

Structural Properties and Electrical Conductivity of Copper Substituted Nickel Nano Ferrites

K. Vijaya Kumar, Rapolu Sridhar, D. Ravinder, and K. Rama Krishna

Abstract—A series of copper substituted nickel nano ferrites with the compositional formula $Ni_{1-x}Cu_xFe_2O_4$ ($X=0, 0.2, 0.4, 0.5, 0.6, 0.8$ and 1.0) were prepared by the Citrate gel auto combustion technique and sintered at $700^\circ C$ for 5 hr. The X-ray diffractograms (XRD) clearly exhibited the existence of single phase cubic spinel structure. The crystallite size was found in the range of 36-58nm. With the increment of Cu content the X-ray density and porosity were found to increase where as the bulk density was found to decrease. The DC electrical properties were carried out by two-probe method from room temperature to well beyond the Curie temperature. DC electrical resistivity decreases with increase of temperature ensuring the semiconducting nature of the ferrites. The DC electrical conductivity found to increase with increase of Cu content and reaches maximum at $X=1.0$ at which the activation energy for conduction becomes minimum. The activation energy in the ferrimagnetic region is in general lesser than that in the paramagnetic region. The activation energy was found to decrease with the increase of Cu content. The Curie temperature determined from DC electrical properties was found in satisfactory agreement with that determined from Loria technique. The DC electrical resistivity results are discussed in terms of hopping model.

Index Terms—Ni–Cu nano ferrite, x-ray density, bulk density, porosity, DC electrical properties.

I. INTRODUCTION

Spinel ferrites have been studied extensively due to easy to synthesis and abundant uses in technological and industrial applications [1]-[3]. The useful properties of the spinel ferrites mostly depend upon the chemical composition, preparation methods, sintering temperature, nature of the additives and their distribution i.e. tendency to occupy tetrahedral (A) or octahedral (B) site [4]. Ni^{2+} has a strong preference octahedral site (B-site) for the electrical conductivity [5]. Cu^{2+} is the divalent ions which occupy essentially tetrahedral A-site depending on the sample preparation [6] when substituted in ferrites.

Among the spinel structures, nickel ferrite have been widely used in different kinds of magnetic devices, such as

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inductors, magnetic heads, and magnetic devices, such as inductors, magnetic heads, magnetic refrigeration and magnetic resonance imaging. Thus, the magnetic and electric properties of nickel ferrite have been researched and improved. Cu-containing ferrites form an interesting group of ferrites because of their typical electrical and magnetic properties and change in crystal structure on thermal treatment [7].

Ni-Cu ferrites are low cost materials and have important magnetic and electrical properties for technological applications. The electrical conductivity of spinel ferrites is of prime importance as it gives valuable information about the conduction mechanism [8]. Therefore a systematic study of the electrical conductivity of the mixed Ni-Cu ferrite system from room temperature to well beyond Curie temperature was undertaken. The results of such a study presented in this communication are explained on the basis of the hopping model.

II. EXPERIMENTAL DETAILS

Nano ferrite samples with the chemical formula $Ni_{1-x}Cu_xFe_2O_4$ ($X= 0.0, 0.2, 0.4, 0.5, 0.6, 0.8,$ and 1.0) were synthesized by using citrate gel auto combustion technique. The molar quantity of AR grade of Nickel Nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), Copper Nitrate ($Cu(NO_3)_2 \cdot 3H_2O$), Ferric Nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), Citric Acid-Citrate ($C_6H_8O_7 \cdot H_2O$) and Ammonia (NH_3) raw materials were taken as starting material. Metal nitrates and citric acid were dissolved in deionized water. Metal nitrate solutions were mixed with citric acid solution in 1:3 molar ratio of nitrate to citric acid. The p^H value of the solution was adjusted to 7 using ammonia. The solution was first heated at $80^\circ C$ to transform into gel and then ignited in a self-propagating combustion manner to form a fluffy loose powder. The as-burnt ferrite powders were grained by agate motor then calcined at $700^\circ C$ for 5hr. the calcined ferrite powders were again grained by agate motor. As this method is a chemical route it requires no ball milling hence little scope of contamination, and better homogeneity. The sintered powders were mixed with 2% of PVA as a binder and uniaxially pressed at a pressure of about $3-5 \text{ tons cm}^{-2}$ to form pellets of 10 mm diameter and 2–3 mm thickness. These pellets were finally sintered at $1050^\circ C$ for 12 h in a programmable furnace to remove the organic binder.

