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Influence of Cu^{2+} ion on Electrical and Dielectric Properties of Ni-Zn Spinel Ferrite

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ABSTRACT

Nanocrystalline spinel ferrites with the general formula $Ni_{0.65-x}Cu_xZn_{0.35}Fe_2O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) were prepared by sol-gel auto-combustion method. Single phase cubic spinel structure of given ferrite were confirmed by X-ray diffraction techniques. Lattice constant was found to be increases by increasing Cu^{2+} ion concentration. This increasing lattice constant can be observed due to large ionic radii of Cu^{2+}(0.72Å) ions as compared to ionic radii of Ni^{+2}(0.69Å) ions. Particle size increases from 34.23nm to 69.21nm by increasing Cu^{2+} concentration. Resistivity and transport properties such as dielectric constant, dielectric loss and loss tangent were measured as function of varying frequency and composition. From this study, it could be observed that the AC resistivity, dielectric constant, dielectric loss and loss tangent decreases with increasing frequency and Cu^{2+} ion concentration. These variations can be explained through the Maxwell-Wagner type interfacial polarization and Fe^{2+}/Fe^{3+} ionic concentration as well as electronic hopping frequency between Fe^{2+} and Fe^{3+} ions in present system.

KEYWORDS: *Nanocrystalline, Ni-Cu-Zn ferrite, X-ray diffraction, resistivity, dielectric properties.*

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I. INTRODUCTION

Nanocrystalline ferrite materials have many applications in making cores of audio frequency and high frequency transformers, chokes, permanent magnets, microwave absorbers, wave guides and chlorine gas sensors, high density information storage, color imaging, bioprocess, medical diagnosis, electromagnetic wave absorption, etc. Multi layer chip indicator (MLCI) has recently been developed as one of the key surface mounting devices [1]. Nanocrystalline Ni-Cu-Zn ferrites are very attractive soft magnetic materials for their high frequency application, high electrical resistivity, low dielectric loss and chemical stability. Due to their reduced sizes, the nanocrystalline materials passes novel and improved properties in comparison to bulk materials, which have been extensively used in electronic devices for high frequency telecommunications [2]. Very fine ferrite particles can be produced by the chemical co-precipitation and sol–gel methods [3–5]. Several researchers have reported the synthesis of Ni-Zn ferrites using different techniques like, ceramic [6], hydrothermal [7], combustion [8], co-precipitation [9], spark plasma sintering [10], micro emulsion [11] and ball milling etc. The size and shape of the ferrite particles are dependent on the synthesis process. Sol-gel autocombustion method is a simple process, which offers a significant saving in time and energy consumption over the traditional methods.

In this paper our aim is to study the variation of ac resistivity and dielectric properties with varying frequency from 100Hz to 5 MHz with influence of Cu^{2+} ion on Ni-Zn ferrite.

II. METHODOLOGY

The Nanocrystalline spinel ferrite system of $Ni_{0.65-x}Cu_xZn_{0.35}Fe_2O_4$ where x= 0.0 to 0.5 were prepared by sol-gel auto-combustion method using metal nitrates and citric acid. Citric acid $C_6H_8O_7$, ferric nitrate $Fe(NO_3)_3.9H_2O$, nickel nitrate $Ni(NO_3)_2.6H_2O$, zinc nitrate $Zn(NO_3)_2.6H_2O$ and copper nitrate $Cu(NO_3)_2.3H_2O$ were used as a raw materials with molar ratio of metal nitrates to citric acid 1:3. All nitrates and citric acid were dissolved in distilled water and stirred continuously. During the constant stirring ammonia solution was added drop wise to adjust PH up to 7. Then the solution was heated at 100°c to transform into gel. The gel burnt in a self propagating combustion manner until all gels were completely burnt to form ashes. The prepared ash powder was ground in a agate mortar and pestle, and then heated in muffle furnace at 500^0c for 5h and cooled slowly to room temperature.

The X-ray diffraction patterns of the ferrite samples were taken in our laborites using desktop Regaku Miniflex II diffractometer with CuKα radiation (λ= 1.54056 Å) in the range of 2θ from 20° to 80°. AC electrical resistivity was measured by using two probe methods. Dielectric constant, dielectric loss factor and loss tangent were measured at room temperature and varying frequency from100Hz to 5MHz using LCRQ meter.

