



SYNTHESIS AND CHARACTERIZATION OF Cu-Cr NANOFERRITE USING MICROWAVE AUTO COMBUSTION TECHNIQUE.

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Abstract:

Nanoscale materials are found to be of great importance and significance, especially in the development of specialized applications. The nanoferrites of Copper-Chromium with generic formula $\text{CuCr}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0,0.5$) were synthesized by microwave assisted sol-gel auto combustion method. The synthesized samples are annealed at 800°C and characterized using X-ray diffractometer (XRD) and transmission electron microscope (TEM). The XRD patterns confirm the formation of single phase cubic ferrite. The value of lattice parameter 'a' reveals the formation of spinel ferrite. The morphological investigations were done by TEM. The TEM imaging demonstrates the formation of nanosize particles. It is also observed that these ferrites show semiconductor behavior. The electrical studies confirm the semiconducting nature of synthesized sample under the influence of high temperature. The dielectric constant was explained on the basis of Maxwell interface polarization in accordance with Koop's phenomenological model.

Keywords:

Nanoferrite, XRD, TEM, ferrimagnetic, sol-gel auto combustion etc.

Introduction

Ferrites are chemical compounds with the formula AB_2O_4 , where A and B represent various metal cations; usually including iron. Ferrites are usually non-conductive ferromagnetic ceramic compounds derived from iron oxides as well as oxides of other metals. The structure consists of a cubic closed packed case of oxygen ions with the metallic ions occupying the tetrahedral A and octahedral B interstitial sites. The electromagnetic properties of ferrite materials can be affected by different operating conditions like field strength, frequency, temperature, pressure and time.





Spinel ferrites are naturally occurring ferrite i.e. $\text{FeO} \cdot \text{Fe}_2\text{O}_3$. the spinel ferrite structure is derived from mineral spinel that crystallizes in cubic system. Spinel ferrites have general formula $\text{FeO} \cdot \text{Fe}_2\text{O}_3$; where, Me is a divalent metal ion.

In cubic closed packed structure there is occurrence of two kinds of interstitial sites, namely tetrahedral and octahedral sites which are surrounded by 4 and 6 oxygen atoms respectively. In the above cubic structure unit cell, 64 tetrahedral and 32 octahedral sites are present, of which only 8 and 16 are respectively occupied by metal ions as A and B sites respectively. In unit cell of spinel lattice, 8 tetrahedral and 16 octahedral sites are occupied by metal ions. It should be noted that ferrites can be prepared containing two different kinds of divalent ions and are called as mixed ferrites. To improve electrical properties of Ca ferrites, divalent, depending trivalent and tetravalent ion substitution were studied [1-3].

Experimental:

In the present work an attempt has been made to synthesize spinel ferrite from metal nitrate and fuel urea precursors by microwave –assisted combustion synthesis route using a modified domestic microwave oven having frequency 2.45GHz. The nano-ferrites of $\text{CuCr}_x\text{Fe}_{2-x}\text{O}_4$ with compositions ($x = 0, 0.5$) have been synthesized by a microwave assisted auto combustion method. This process consists of evolution of inorganic network formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel).

Synthesis of ferrite nanoparticles is done in following steps:

The starting materials used were AR grade Copper Nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Chromium Nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), Ferric Nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and Urea (NH_2CONH_2), as given in Table:.1. These salts were dissolved in distilled water with constant stirring to get clear solutions. For synthesis, equimolar solutions of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were mixed in their





stoichiometric ratio and homogenized. The mixture was then heated at 80°C for about eight hours. During the reaction, it was noticed that the solution became viscous (converting to gel). On further heating, brown colored powder was obtained.

The gel was cooled and allowed to fire in microwave oven to remove the water from the gel. The obtained powder was crushed in pestle mortar to get fine nanoparticles. This powder was calcined at 800 °C for 2 hours by slowly rising the temperature in a step of 100°C per hour by using high-temperature Muffle furnace. Finally ferrite nanoparticles were obtained. The samples were then characterized through various characterization techniques.

