



D. C. ELECTRICAL PROPERTIES OF CHROMIUM SUBSTITUTED COPPER NANO-FERRITE

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Abstract: A series of polycrystalline spinel ferrite, formula $\text{CuCr}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8,$ and 1.0) were synthesized by using self-propagating sol-gel auto combustion method and were studied by using X-ray diffraction (XRD) analysis. The calculated lattice constant from XRD shows that the values of the lattice constant decrease with an increase in Cr^{3+} ion content x . The XRD data confirmed the formation of the single-phase cubic spinel structure of the prepared samples. The DC electrical resistivity of all samples is taken at room temperature 300-800 K by using two probe methods. The values of activation energy are greater in the paramagnetic region than that of the ferrimagnetic region. Using D.C. electrical resistivity and the Loria method, the Curie temperature (T_c) of all samples was investigated. The values of ' T_c ' obtained from both the methods are very close to each other which is attributed to the transition from ferrimagnetic region to paramagnetic region.

Keywords: X-ray diffraction, lattice constant, activation energy, Curie temperature.

1. INTRODUCTION

Nowadays magnetic materials are at the apex of nanotechnology. Ferrite is one of the important magnetic materials which have very good electric as well as dielectric properties. Ferrite material is one of the important components in the latest electronic products, such as cell phones, computers, video cameras, memory devices, etc. They require small dimensions and all light weights and have better functions. The soft ferrites exhibit two antiferromagnetic coupled sub-lattices namely tetrahedral (A) and octahedral [B] site [1, 2].

The polycrystalline ferrite has very good structural, magnetic, electrical, and dielectric properties that are dependent on several factors, such as the method of preparation and substitution of different ions. The usefulness of ferrites is influenced by the physical and chemical properties of the materials. The physical properties of polycrystalline ferrites are very sensitive to the microstructure. The grain and grain boundary are the two main components that determine the microstructure. Soft

ferrites remain of great interest because of their high initial permeability over a large frequency range leading to widespread applications e.g. inductor cores in RF systems, recording heads, and microwave devices. Soft ferrites are commercially important materials because of their excellent magnetic, electrical, and dielectric properties [3].

The general formula of ferrite material is MFe_2O_4 where, $\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Fe}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+}$, etc. nano-crystals attract great research interest due to their potential applications in Ferrofluids, magnetic fluids, magnetic recording media, magnetic resonance image, remarkable chemical stability, and a mechanical hardness, which make it possible material for high-density recording media [4]. The present study aims to focus systematically on the electrical properties of chromium substituted copper ferrite prepared by the sol-gel auto combustion method.

2. EXPERIMENTAL

2.1. Material and sample preparation

A series of chromium substituted copper nano-ferrites having the chemical formula $CuCr_xFe_{2-x}O_4$ (as $x = 0.0$ to 1.0 in the step of 0.2) were prepared by sol-gel auto combustion method. The starting materials having high purity (99 %, S. D. fine, India) were copper nitrate: $Cu(NO_3)_2 \cdot 6H_2O$, ferric nitrate: $Fe(NO_3)_3 \cdot 9H_2O$, chromium nitrate: $Cr(NO_3)_3 \cdot 9H_2O$, citric acid: $C_6H_8O_7 \cdot H_2O$ and ammonia: NH_3 all of 99% pure AR grade. Calculated quantities of metal nitrates were dissolved together in 100ml of distilled water to get a clear solution. An aqueous solution of citric acid was then added to the metal nitrate solution. The molar ratio of citric acid to the total moles of nitrate ions was adjusted to 1:3. A small amount of NH_3 was added dropwise into the solution to adjust the pH value to about 7 so the sample becomes neutral.

A continuous stirring and heating at $90^\circ C$ to the solution on the hot plate with a magnetic stirrer until it becomes a very viscous gel. The powder was annealed in air at a temperature of $500^\circ C$ for six hours with a heating rate of $50^\circ C$ per min to obtain a spinel phase.

2.3. Characterization

The X-ray powder diffraction patterns were recorded on Philips X-ray diffractometer wavelength 1.5418 \AA . The XRD patterns were in the 2θ range of 20° to 80° with a scanning rate of $1^\circ/\text{min}$. All the structural parameters were calculated from the X-ray diffraction analysis. The D.C. electrical resistivity of all the samples at temperature range, $300\text{-}800\text{K}$ was measured by the two-probe technique.

3. RESULTS AND DISCUSSION

3.1. Structural analysis

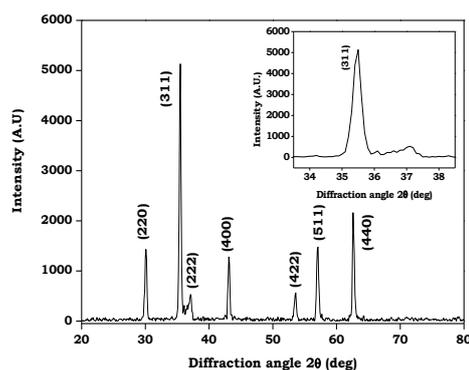


Fig. 1: X-ray diffraction patterns of the $CuCr_xFe_{2-x}O_4$ ($x = 0.2$) nano-ferrite.