III. RESULTS AND DISCUSSION

3.1 X-ray Diffraction

The X-ray diffraction pattern of $Ni_{0.65-x}Cu_xZn_{0.35}Fe_2O_4$ ferrite for x= 0.0, 0.2 and 0.4 is as shown in figure 1. From figure 1, it can be observed that all the peaks could be indexed with cubic spinel ferrite structure showing that all the

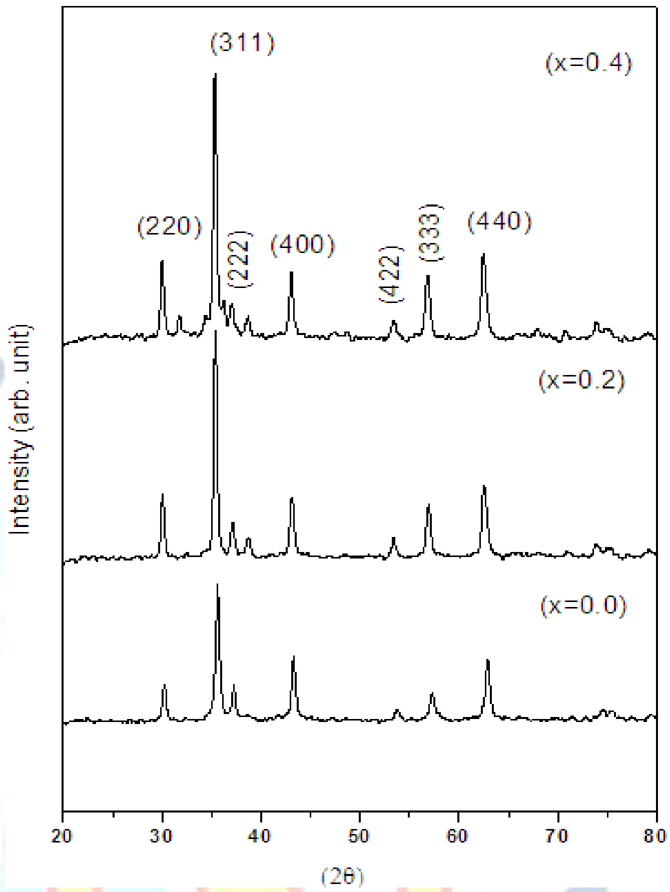

Figure 1 X-ray diffraction pattern for $Ni_{0.65-x}Cu_xZn_{0.35}Fe_2O_4$ ferrite system.

samples were formed in single phase and were well crystalline in nature.

By knowing the values of interplanar distance (d) and Miller indices (h, k, l) lattice constant a calculated by using formula,

$$a = \frac{d}{\sqrt{h^2+k^2+l^2}} \quad ------(1)$$

Lattice constant can be increases by increasing Cu^{2+}ion concentration. This increase in lattice constant is due to increasing ionic radii of Cu^{2+}(0.72Å) as compared to ionic radii of Ni^{+2} (0.69Å). The value of lattice constant is as shown in table 1. From table 1 it can be observed that, the lattice constant increases from a value 8.3412Å to 8.4153 Å linearly by increasing Cu^{2+} ion concentration.

The FWHM of the most intense peak can be used to get average particle size using Scherer's equation [12],

$$t = \frac{0.9\lambda}{\beta \cos\theta} ---------- (2)$$

Where, λ is the wavelength of x-ray radiation (CuKα, 1.54056 Å), β is full width at half of the intensity maximum of plane in radian and t is diameter of crystal particle. The crystallite size of

Table 1 Variation of lattice constant and particle size with composition

Composition (x)	Lattice constant a in(Å)	Particle size t in (nm)
0.0	8.3412	34.23
0.1	8.3752	37.28
0.2	8.3821	45.13
0.3	8.3965	57.44
0.4	8.4045	62.51
0.5	8.4153	69.21

the as-burnt powder estimated from the X-ray diffraction by considering the peak [311]. The particle size increases by increasing Cu^{2+} ion concentration. The obtained value of particle size is as shown in table 1. From table 1 it can be observed that particle size increases from 34.23nm to 69.21nm. This reveals that synthesized powder has nano-sized crystallites.

