-ray density depends on the molecular weight and lattice parameter of the sample. Volume of the unit cell also decreased since it depends on lattice parameter. It is also observed that experimental density less than X-ray density of the sample. The experimental density and lattice parameters of the preparedsample with Cu substituted compositions were shown in Figure3

3.2.Optical Studies

Optical studies related to prepared nano-ferrites was performed taking BaSO4 as reference with absorbance verses wavelength by using the technique of UV–DRS.During absorption,molecules of electron absorb energy in the form ofUV or visible light exciting the electron to higher orbit[19].Cu substituted Ni-Zn ferriteshas wave length 499 nm and it is a visible region.

Awavelength of 499nm was observed for particles under study in Figure 4.Increase in Cu concentration decreases wavelength and the absorption edge shifts from 499nm to 485 nm. In case of Cu substitutedNi-Zn ferrite for composition x=0.2 blue shiftis observed which may be due to increase in particle size leading to expansion of band gap [20].The Synthesized samples Band gap energy calculated from following questionB.E=1240/λ[21].The calculated band gapenergy of pure $Ni_{0.2}Zn_{0.8}\ Fe_2O_4$ was 2.48ev.The band gap energy is increased with increasing of dopant concentration of Cu,i.e 2.48 to2.55ev,it could be due to partial size, method of synthesis and lattice parameters of the samples. The observed values of cut off wave length and band gap energy were tabulated in Table 2

3.3.High Temperature Thermo ElectricPower

The values of Seebeck Coefficient have been given Table 3. It can be seen from the table that the values of Seebeck Coefficients are positive. Depending on the sign of Seebeck coefficient current nano-ferrites under study are classified as P-type semiconductors. All composition of Ni-Zn-Cu nano-ferrites are useful in Semi conductor industry.

Thermoelectrical power for current samples has been obtained using differential method between $200^{0}C$ -600 ^{0}C.In view of higher stability, the thermo emf for all samples is carried out in cooling cycle.Seebeck coefficients for these these nano-

ferrites are derived from observed thermo e.m.fvalues and are tabulated in Table3.

Table 3 indicate that seebeckcoefficients for all samples are positive indicating majority of charge carriers to be holes. The existence of Ni on B-sites favorconduction mechanism

$$Ni^{2+} + Fe^{3+} \rightarrow Ni^{3+} + Fe^{2+}$$

This is due to copper ions occupying B-sites and transferring Fe^{3+} ions to A-site thereby decreasing Fe^{3+} ions in B-site with increasing Cu concentration.

Seebeck coefficient (S) for cubic spinal systemis given by

S= Total number of Fe^{3+} ions on B-sites/ Total number of Fe^{2+} ions on B-sites

Increase in Cuconcentration decreases the number of Fe^{2+} ions on B-sites increasing the seebeck coefficient in Ni-Zn ferrites as per the definition of S above.The variation of Seebeck Coefficient(S) with temperature for all samples was shown in Figure5 which indicated positive value between lowto high temperature but for pure Ni-Zn ferrite it is negative to positive with increasing temperature. Swas positive value for all ferrite samples under study. These samples exhibit the characteristics of p type semiconductor in high temperature region excepting pure Ni-Zn ferrites. Pure samples at low temperatures behave like n-type semiconductor. With increase in temperature,itbehaves like p-type semiconductor due to predominant conduction mechanism.Figure5. indicate measurements of thermo electric power carried out between 200^0C-600^oCusing differential method. Thermoelectric power exhibits a clear transition at Curie temperaturejust like magnetic properties. Minimum value of seebeck coefficient at Tc indicate the influence of magnetic ordering on thermoelectric power of current samples under investigation[22]

3.4.High Temperature Electrical conductivity

The electrical conductivity of the prepared nano-ferrite samplesfrom under room temperature to 530^OC was reported.It reduces with enhanced temperature for every sampleindicating semiconducting nature.Figure6 shows the plot of Log (σT)vs 1000/Tindicating a curve from which samples thermal activation energy can be derived from slope. As per the plot electrical conductivity of Cu substituted Ni-Zn nano ferrites show discontinuity having two different regions with variation in activation energies resulting in paramagnetic and ferrimagnetic regions. As per magnetic semiconductor theory, ferrimagnetic and paramagneticrepresent ordered
and disordered regions[23]. Hence extra energy is required for conduction in paramagnetic region than ferrimagnetic region. Hence, the activation energy in the paramagnetic region (EP) is found greater than the ferrimagnetic region (EF). Similar results were reported by others in Zn-Ni ferrites [24]. The activation energy values in the paramagnetic region and ferromagnetic region with Curie temperature values are tabulated in Table4

IV. CONCLUSIONS:

XRD pattern for investigative samples confirmed single phase cubic spinal structure.

