Role of Cr^{3+} Substitution on Electrical and Dielectric Behavior of Cu-ferrite Nanoparticles

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Abstract: Chromium substituted copper ferrite nano particles with generic formula $CuCrxFe2-xO4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) have been synthesized successfully in nano-crystalline form by wet chemical co-precipitation method. The as prepared powder of $CuFe2-xCrxO4$ was sintered at 800 0C for 12 h. X-ray diffraction (XRD) technique was employed to investigate the structural properties and to check the phase purity of the prepared samples. The analysis of XRD patterns revealed the formation of single phase cubic spinel structure for all samples. The average crystallite size of all samples was estimated using Scherrer's formula and it is in the order of 30-40 nm. The lattice parameter obtained by using XRD data decreases with chromium substitution. The temperature dependence of d. c. electrical resistivity of all samples was studied by using two probe methods. The resistivity increases with increase in chromium substitution and as temperature increases resistivity decreases. The dielectric properties were investigated as a function of frequency at room temperature using LCR-Q meter. The dielectric constant (ε'), dielectric loss (ε'') and dielectric loss tangent ($\tan\delta$) decreases with increase in frequency.

Keywords: Resistivity, Spinel ferrite, Nano-crystalline, X-ray diffraction.

I. INTRODUCTION

Magnetic semiconductor ferrites have a wide spread role in many technological applications due to their interesting magnetic properties, high electrical resistivity, and low eddy current and dielectric losses. The interest in ferrite emerges from their versatile applicability in radio to microwave frequency regions. Ferrites have low conductivity and the order of magnitude of the conductivity greatly influences the electrical and dielectric behaviour [1-4]. The polycrystalline ferrites which have many applications at microwave frequencies are very good dielectric materials. The electrical and dielectric properties of ferrites are dependent on various factors like method of preparation, sintering temperature, sintering atmosphere, sintering time and chemical composition [5-7]. The reduction of Fe^{3+} ions to Fe^{2+} ions takes place without disturbing the lattice configuration.

The electrical transport properties of ferrites provide information suitable for the specific applications of ferrite in electrical and electronic devices. High electrical resistivity and low eddy current losses at high frequencies make them widely usable for the cores of high frequency electromagnetic devices [8, 9].

According to the literature report $CuFe_2O_4$ is a unique ferrite for the reason that it shows tetragonal structure in pure form. The presence of Jahn-Teller ions (Cu^{2+}) in copper ferrite may give rise to very interesting electrical properties. In the literature studies concerning the electrical and dielectric properties of copper and substituted copper ferrite prepared by ceramic technique has been reported [10,11].

Magnetic nano-particles of spinel ferrites (MFe_2O_4) are of great importance due to their numerous applications in magnetic fluids, high frequency magnets, microwave absorber, high density data storage, drug delivery system from magnetic resonance image etc.[12,13]. The increased interest in nano-sized material is due to their unusual physical and chemical properties in comparison with bulk analogous which are attributed to the increased surface area along with decreased particle size and size effect [14,15]. The electrical properties of spinel ferrites in the nano regime are totally different when compared with their bulk counter parts at micrometric regime. The electrical and dielectric properties are greatly influenced when the particles size is reduced from micro to nano level. The modified electrical and dielectric properties of the nano size spinel ferrites have been effectively used in various dielectric based materials like capacitors, optical factors etc [16]. It is interesting to understand the electrical and dielectric properties of nano-crystalline copper and substituted copper ferrite. The substitution of chromium ions in place of Fe^{3+} in copper ferrite results in decreasing Fe^{2+} ions at octahedral [B] sites. In this study, we have investigated the effect of chromium substitution on the electrical and dielectric properties of copper ferrite and results are presented.

II. EXPERIMENTAL

A. Sample preparation

The samples of spinel ferrite system having chemical formula $CuCr_xFe_{2-x}O_4$ with (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) were prepared by wet chemical co-precipitation method. The starting materials having purity (99 %, s. d. fine, India) used were zinc sulphate ($ZnSo_4.7H_2O$), ferrous sulphate ($FeSo_4.7H_2O$), and chromium sulphate $Cr_2 (So_4)_3.6H_2O$.