3.2 A C Resistivity

The frequency dependence of ac resistivity (ρ_{ac}) was calculated by using relation [13],

$$\rho = \frac{A}{2\pi f tan\delta ct} - - - - - - - - - - (3)$$

Where tanδ is the dielectric loss tangent, f is the frequency, C is the capacitance, A and t is the area and thickness of the sintered pellet respectively.

The variation of ac resistivity ($Log\rho_{ac}$) with frequency (Logf) is as shown in figure 2.

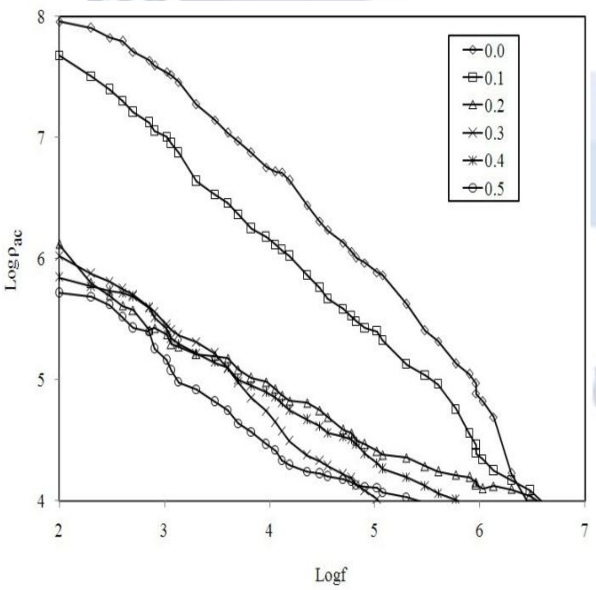

Figure 2 Variation of ac resistivity with frequency for $Ni_{0.65-x}Cu_xZn_{0.35}Fe_2O_4$ ferrite system

From figure 2, it can be observed that the resistivity of all the compositions decreases with the increasing frequency which is the normal behavior of ferrites. At low frequency resistivity is very large and decreases with increasing frequency and acquires minimum value. These decreases in resistivity with Cu^{2+} concentration was due to the increase in grain size of the ferrites. Grain boundaries were highly dislocated areas with trapped imperfections, such as porosity, dislocations etc. The more dispersion is observed at low-frequency side which could be due to the difference in the concentration of Fe^{3+}/Fe^{2+} and other ions in the different samples. This dispersion is due to the presence of large number of Fe^{2+} ions which in favour of the polarization as well as conduction mechanisms.

The conduction mechanism in the ferrites can be explained on the basis of hopping of charge carriers between Fe^{3+} and Fe^{2+} ions on octahedral sites [14]. The increase in frequency of the applied field enhances the hoping of charge carriers resulting in an increase in the conduction process thereby decreasing the resistivity. At high frequency resistivity becomes negligibly small and remains constant because the hopping frequency no longer follows the external applied field and lags behind it. The compositional variation of resistivity at frequency 100Hz is as shown in table 2.

Table 2 Variation of ac resistivity (ρ_{ac}), dielectric constant (ε′), dielectric loss (ε″) and loss tangent (tanδ) for $Ni_{0.65-x}Cu_xZn_{0.35}Fe_2O_4$ system.

Compositions (x)	Ac resistivity (ρ_{ac}) Ω-cm	dielectric constant (ε′)	dielectric loss (ε″)	loss tangent (tanδ)
0.0	9.10×10^7	1.41×10^5	2.67×10^5	1.886
0.1	4.74×10^7	1.38×10^5	1.91×10^6	13.900
0.2	1.32×10^6	3.55×10^5	4.33×10^6	12.195
0.3	1.05×10^6	2.34×10^5	4.33×10^5	1.852
0.4	7.01×10^5	2.85×10^5	8.14×10^5	2.857
0.5	5.24×10^5	2.02×10^5	3.67×10^5	1.818

From table 2 it was observed that, the value of resistivity decreases from 9.10×10^7 to 5.24×10^5Ω-cm with addition of Cu^{2+} ion concentration. These decrease in resistivity with addition of Cu^{2+} ion concentration representing semiconducting behavior of ferrite material.