Doping copper in Ni-Zn ferrite system decrease lattice parameter and increase x-ray density.

Crystallite size of the sample ranges between14.7nm -34.5 nm.

Optical studies by UV–DRS decrease in wavelength with increase in Cu concentration. The absorption edge shifts from 499nm to 485 nm.

Thermo electric power measurements are taken up in the range of 200^0C-600^oC using differential method.

Seeback coefficient attained positive value for all ferrite samples under study. This indicated p-type semiconducting nature in high temperature region for prepared samples with exception of pure Ni-Zn ferrites.

Depending on the sign of Seebeck coefficient current nano-ferrites under study are classified as P-type semiconductors. All composition of Ni-Zn-Cu nano-ferrites are useful in Semi condutor industry.

Electrical conductivity of the prepared sample between room temperature to530^OC clearly indicated decrease in electrical conductivity with increase in temperature for all samples indicating semiconducting nature of the prepared ferrite samples resulting to para and ferrimagnetic regions.

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Figure 1. Flow Chart for Citrate gel auto combustion method

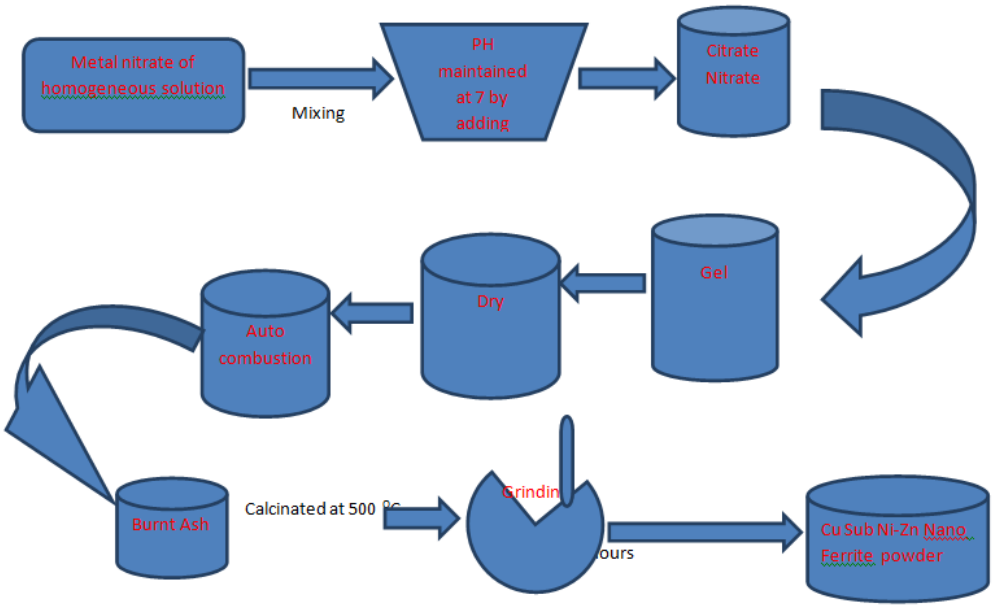
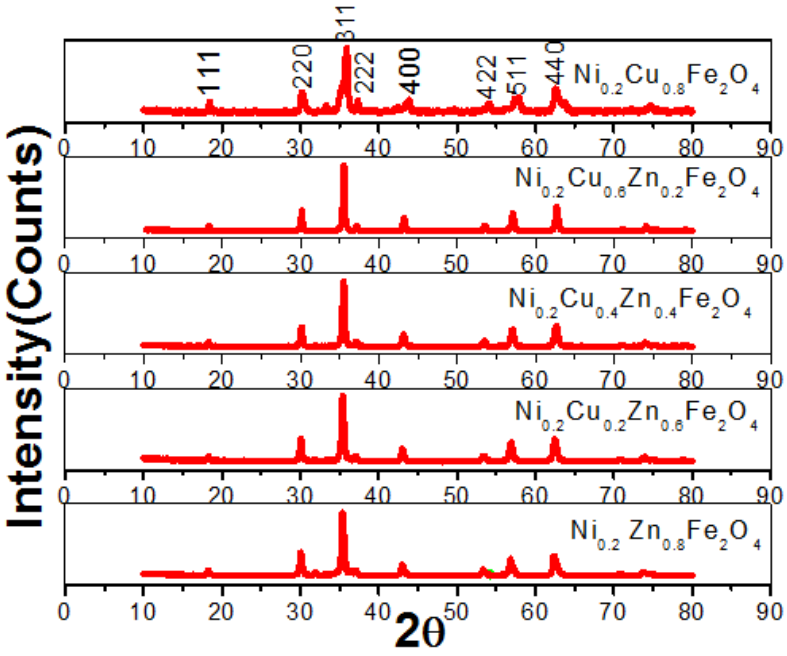