The structural characterization was carried out using X-Ray Diffractometer Bruker (Karlsruhe, Germany) D8 advanced system with a diffracted beam monochromatic K_α radiation ($\lambda = 1.5405 \text{ \AA}$) radiation source between the Bragg Angles 20° to 80° in steps of $0.04^\circ/\text{Sec}$. The bulk density ρ_m , X-ray density ρ_x and porosity P as function of Cu

concentrations were estimated as follows. The bulk density, ρ_m was determined using formula

$$\rho_m = \frac{m}{\pi r^2 h}$$

where m is the mass, r the radius and h the height of the sample. The X-ray density ρ_x of the prepared samples was calculated by the relation

$$\rho_x = \frac{8M}{Na^3}$$

where M is the molecular weight of the samples, N is the Avogadro's number and a is the lattice constant. Each cell has 8 formula units.

The porosity P of the ferrite nanoparticles was then determined using the relation [9]

$$P = 1 - \frac{\rho_m}{\rho_x}$$

where ρ_m and ρ_x are the bulk and X-ray densities, respectively.

The DC electrical properties were carried out as a function of composition and temperature by the two probe method [10] from room temperature to well beyond the Curie temperature.

The relationship between resistivity and temperature may be expressed as [11]

$$\rho = \rho_{oe} \Delta E / k_B T$$

where ρ is the dc electrical resistivity at temperature T , K_B the Boltzmann constant and ΔE the activation energy corresponding to the electrical process.

TABLE I: PARTICLE SIZE, X-RAY DENSITY, BULK DENSITY AND POROSITY WITH COMPOSITION OF MIXED NI-CU NANO FERRITES

Composition (x)	Particle Size (nm)	X-ray density (gm/cm ³)	Bulk density (gm/cm ³)	Porosity (%)
0	58.91	5.356	5.07	5.339
0.2	46.3	5.396	4.976	7.782
0.4	49.2	5.429	4.943	8.952
0.5	37.3	5.452	4.937	9.446
0.6	36.9	5.48	4.892	10.730
0.8	43.33	5.543	4.862	12.286
1	36.7	5.669	4.844	14.553

III. RESULTS AND DISCUSSION

A. X-Ray Analysis

The X-ray diffraction patterns for $Ni_{1-x}Cu_xFe_2O_4$ ($0 \leq X \leq 1$) was sintered at 700°C are shown in Fig. 1. The X-ray patterns show all sample are existence of the single phase of cubic spinel structure [12] with the reflection the samples planes (111), (220), (311), (400), (511) and (440). It can be seen from the table I the values of the particle size varies from 36.7 nm to 58.91 nm. Though all the samples were prepared

under identical condition, the crystallite size was not the same for all Cu concentrations. This was probably due to the preparation condition followed here which gave rise to different rate of ferrite formation for different concentrations of Cu, favoring the variation of crystallite size. Fig. 2 indicate that the X-ray density (D_x) increases from 5.356 gm/cm³ to 5.669 gm/cm³ and bulk density (D) decreases from 5.07 gm/cm³ to 4.844 gm/cm³ with the increase in Cu ion content, this can be attributed to the atomic weight and density of Copper (63.546, 8.96 gm/cm³) which are higher than those of nickel (53.933, 8.91 gm/cm³), the oxygen ions which diffuse through the material during sintering also accelerate the densification of the material. The X-ray density is higher than the apparent value due to the existence of pores which depends on the sintering condition. Fig. 3 indicates that the porosity increases by Cu content increase which reflects the similar behavior of X-ray density, it is due to the larger ionic radius of Cu (0.73 Å) compared to Ni (0.69 Å).

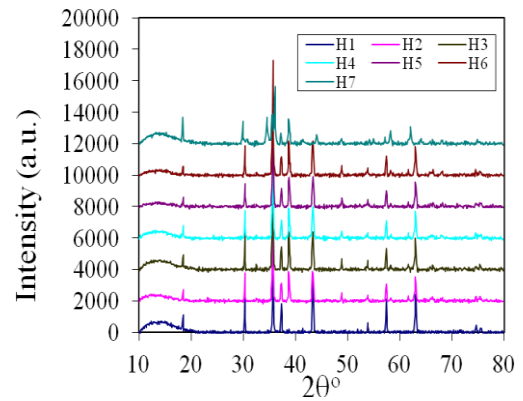


Fig. 1. X-ray diffraction pattern of $Ni_{1-x}Cu_xFe_2O_4$ ferrites (where $X=0$:H1, 0.2:H2, 0.4:H3, 0.5:H4, 0.6:H5, 0.8:H6 and 1.0:H7).