3.3 Dielectric Properties:

The dielectric constant (ε′) was calculated by using relation,

$$\varepsilon' = \frac{C\,t}{\varepsilon_{0A}} \text{ ------------- }(4)$$

where C is capacitance, t is thickness of the pellet, A is area of the flat surface of the pellet and ε_o is permittivity of free space ($\varepsilon_o = 8.85 \times 10^{-12}$ C^2/Nm^2).

The dielectric loss (ε″) was calculated using the relation,

$$\varepsilon'' = \frac{1}{2\pi.1000.\varepsilon_0}\sigma \text{ ------- }(5)$$

Where σ is the AC conductivity.

The value of loss tangent (tanδ) was calculated using the relation,

$$tan\delta = \frac{\varepsilon''}{\varepsilon'} \text{ ------------ }(6)$$

The variation of dielectric constant (ε′), dielectric loss (ε″) and loss tangent (tanδ) with log frequency is shown in the figure 3, 4 and 5 respectively.

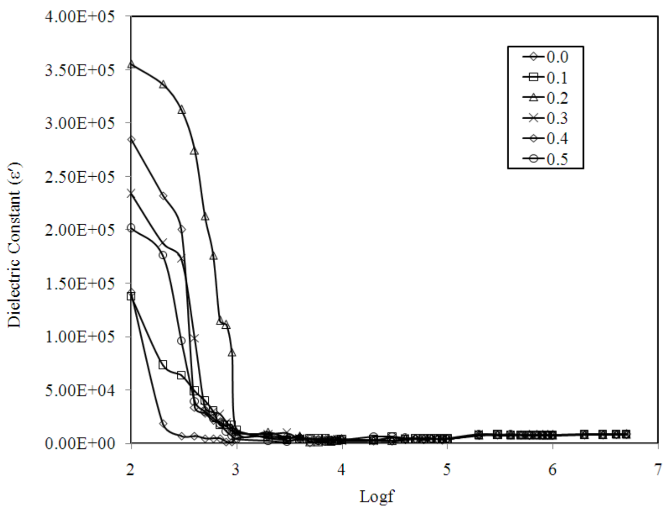

Figure 3 Variation of dielectric constant (ε') with frequency for $Ni_{0.65-x}Cu_xZn_{0.35}Fe_2O_4$ ferrite system

The value of dielectric constant (ε′), dielectric loss (ε″) and loss tangent (tanδ) is much higher at lower frequencies and it decreases with the increasing frequency. It decreases rapidly up to 1 kHz, followed by slow decrease up to 10 kHz, and nearly constant above 10 kHz. At very high frequencies, its value is so small that it becomes independent of frequency. The variation in dielectric constant may be explained on the basis of space charge polarization.
According to Maxwell and Wagner two-layer model [15-16], the space charge polarization is produced

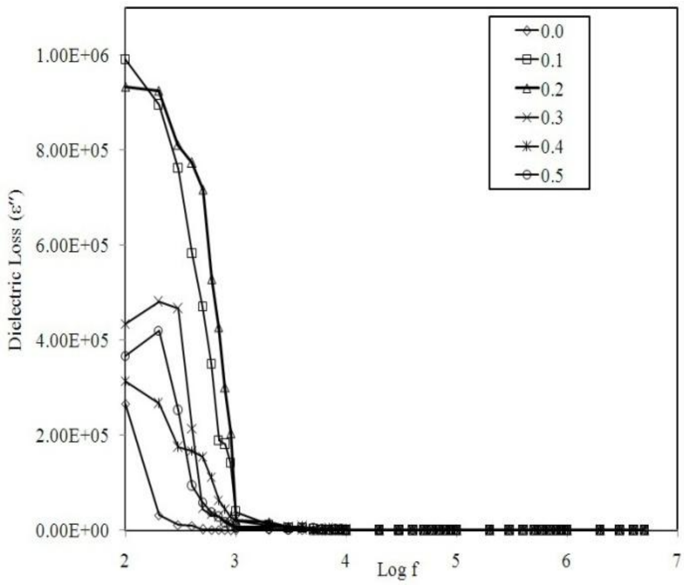

Figure 4 Variation of dielectric loss (ε") with frequency for $Ni_{0.65-x}Cu_xZn_{0.35}Fe_2O_4$ ferrite system