The samples with variable composition x = 0.0 -1.0 were prepared by air oxidation of an aqueous suspension containing Zn^{2+}, Fe^{3+}, Cr^{3+} cations in the proper proportion.

177

The starting solutions were prepared by mixing 50 ml of aqueous solution of ferrous sulphate, chromium sulphate and zinc sulphate in stoichiometric proportion. Two molar (2M) solution of NaOH was prepared as precipitant. It has been suggested that the solubility product constant (K_{SP}) of all the constituent always exceeds when the starting solution is added into the precipitant. Therefore, in order to achieve simultaneous precipitation of all the hydroxides $Zn(OH)_2$, $Fe(OH)_3$ and $Cr(OH)_3$ the starting solution (pH ~ 3) was added to the solution of NaOH and a suspension (pH~11) containing dark intermediates was formed. The suspension was heated and kept at temperature of 60 ^{0}C; oxygen gas was bubbled uniformly into the suspension to stir it and to promote oxidation reaction, until all the intermediate precipitates changed into the dark brownish precipitates. The samples were filtered and washed several times by distilled water. The final product was heated at 150 ^{0}C to remove water molecules, finally annealed at 800 ^{0}C for 12 h and was used for different characterization. The XRD pattern was recorded at room temperature to investigate the formation of single phase structure and other structural parameters.

B. Electric measurement

The temperature dependence of d. c. electrical resistivity of all the samples of spinel ferrite system $CuCr_xFe_{2-x}O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) were studied by using two-probe method. The sample was held in specially designed sample holder which consists of two brass electrodes. Silver paste was applied on the two surfaces of the disc shaped pellet for good electric contact and then, whole assembly was placed in a furnace. The temperature of the sample was measured by chromel-alumel thermocouple with an accuracy of $\pm$ 5 K. The temperature of the furnace was controlled by digital temperature controller. The electrical resistivity of all the samples was measured using resistance 'R' and dimensions of disc shaped pellet in the temperature range 300 K-800 K.

C. Dielectric measurement

The measurements of dielectric properties were carried out as a function of temperature and frequency both measured using LCR-Q meter (HP Make, 4192A). The measurements were performed on disc shaped pellet of 10 mm diameter and 2 mm thickness using two-probe method. The measurements of frequency dependence dielectric properties were carried out from 100 Hz to 1MHz at room temperature.
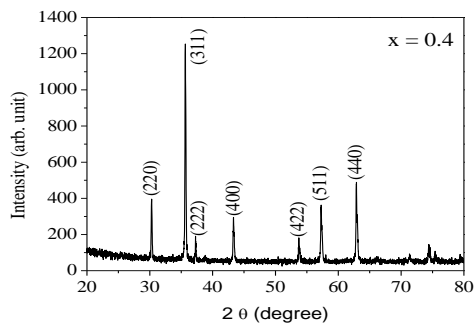

Fig. 1 X-ray diffraction pattern for typical sample x = 0.4 of $CuCr_xFe_{2-x}O_4$ system

From Table 1, it is observed that lattice constant decreases with increase in Cr^{3+} ion concentration. The decrease in lattice constant is attributed to difference in ionic radii of Cr^{3+} ions (0.615Å) and Fe^{3+} ions (0.645Å). In the present study

Cr^{3+} ions replaces Fe^{3+} ions. The ionic radius of Cr^{3+} ions is smaller than that of Fe^{3+} ions, hence lattice constant decreases. Similar behavior of lattice constant was reported in the literature [18].

Table 1: Lattice constant (a), particle size (t), X-ray density (dx), bulk density (d_B) and porosity for $CuCr_xFe_{2-x}O_4$ system

Comp. x	Lattice constant 'a' A.U.	Particle size 't' nm	X-ray density 'dx' gm/cm³	Bulk density 'd_B' gm/cm³	Porosity 'p' %
0.0	8.221	39	5.649	3.799	11
0.2	8.275	35	5.394	3.640	13
0.4	8.250	38	5.383	3.827	10
0.6	8.220	36	5.345	3.762	11
0.8	8.195	42	5.332	3.740	13
1.0	8.182	39	5.319	3.657	12

The X-ray density of all the samples was estimated using the relation, $dx = 8M/Na^3$, where 'M' is the molecular weight and 'a' is lattice constant. The values of X-ray density are given in Table 1. It is evident from Table 1 that, X-ray density decreases with increase in Cr^{3+} ions substitution. The decrease in X-ray density is attributed to decrease in lattice constant. The bulk density of all the samples was estimated through Archimedes principle [19]. The porosity was also determined from the values of X-ray density and bulk density. The values of bulk density and porosity are presented in Table 1. It is observed that the bulk density is 85 to 90 percent of X-ray density. The porosity varies between 10 to 15 percent.