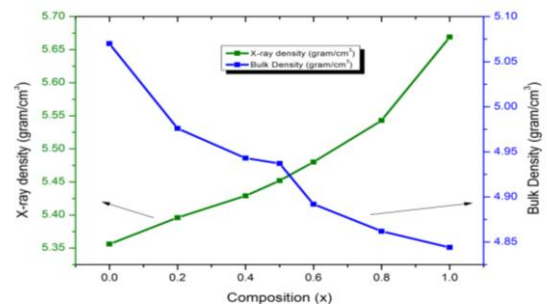


Fig. 2. Variation of X-ray density and Bulk Density with Cu concentration.

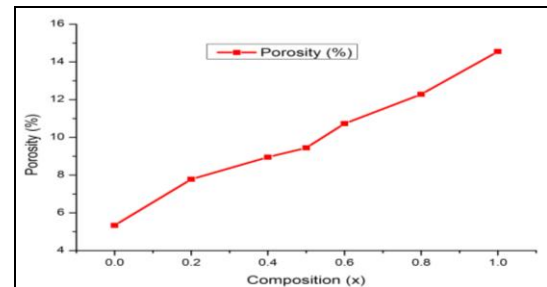


Fig. 3. Variation of Porosity with Cu concentration electrical properties.

B. Temperature-Dependant of DC Resistivity

The temperature-dependant of dc resistivity was measured as a function of temperature for all samples from room temperature to well beyond Curie temperature, which is

described in Fig. 4 follows Arrhenius plot. It showed that the resistivity of the prepared Ni-Cu nano ferrite materials decreased with increasing temperature for each sample. This proved the semiconductor nature of synthesized samples [13].

From Fig. 4 the change of slope is attributed to change in conductivity mechanism. The conduction at a lower temperature (below curie temperature) is due to hopping of electrons [14] between Fe^{2+} and Fe^{3+} ions, whereas at a higher temperature (above curie temperature) due to hopping of polarons [15]-[17].

TABLE II: ELECTRICAL PROPERTIES WITH COMPOSITION OF MIXED NI-CU NANO FERRITES

Sl. No	Composition (x)	Para Region (E_p) eV	Ferro Region (E_f) eV	Activation Energy (ΔE) eV	Conductivity (σ) ($\Omega^{-1}\text{-cm}^{-1}$) (Room Temp)
1	0	0.698	0.369	0.329	8.04×10^{-05}
2	0.2	0.717	0.402	0.315	5.28×10^{-04}
3	0.4	0.75	0.454	0.296	6.38×10^{-04}
4	0.5	0.788	0.502	0.286	6.74×10^{-04}
5	0.6	0.836	0.566	0.27	8.08×10^{-04}
6	0.8	0.859	0.609	0.25	2.02×10^{-03}
7	1	0.954	0.731	0.223	4.71×10^{-03}

C. Composition Dependence of DC Electrical Conductivity

DC electrical conductivity of the Ni-Cu system was found to increase from $8.04 \times 10^{-05} (\Omega\text{-cm})$ to $4.71 \times 10^{-03} (\Omega\text{-cm})$ at room temperature with the increase in Cu concentration from 0.0 to 1.0 as given in Table II. This increase in conductivity is due to the fact that Cu has smaller value of resistivity ($1.7 \times 10^{-6} \Omega\text{-cm}$) as compared to that of Ni ($7.0 \times 10^{-6} \Omega\text{-cm}$) [18]. The increase in conductivity may be due to the hopping of electrons between $Fe^{2+} \leftrightarrow Fe^{3+}$ on tetrahedral sites that increases the conduction as Cu is added, which are produced during sintering [13]. The decrease in resistivity may also be due to $Cu^{2+} \rightarrow Cu^+$ transition with the variation of Cu content in Ni-Cu ferrite [19].

D. Composition Dependence of Activation Energy (ΔE)

The activation energies in the ferrimagnetic and paramagnetic regions are calculated from the slopes of plots of $\ln(\rho T)$ versus $10^3/T$ and presented in Table II. The activation energy in the paramagnetic region is higher than that in the ferrimagnetic region. The activation energies of prepared samples as determined by the difference between the activation energies in the paramagnetic and ferrimagnetic regions (ΔE) which is given in column (5) of Table II. The Fig. 6 shows the variation the activation energy in the paramagnetic region, ferrimagnetic region. The value of activation energy of samples decreased from 0.329eV to 0.223eV as the Cu concentration is increased from 0.0 to 1.0. High activation energy goes hand in hand with a low conductivity of the ferrites. Similar result was observed by samokhrlov and rustmov [20]. The decrease in activation energy may be attributed to the creation of small number of oxygen vacancies [13]. It may also be justified due to the

decrease in resistivity with the increase in Cu concentration because activation energy behaves in the similar way as that of dc electrical resistivity as reported by others [13], [21]. The decreasing trend of activation energy with the increase in Cu concentration may also be due to dominant role of Cu in conductivity.