Table-1: Preparation details of $\text{CuCr}_x\text{Fe}_{2-x}\text{O}_4$ series

Sr. No.	Chemical Composition	Reacting Nitrate
1	CuFe_2O_4	$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
2	$\text{CuCr}_{0.5}\text{Fe}_{1.5}\text{O}_4$	$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

Result & Discussion

The XRD pattern as shown in the fig. 1 confirm that the investigated sample of CuFe_2O_4 revealed a cubic spinel structure without any impurities. The analysis of XRD pattern reveals that, the main peaks in the pattern correspond to the cubic spinel phase, without any ambiguous reflections. The peaks considered to denote the spinel phase appears at 30.70° , 35.56° , 43.18° , 57.24° and 62.88° , which are well indexed to the crystal plane of spinel ferrite (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (5 2 2) respectively. The average particle size of the samples calculated by using Scherrer formula was found to be in the



range of 24 nm to 33 nm [4]. The lattice parameter and x-ray density as a function of Cr concentration was tabulated in the table 2. The lattice parameter 'a' was found to be linear while the x-ray density was found to be decreasing with the increasing concentration of Cr. Since the ionic radii of Cr^{+3} is slightly small as compared to the ionic radii of Fe^{+3} . The values of lattice parameter, x-ray density, bulk density and porosity were mentioned in the following table number 3.

Table No. 3: Different parameters of $\text{CuCr}_x\text{Fe}_{2-x}\text{O}_4$

Concentration	a (Å)	Vol(Å)	x-ray density (gm/cm ³)	bulk density (gm/cm ³)	Porosity (%)	Particle Size (nm)
$x=0$	8.3681	585.977	5.3128	1.6834	68.31	33
$x=0.5$	8.3030	572.407	5.2902	1.5308	63.65	24

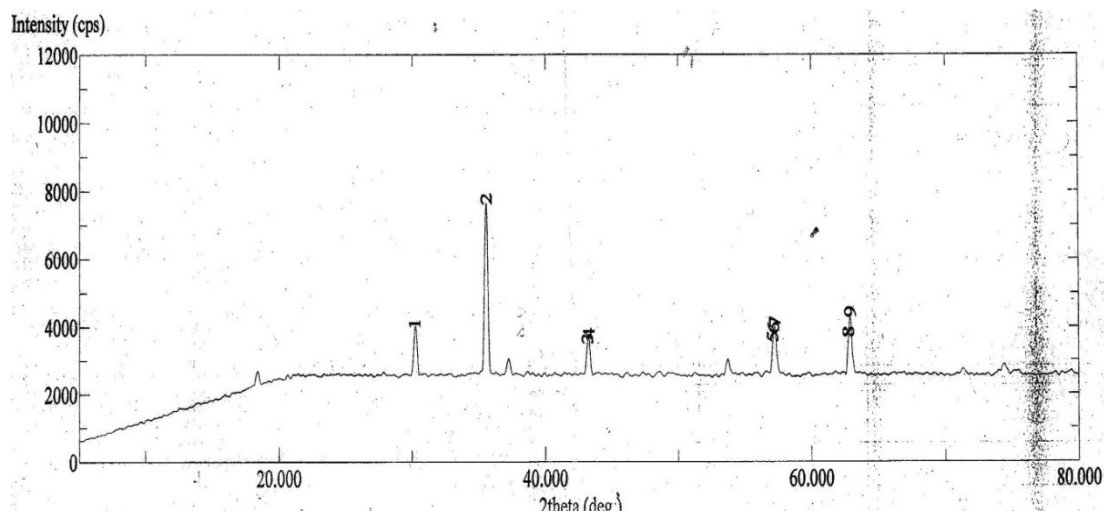


Figure 1:- X-ray diffraction spectrum of $\text{CuCr}_{0.5}\text{Fe}_{1.5}\text{O}_4$

Lattice parameter

$$a = 8.3681 \pm 0.01 \text{ \AA}$$

Sr. No.	2 θ	dobs (Å)	dcal (Å)	I/I ₀	H	K	L
1	30.70	2.9569	2.9568	52	2	2	0
2	35.56	2.5235	2.5244	100	3	1	1
3	43.18	2.0934	2.0933	46	4	0	0
4	57.24	1.6081	1.6081	53	5	1	1
5	62.88	1.4768	1.4575	57	5	2	2