Figure 2.XRD Pattern of Cu Substituted Ni-Zn nano-ferrites



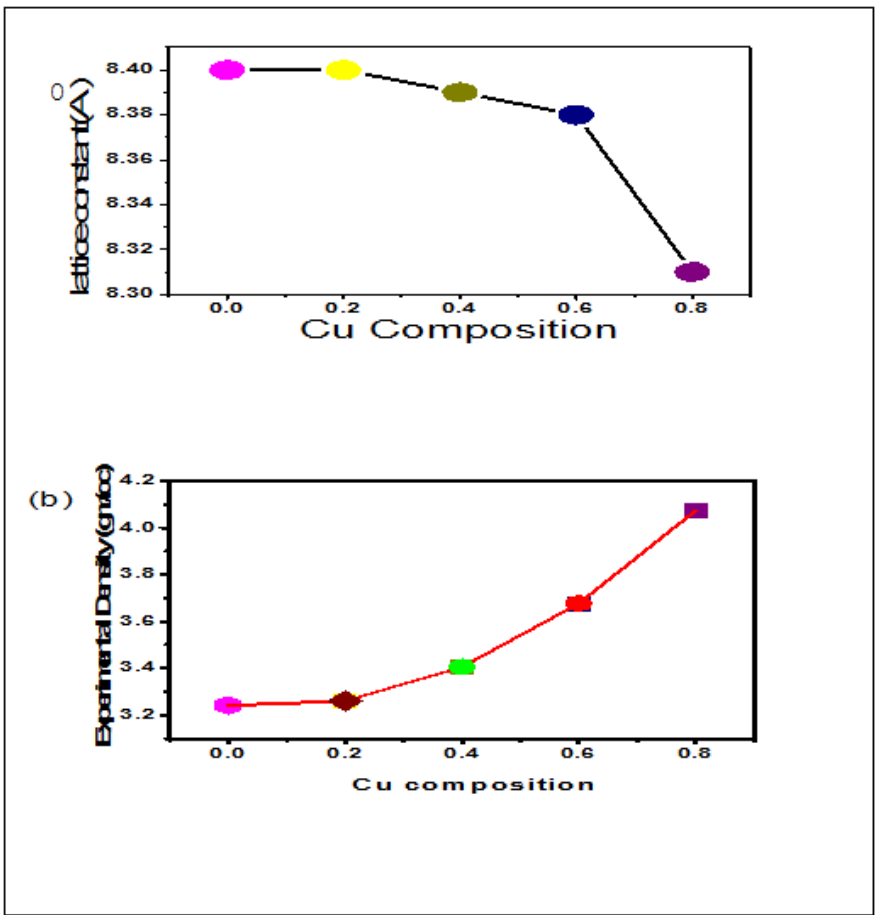


Figure 3. Variation of (a)Lattice parameter and (b)Experimental density with composition of Ni0.2CuxZn0.8-xFe2O4 nano ferrites.