Table 2 gives the values of d. c. electrical resistivity as a function of chromium composition x.

Comp. x	R (MΩ)	ρ x 10⁵ (Ω-cm)	Activation energy (eV)		ΔE (eV)
			E_F	E_P	
0.0	1.33	2.36	0.38	0.52	0.14
0.2	1.35	2.38	0.25	0.36	0.11
0.4	1.36	2.40	0.26	0.37	0.11
0.6	1.36	2.41	0.27	0.40	0.13
0.8	1.37	2.43	0.30	0.44	0.14
1.0	1.39	2.46	0.302	0.46	0.16

Table 2: Resistance (R) and resistivity (ρ) at room temperature, activation energy in ferrimagnetic (E_F) and paramagnetic (E_P) region for $CuCr_xFe_{2-x}O_4$ system

It can be seen from Table 2 that resistivity increases with chromium composition. In the present ferrite system of $CuCr_xFe_{2-x}O_4$, Fe^{3+} ions are replaced by Cr^{3+} ions. The substitutional ions (Cr^{3+}) have strong preference towards octahedral [B] site. These chromium ions do not participate in the conduction process but it limits the degree of $Fe^{2+} \leftrightarrow Fe^{3+}$ exchange conduction phenomena by blocking of Fe^{2+} to Fe^{3+} ions [20], this interesting results shows increase of resistivity with increasing chromium composition.
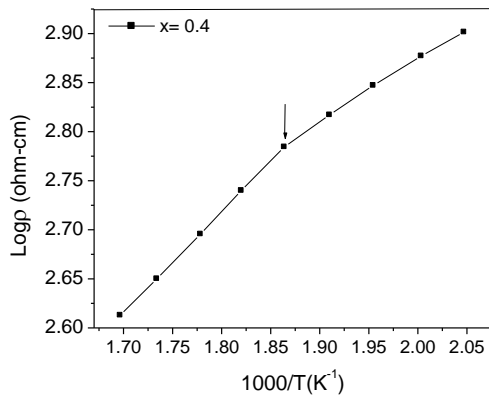
Fig. 2 Log ρ vs 1000/T for typical sample x = 0.4 of $CuCr_xFe_{2-x}O_4$ system

Fig. 2 displays the plot of logarithm of resistivity versus reciprocal of temperature for typical sample (x=0.4). As expected for semiconductors the resistivity of ferrites increases with increase in temperature. It can be seen from Fig. 2 that there are two temperature regions (high temperature and low temperature region). The activation energy for two different regions observed in resistivity plots is different. It is observed from Fig 2 that at low temperature there is no much variation in the resistivity. The conduction phenomenon in this region is attributed to impurities. At higher temperature regions conductivity is attributed to a thermally activated mobility of charge carriers. The activation energy for both the regions has been calculated using the relation, $\rho = \rho_0 \exp(E_g / kT)$, were the symbols have their usual meaning. The results of activation energy are presented in Table 2. It is evident from Table 2 that the activation energy of paramagnetic region (E_p) is greater than that of ferrimagnetic region (E_f). Our results on electrical properties are in good agreement with the other reported nano-size spinel ferrite systems [21].
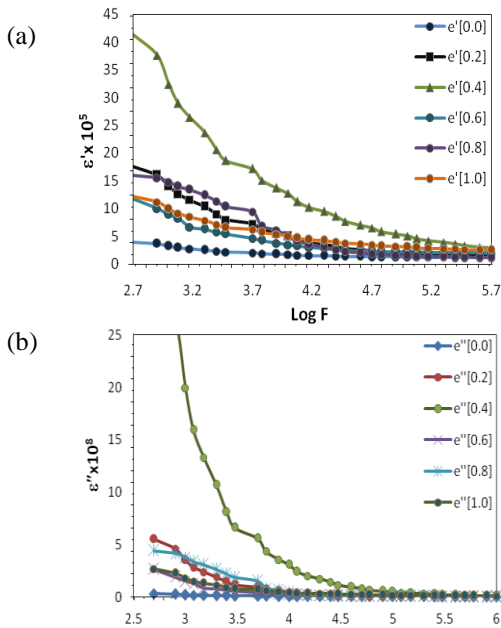
(a)