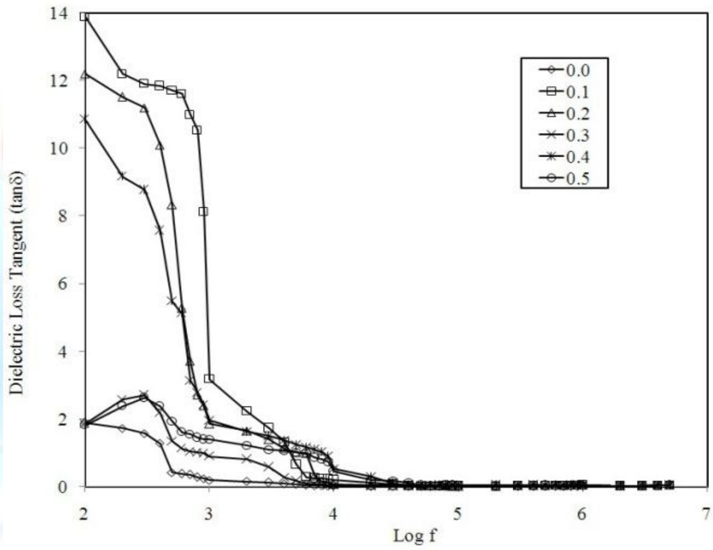

Figure 5 Variation of dielectric loss tangent (tanδ) with frequency for $Ni_{0.65-x}Cu_xZn_{0.35}Fe_2O_4$ ferrite system

in a dielectric material due to the presence of higher conductivity phases (grains) in the insulating matrix (grain boundaries).

The compositional dependence can be explained by using the assumption that the mechanism of dielectric polarization. It has been concluded that the electron exchange between Fe^{2+} and Fe^{3+} results in the local displacement of charges in the direction of an electric field, which is responsible for the polarization mechanism in ferrites [17]. With increasing the frequency of externally applied electric field, the electronic exchange between Fe^{2+} and Fe^{3+} cannot follow the alternating electric field, which results decrease in dielectric constant.

From figure 4, it can be seen that dielectric loss (ε″) decreases with increasing frequency. According to Smith and Wijn [18] for the same temperature, the ratio between the dielectric constant to the ac conductivity is inversely proportional to the applied frequency.

The dielectric loss tangent (Fig.5) in ferrites is considered to be originated from two mechanisms as electron hopping and charged defect dipoles. The former contributes to the dielectric loss tangent mainly in the low frequency range. In high frequency range, the dielectric loss tangent mainly results from the response of defect dipoles to the field. These dipoles in ferrites are formed due to the change of cation valence state, such as Fe^{3+}/Fe^{2+}, Ni^{3+}/Ni^{2+} and Cu^{2+}/Cu^{1+}, during sintering under oxygen partial pressure. The relaxation of dipoles under electric field is decreases with increasing frequency, resulting in the decrease of dielectric loss tangent in high frequency range.

The compositional dependence of dielectric constant (ε′), dielectric loss (ε″) and loss tangent (tanδ) is as shown in table 2. From table 2 it can be seen that ε′,ε″, and tanδ increases with increasing Cu^{2+} ion concentration. The number of vacancies may be established at the iron site as Cu^{2+} content increases. Such vacancies initiate the thermal dissociation of oxygen, which in turn increases the number of electrons [29]. Also, a number of Fe^{2+}ions may be formed during the sample preparation. Such mechanisms will increase the hopping process and may account for the increase in ε′, ε″and tanδ with addition of Cu^{2+} concentration.

IV. CONCLUSIONS

From this work it can be concluded that, X-ray diffraction pattern shows cubic spinel structure. The lattice constant increases with increasing Cu^{2+} ion concentration. Particle size increases from a value 34.23nm to 69.21nm behave nanocrystalline material. The ac resistivity decreases with increasing frequency. At low frequency resistivity is very large. At high frequency resistivity is decreases and this decrease in resistivity is negligibly small. Among the Ni-Cu-Zn ferrites the specimen with the composition $Ni_{0.65}Zn_{0.35}Fe_2O_4$ exhibits highest value of electricity resistivity (ρ_{ac} = $9.1\times10^7\Omega$-cm) and it decreases with addition of Cu^{2+} content. The decrease in resistivity with Cu^{2+} content was due to the increase in grain size of the ferrites. The dielectric constant, dielectric loss and loss tangent decreases with the increase of frequency for all samples and dielectric dispersions is observed with increasing Cu^{2+} Concentration.

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