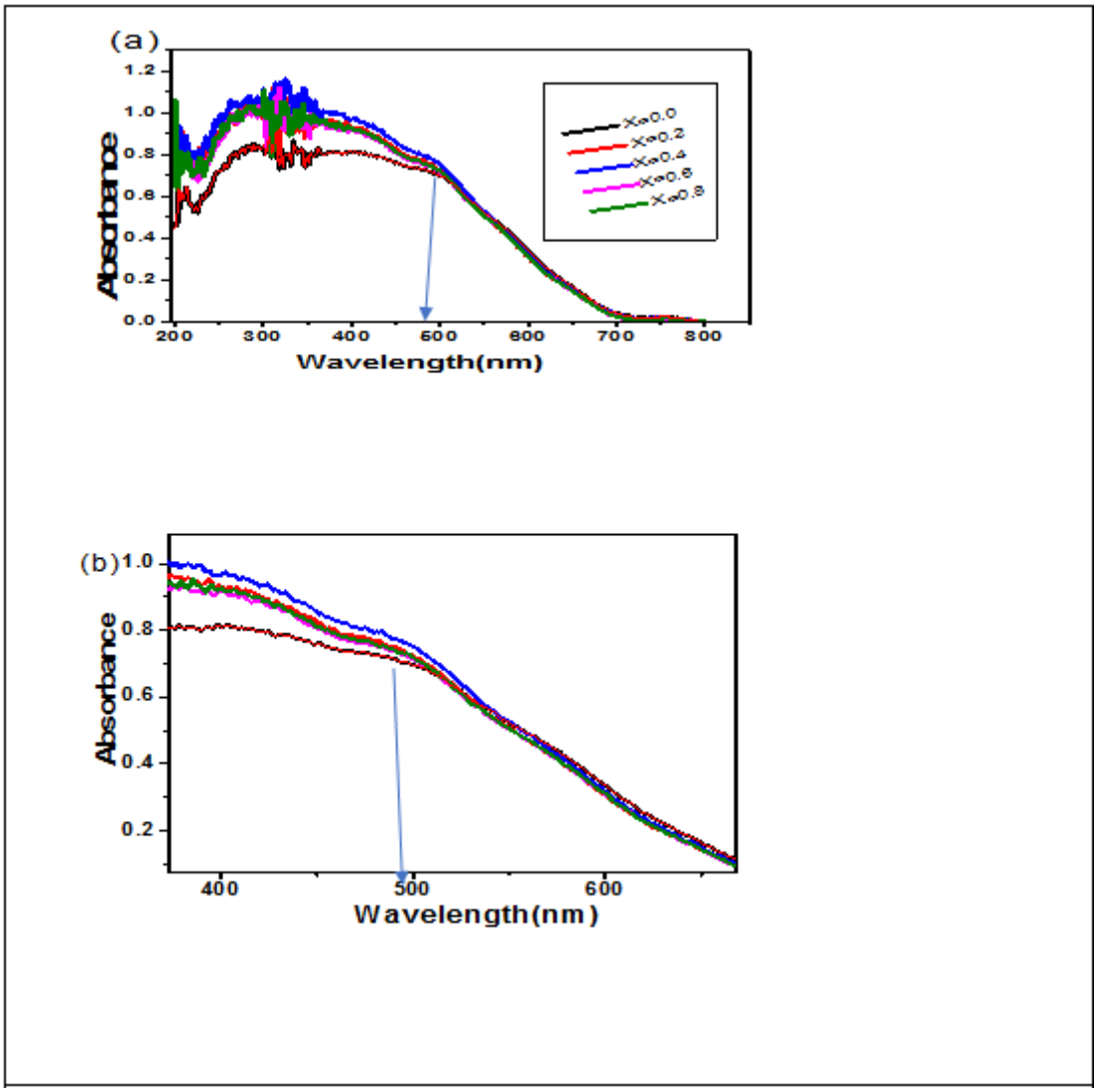
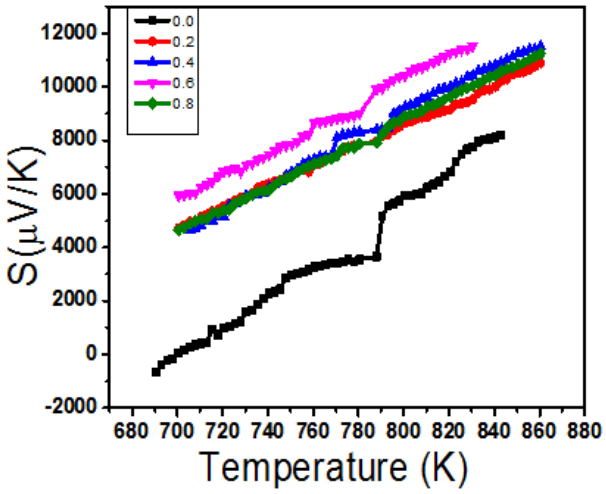
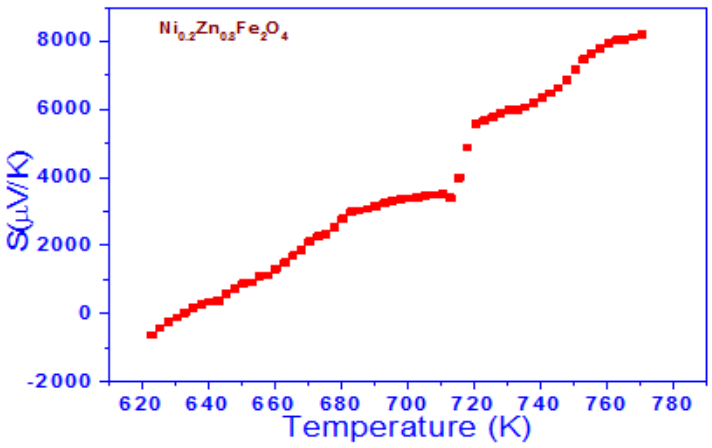
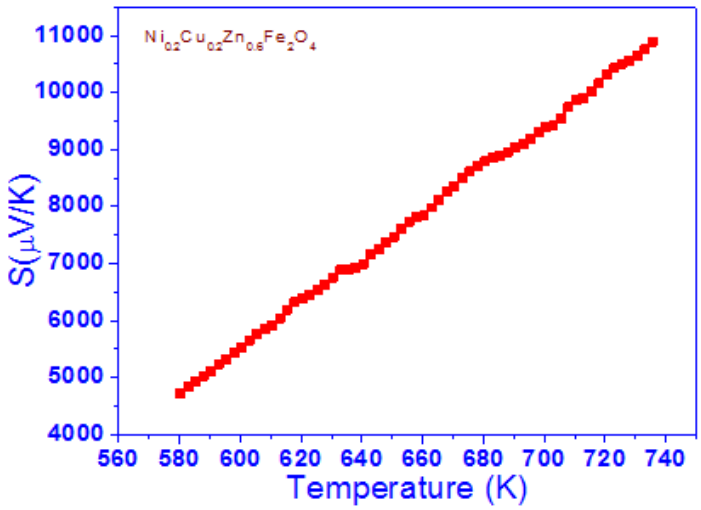