(b)

Fig. 3 Dielectric constant (ε') and dielectric loss (ε'') as a function of frequency with constant temperature for x = 0.0-1.0 of $CuCr_xFe_{2-x}O_4$ system

Fig. 3 (a) and (b) shows the variation of dielectric constant (ε') and dielectric loss (ε'') as a function of frequency. The

frequency dependence of dielectric constant for $CuCr_xFe_{2-x}O_4$ is in very good agreement with the well known spinel ferrites [22] for which dielectric constant decreases continuously with increase in frequency. It can be seen from Fig. 3 (a) and (b), both dielectric constant and dielectric loss decreases with increase in frequency much rapidly at lower frequency region. As frequency further increases dielectric constant and dielectric loss both remains almost constant. All the samples revealed the dispersion due to Maxwell-Wagner interfacial polarization [23, 24] in agreement with Koop's phenomenological theory [25]. The dielectric behavior may be explained qualitatively by supposing the mechanism of polarization process in ferrite is similar to that of conduction process. As temperature increases, electrical conductivity increases due to increase in thermal activity and drift mobility of electrical charge according to hopping conduction mechanism.

By the electronic exchange $Fe^3 \leftrightarrow Fe^2 + e^-$ one obtains local displacement of electron in the direction of applied electrical field. It is well-known fact that effect of polarization is to reduce the field inside the media. The decrease in polarization of the dielectric constant with increase in frequency is due to fact that at the certain frequency of the electrical field, electron exchange between ferrous and ferric ions cannot follow the alternating field. Therefore, dielectric constant of material may decreases substantially as frequency increases.
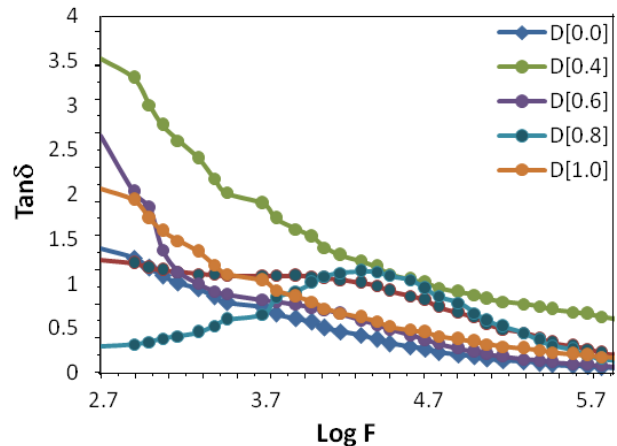

Fig. 4 Dielectric loss tangent (tanδ) as a function of frequency with constant temperature for x = 0.0-1.0 of $CuCr_xFe_{2-x}O_4$ system

The variation of dielectric loss tangent with frequency at room temperature for all the samples of $CuCr_xFe_{2-x}O_4$ is shown in Fig. 4 It is observed from Fig. 4 that, dielectric loss tangent decreases exponentially with increase of frequency and attains constant value at higher frequency. According to Iwauchi [26] there is a strong co-relation between the conduction mechanism and dielectric behaviour ferrites. A maximum value of dielectric loss tangent can be observed when the hopping frequency is approximately equal to that of externally applied electric field.

II. CONCLUSIONS

The prepared chromium substituted copper ferrite system shows single phase cubic spinel structure in nano-crystalline nature (particle size up to 40 nm.).

179

The electrical resistivity measurements shows that the resistivity increases with chromium composition and decreases with increase in temperature confirmed from logarithm of resistivity versus temperature plots. The conduction mechanism can be explained on the basis of hopping mechanism of polaron as activation energy values are found to be less than 0.2 eV. The dielectric behaviour shows strong frequency as well as composition dependence. The dielectric constant (ε'), dielectric loss (ε'') and dielectric loss tangent ($\tan\delta$) all decreases with increase in frequency.

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