Table 2:- X-ray Diffraction result of $\text{CuCr}_{0.5}\text{Fe}_{1.5}\text{O}_4$

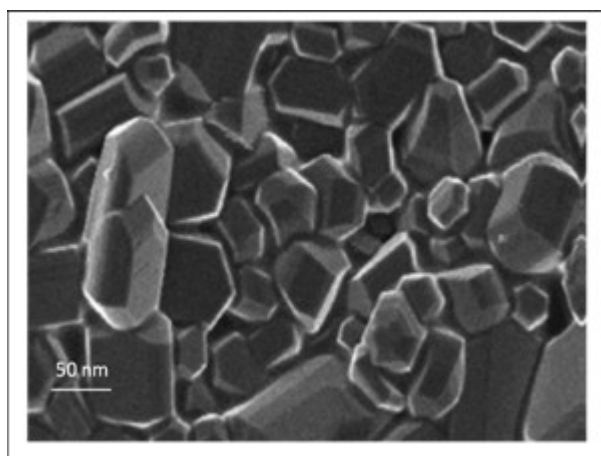


Figure 2:- TEM Image of $\text{CuCr}_{0.5}\text{Fe}_{1.5}\text{O}_4$

TEM has provided more reliable particle morphology of the synthesized sample. The TEM of the sample has confirmed the ability to produce cubic crystal structure in nanorange. These cuboids are nearly cubic in shape and are formed exactly as obtained by Xiang-ming Lu (2007). The surface grains are smooth, grain edges are sharp. TEM of the sample shows that cuboid stack on top of each other due to their magnetic attraction and exhibit a partially sintered nanostructure. The TEM micrographs of $\text{CuCr}_{0.5}\text{Fe}_{1.5}\text{O}_4$ of sample is given in the above figure. From the micrograph it is observed that the mixed



oxide particles are finely dispersed in the polymer matrix and are spherical in shape within a narrow size range. However in the case of heating sample at 800°C, the micrograph shows spherical particles with a particle size distribution of 21 nm to 47 nm as shown in the figure 2.

The temperature dependence of electrical conductivity was studied in the temperature range of 300K to 700K. The samples studied have better electrical properties. On the basis of previous research investigations carried out, it could be quoted that the electrical properties of the ferrite materials depend upon chemical composition, method of synthesis, sintering temperature and of course grain size. The D.C. conductivity as a function of temperature may be written as

$$\sigma_{dc} = \sigma_0 \exp(-E_a / K_B T)$$

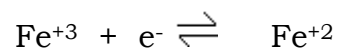
Where, E_a is the activation energy for conduction,

K_B is Boltzmann's constant

σ_0 is conductivity extrapolated to $1/T = 0$

T is absolute temperature.

It is clear from the Figure:-3 that by increasing temperature, the conductivity of ferrite increases. It indicates that these ferrites have semiconductor like behaviour as reported by Smit et al (1959). As studied by Verwey et al (1950), the conduction in ferrite at room temperature is due to the impurities, whereas at the high temperature it is due to the polaron hopping. Similarly, the electronic conduction in ferrite is mainly due to hopping of electrons between ions of some element present in more than one valance state, distributed randomly over different lattice sites. In this case it is suggested as follows,



The linearity in the graph of $\log \sigma$ Vs $(1/T)$ breaks at a particular temperature, which is in the neighborhood of magnetic transition temperature of ferrite.

The activation energy calculated from the graph of $\log \sigma$ Vs $(1/T)$ shows that it is different in two region, it is lower in the low temperature region while in the high temperature region it is little higher, as tabulated in Table: 3. The change



in activation energy is due to transition from ordered (Ferrimagnetic) to disordered (Paramagnetic) state.