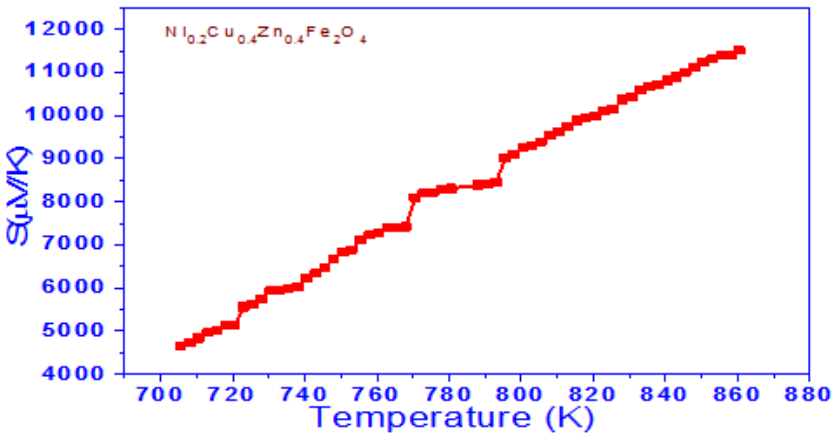
Figure 4(a-b). UV–visible spectra of nano-crystalline $Ni_{0.2}Cu_xZn_{0.8-x}Fe_2O_4$