The X-ray diffraction (XRD) patterns of the $CuCr_xFe_{2-x}O_4$ nano-particles are shown in Fig.1 for a typical $x=0.2$ sample. The entire XRD patterns show the reflections belonging to cubic spinel structure; no extra peaks have been observed in the XRD patterns. The single-phase formations of compounds under investigation were confirmed from the analysis of the

XRD pattern. In inset of Fig.1, the intensity of the (311) plane is more as compared to other planes like (220), (222), (400), (422), (511), and (440) and is chosen for the determination of crystallite size.

Using XRD data, the variation of lattice constant 'a' with an increase in chromium content 'x' shows that, lattice constant decreases with an increase in Cr^{3+} content x as shown in Table 1. The observed behavior of the lattice constant can be explained based on the relative sizes of ionic radii. The ionic radius of Cr^{3+} (0.63 \AA) ions is smaller than the ionic radius of Fe^{3+} (0.64 \AA) ions. Replacement of larger Fe^{3+} cations by smaller Cr^{3+} cations in the copper ferrite causes a decrease in lattice parameters. A similar variation of lattice parameters was observed for other Cr^{3+} ions substituted spinel ferrites [5, 6].

3.2. D.C. Electrical resistivity

The temperature dependence of D.C. electrical resistivity of all the samples of the series $CuCr_xFe_{2-x}O_4$ was studied in the temperature range of $300\text{-}800\text{K}$ of all the samples was studied by the two-probe method. The sample was held in a specially designed sample holder which consists of two brass electrodes; silver paste was applied on the two surfaces of the circular pellet for good ohmic contact. The whole assembly is placed in a furnace. The temperature of the sample was measured by chromel-alumel thermocouple with an accuracy of $\pm 5 \text{ K}$. The temperature of the furnace was controlled by the digital temperature controller. A slow rate of temperature change was maintained throughout the experiment. The measurements were carried out from room temperature to beyond Curie temperature, in the step of 10K . The resistivity (ρ) of all the samples was calculated from dimensions and resistance of the pellet by using the relation,

$$\rho = \left(\frac{\pi r^2}{t} \right) R \quad \text{Ohm - cm}$$

where r is the radius of the pellet, t is the thickness of the pellet, R is the resistance of the pellet. The D. C. electrical resistivity measurements of chromium substituted copper ferrite ($CuCr_xFe_{2-x}O_4$) spinel ferrite system were calculated by measuring the values of resistance 'R'.

Table 1: Variation in the values of Lattice constant (a), Resistance (R), and DC Resistivity (ρ) at room temperature of $CuCr_xFe_{2-x}O_4$ system

Cr content x	Lattice constant (a) A.U.	Resistance (R) Ω	DC Resistivity (ρ) $\Omega\text{-cm}$
0.0	8.3886	1332570	235468
0.2	8.3582	1356398	238132
0.4	8.3345	1355132	239856
0.6	8.3211	1363458	241345
0.8	8.3109	1374201	243036
1.0	8.3057	1391242	245987

Table 1 gives the values of D. C. resistivity as a function of composition shows that the resistivity increases with chromium content x.

To understand the D. C. electrical behavior of the samples, the variation of logarithm of resistivity versus reciprocal of temperature has been studied. **Fig. 2** displays the plots of the logarithm of resistivity (logρ) versus reciprocal of temperature (1000/T) for typical samples x=0.2 and x=0.4. The plots exhibit a break near Curie temperature dividing the curve into two regions namely ferrimagnetic and paramagnetic regions.

The variation of resistivity as a function of temperature is also studied. It can be seen from **Fig. 2** that D.C. resistivity decreases with the increase in temperature, indicating the semi-conducting nature of the ferrite system. The resistivity - temperature behavior obeys the relation [7],

$$\rho = \rho_0 \exp\left(\frac{-\Delta E}{kT}\right) \text{ Ohm-cm}$$

where ρ is the resistivity at absolute temperature T, ΔE is the activation energy and k is the Boltzmann constant. Each sample shows a break near the Curie temperature which is attributed to the transition from ferrimagnetic region to paramagnetic region. Using the above equation and the resistivity plots, the activation energy in the ferrimagnetic and paramagnetic region was calculated and the values of activation energies are tabulated in **Table 2**.