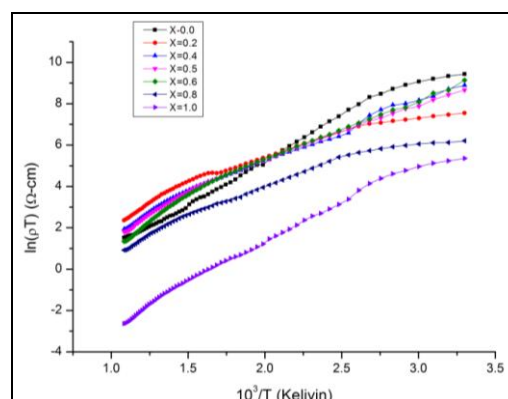


Fig. 4. Variation of DC resistivity with inverse temperature.

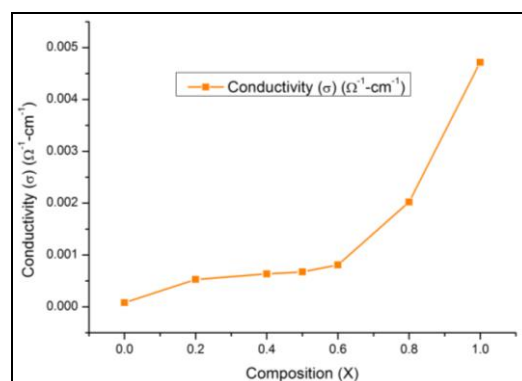


Fig. 5. Variation of electrical conductivity with Cu concentration.

TABLE III: CURIE TEMPERATURES OF MIXED NI-CU NANO FERRITES

Sl. No.	Composition (x)	dc resistivity	Loria technique
			Curie temperature (T_c) (Kelvin)
1	0	812.08	808
2	0.2	738.22	736
3	0.4	730.19	726
4	0.5	688.42	686
5	0.6	676.59	674
6	0.8	665.42	668
7	1	646.20	648

E. Composition Dependence of Curie Temperature

From the plots of $\ln(\rho T)$ with reciprocal of temperature as shown in Fig. 4, at particular temperature indicating that sample changing from ferrimagnetism to paramagnetism, this temperature is known as Curie temperature. The Curie temperatures of the samples are presented in the Table III. It is clear the Curie temperature decreases from 812.08 K to 646.20 K as Cu^{2+} composition increasing from $X = 0.0$ to 1.0. These values are good agreement with Curie temperature determined by Loria technique. The Fig.7 Shows that the variation of Curie temperature with composition in dc resistivity and Loria technique.

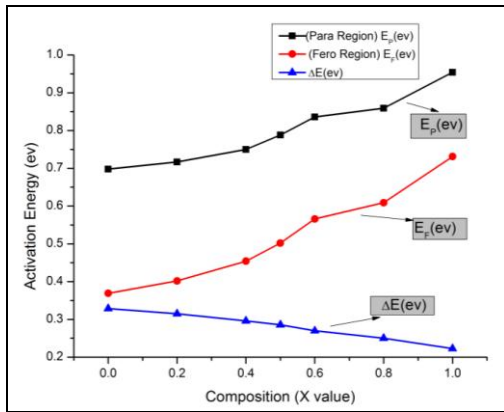


Fig. 6. Variation of para region(E_p), ferro region(E_f) and activation energy (ΔE) with Cu concentration.

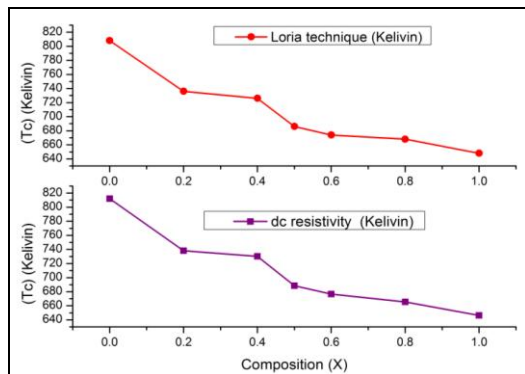


Fig. 7. Variation of curie temperature with Cu concentration.

IV. CONCLUSION

The substitution of Cu in the $Ni_{1-x}Cu_xFe_2O_4$ ferrites causes appreciable changes in its structural and electrical properties. All samples have existence of single phase cubic spinel structure with the increase of x-ray density and porosity whereas decrease of bulk density, conductivity and activation energy with increasing Cu contents. DC electrical resistivity decreases with the increase in temperature which confirms the semiconductor like behavior of the sintered materials. The activation energy in the ferrimagnetic region is in general less than that in the paramagnetic region. The Curie temperature determined from DC electrical properties was found in satisfactory agreement with that determined from Loria technique.

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