Figure 5. Dependence of Seebeck Coefficient on Temperature forCu substituted Ni-Zn nanoferrites




$Ni_{0.2}Zn_{0.8}Fe_2O_4$
S(μV/K)
Temperature (K)


$Ni_{0.2}Cu_{0.2}Zn_{0.6}Fe_2O_4$
S(μV/K)
Temperature (K)


$Ni_{0.2}Cu_{0.4}Zn_{0.4}Fe_2O_4$
S(μV/K)
Temperature (K)

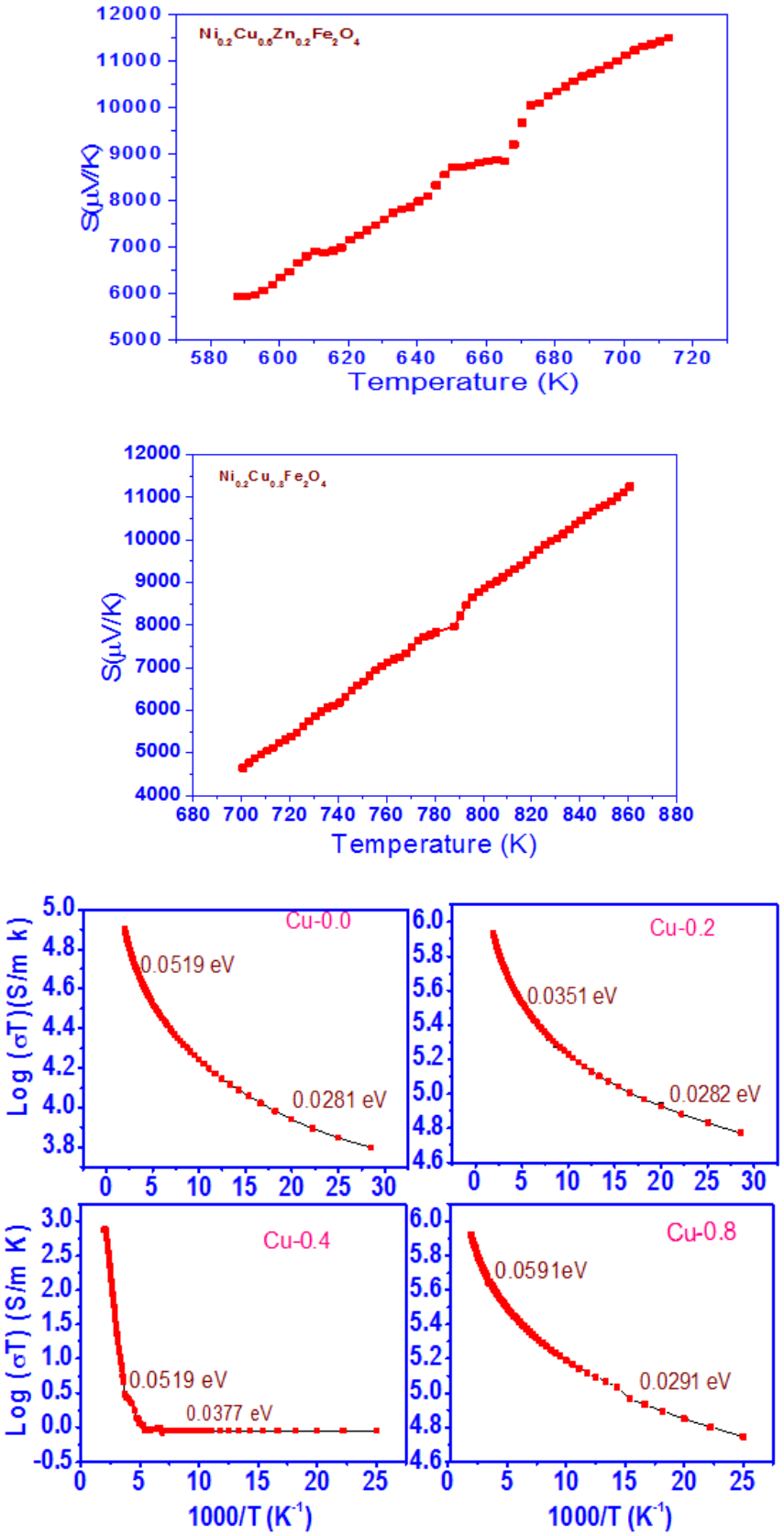


Figure 6 Temperature variation of Electrical conductivity of $Ni_{0.2}Cu_xZn_{0.8-x}Fe_2O_4$ nano ferrites.

Table1. Structural parameters of the prepared Cu substituted Ni-Zn nano ferrite sample

S.no	Composition	Mol.Wt(gm/mol)	Crystallite size(nm)	Lattice constant (A^o)	X-ray density(d_x) (gm/cc)	Volume $(A^o)^3$	Ex. density(d_e) (gm/cc)
1	$Ni_{0.2}Zn_{0.8}Fe_2O_4$	239.73	22.7	8.40	5.35	594.2	3.2
2	$Ni_{0.2}Cu_{0.2}Zn_{0.6}Fe_2O_4$	239.36	25.2	8.40	5.36	594.07	3.3
3	$Ni_{0.2}Cu_{0.4}Zn_{0.4}Fe_2O_4$	239	24.1	8.39	5.38	589.8	3.4
4	$Ni_{0.2}Cu_{0.6}Zn_{0.2}Fe_2O_4$	238.63	34.5	8.38	5.39	588.2	3.6
5	$Ni_{0.2}Cu_{0.8}Fe_2O_4$	238.26	14.7	8.31	5.50	574.5	4.1

Table 2.$Ni_{0.2}Cu_x\ Zn_{0.8-x}\ Fe_2O_4$ nano ferrites Cut off wave length with Band gap energy