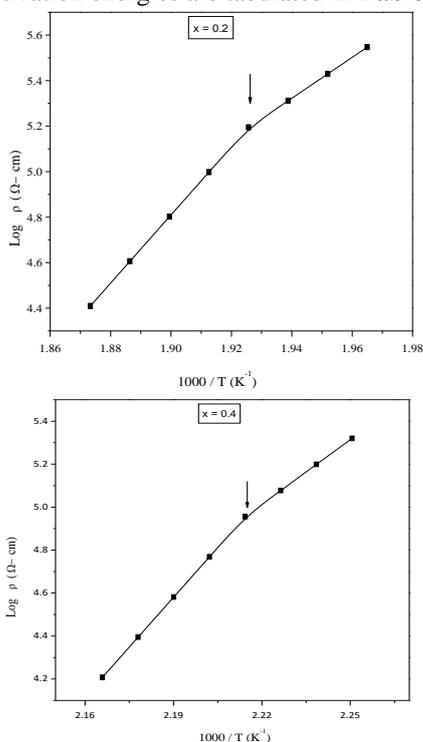


Fig.2: Logρ versus 1000/ T of CuCr_xFe_{2-x}O₄ (x= 0.2 and x=0.4) ferrite system

The activation energy observed for all the ferrite samples indicates the small polaron hopping type of conduction mechanism in ferrites. The

activation energy in the paramagnetic region is higher than that in the ferrimagnetic region. The lower activation energy in the ferromagnetic region is attributed to the magnetic spin disordering effect due to a decrease in the concentration of current carriers, while the change in activation energy is attributed to the change in conduction mechanism. The change in activation energies (ΔE) in eV of prepared samples as determined by the difference between the activation energies in the paramagnetic (E_P) and ferrimagnetic regions (E_F) shows conduction mechanism.

Table 2: Variation of activation energy in the ferrimagnetic and paramagnetic region and Curie temperature of CuCr_xFe_{2-x}O₄ (0.0 ≤ x ≤ 1.0) ferrite system

Cr content x	Activation energy (eV)			Curie temperature	
	E _F	E _P	ΔE	DCR	Lorica
0.0	0.228	0.326	0.098	753	710
0.2	0.256	0.364	0.108	702	682
0.4	0.264	0.374	0.110	653	623
0.6	0.269	0.398	0.129	604	565
0.8	0.301	0.443	0.142	553	510
1.0	0.312	0.475	0.163	423	415

In the present study, Fe³⁺ ions are replaced by Cr³⁺ ions. The substitutional ions (Cr³⁺) have a strong preference for octahedral B-site which leads to Fe³⁺ ions at B-site. These chromium ions do not participate in the conduction process but it limits the degree of Fe²⁺ ↔ Fe³⁺ conduction by blocking Fe²⁺ to Fe³⁺ ions [8]. This results in an increase in resistivity with increasing chromium concentration. Similar behaviour was also reported in chromium substituted nickel-zinc ferrite [9] and other well-known ferrites [10, 11]. These plots obey the Arrhenius relation indicating the semiconducting behaviour of the samples.

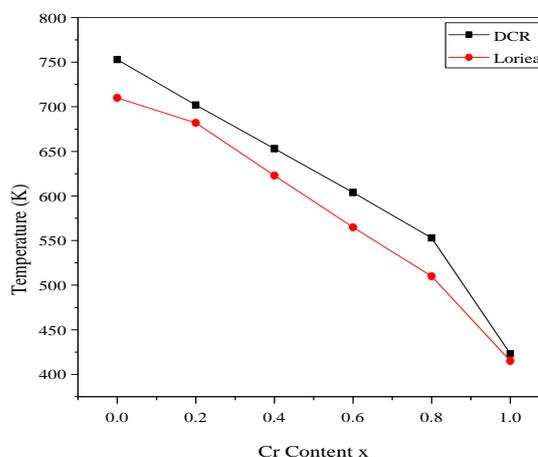


Fig.3: Curie temperature CuCr_xFe_{2-x}O₄ (0.0 ≤ x ≤ 1.0) nano-ferrite

Fig.3 shows that, the variation of Curie temperature 'T_c' using DC electrical resistivity and Loria technique with different Cr content x. It is clear from the graph that the values of Curie temperature from both methods are very close to each other. The value from the DCR method is slightly greater than the values obtained from the Loria method. This change is due to the surrounding variation in room temperature.

4. CONCLUSIONS

The chromium substituted copper ferrite system is successfully prepared by the sol-gel auto combustion technique. The prepared chromium substituted copper ferrite system shows a single-phase cubic spinel structure. The lattice constant decreases with Cr³⁺ ions substitution. The experimental data of electrical properties leads to electrical resistivity measurements to show that the resistivity increases with composition for chromium substituted copper ferrite. The electrical resistivity decreases with an increase in temperature as can be seen from the logarithm of resistivity versus temperature plots for chromium substituted copper ferrite. The values of Curie temperature obtained from the DCR method and Loria technique are in very close agreement with each other. The conduction mechanism can be explained based on the hopping of polaron as activation energy values are found to be less than 0.2 eV.

[12].

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