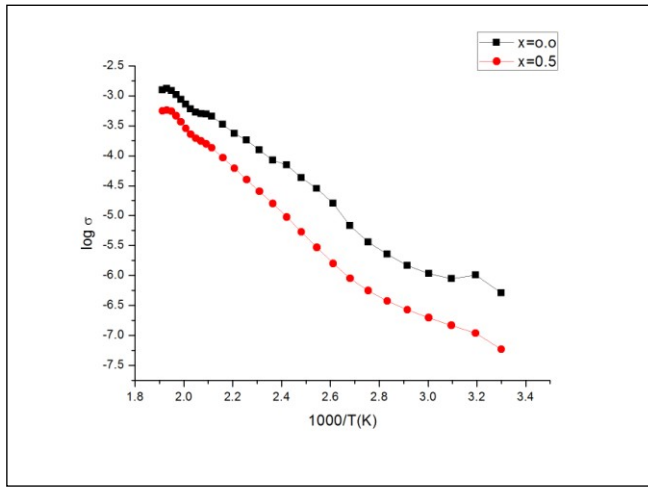


Figure 3:- Variation of $\log \sigma$ Vs $(1/T)$ of $\text{CuCr}_x\text{Fe}_{2-x}\text{O}_4$

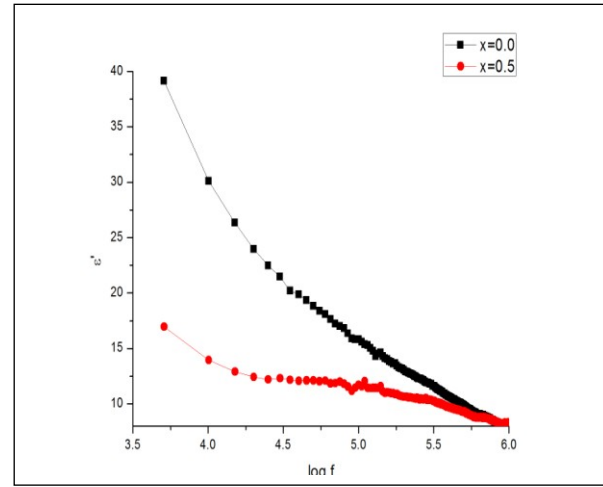


Figure 4:- Variation of ϵ' Vs $\log f$ of $\text{CuCr}_x\text{Fe}_{2-x}\text{O}_4$

S.N	Compound	Tt ($^{\circ}\text{K}$)	Activation Energy ΔE (eV)	
			Ferrimagnetic	Paramagnetic
1)	CuFe_2O_4	488	0.40	1.29
2)	$\text{CuCr}_{0.5}\text{Fe}_{1.5}\text{O}_4$	453	0.82	1.25

Table

4:- Activation Energy of $\text{CuCr}_x\text{Fe}_{2-x}\text{O}_4$

Fig 4 shows the decrease in dielectric constant with increasing frequency exhibit normal ferromagnetic behaviour. The sharp decrease in ϵ' at low frequencies and show almost a frequency independent behavior at high frequencies. The decrease in dielectric constant with frequency can be explained by the mechanism of polarization process in the ferrites is similar to that of conductivity process. The observed variation in ϵ' is qualitatively in accordance with Maxwell Wagner two layer model [5-6], the space charge polarization is due to the inhomogeneous structure of dielectric material. When the frequency of the applied field is increased, the probability of electrons to reach grain boundary decreases. This decreases the polarization and hence the dielectric constant with increasing frequency.



Conclusion :

The nanoferrites of $\text{CuCr}_x\text{Fe}_{2-x}\text{O}_4$ cubic spinel ferrites was successfully synthesized by using microwave sol-gel auto combustion technique. XRD of the investigated samples shows the single phase cubic spinel ferrite. The lattice parameter was found to be decreasing with the increase in Cr^{+3} concentration due to its smaller ionic radii compared to Fe^{+3} . The average particle size of the Cu-Cr nanoferrite is found to be in the range of 24 nm to 33 nm as per Debye Scherrer formula, which was duly confirmed by the TEM analysis. From the electrical studies, it is also observed that these ferrites show semiconductor behaviour under the influence of high temperature. The values of activation energy shows that its value in paramagnetic region is higher than that of ferrimagnetic region and change in this value is attributed to transition from ordered (Ferrimagnetic) to disordered (Paramagnetic) state. The dielectric constant was found to be frequency sensitive. The decrease in the dielectric constant with frequency arises from the two types of charges carriers present in the ferrite.

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