Composition	Cut off wave length	Band gap energy
$Ni_{0.2}Zn_{0.8}\ Fe_2O_4$	499	2.484
$Ni_{0.2}Cu_{0.2}Zn_{0.6}Fe_2O_4$	485	2.556
$Ni_{0.2}Cu_{0.4}Zn_{0.4}Fe_2O_4$	489	2.535
$Ni_{0.2}Cu_{0.6}Zn_{0.2}Fe_2O_4$	487	2.546
$Ni_{0.2}Cu_{0.8}Fe_2O_4$	486	2.551

Table 3. Seebeck Coefficient and Curie temperature of $Ni_{0.2}Cu_xZn_{0.8-x}Fe_2O_4$

S.no	Composition	Curie Temperature (K)	Seebeck Coefficient (s)($\mu V/K$)at 730K
1	$Ni_{0.2}Zn_{0.8}Fe_2O_4$	789	+1600
2	$Ni_{0.2}Cu_{0.2}Zn_{0.6}Fe_2O_4$	780	+ 5910
3	$Ni_{0.2}Cu_{0.4}Zn_{0.4}Fe_2O_4$	765	+ 5930
4	$Ni_{0.2}Cu_{0.6}Zn_{0.2}Fe_2O_4$	779	+ 7070
5	$Ni_{0.2}Cu_{0.8}Fe_2O_4$	781	+ 5830

Table4. Activation energies of $Ni_{0.2}Cu_xZn_{0.8-x}Fe_2O_4$nano-ferrites with Curie Temperatures

S.No	composition	Curie Temp (^oC)	Para Region (E_P) eV	Ferri Region (E_F) eV
1	$Ni_{0.2}Zn_{0.8}Fe_2O_4$	516	0.052	0.028
2	$Ni_{0.2}Cu_{0.2}Zn_{0.6}Fe_2O_4$	507	0.035	0.028
3	$Ni_{0.2}Cu_{0.4}Zn_{0.4}Fe_2O_4$	492	0.052	0.038
4	$Ni_{0.2}Cu_{0.8}Fe_2O_4$	508	0.059	0.029