

# Anomalous Behavior on the Electrical Properties of $\text{Cu}^{2+}$ Substitution in Li-ferrite

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## Abstract

$\text{Li}_{0.5-0.5x}\text{Cu}_x\text{Fe}_{2.5-0.5x}\text{O}_4$  where  $0.1 \leq x \leq 0.3$  in steps of 0.05 have been synthesized by the citrate precursor method. The samples were given heat treatment at a temperature of  $900^\circ\text{C}$ . Technique such as XRD, FTIR, LCR meter and B-H loop tracer were used to characterize the samples. Spinel phase structure was confirmed from the XRD pattern and FTIR spectra. As calculated from the XRD data the average crystallite size were found to be in the nanometer range. FTIR analysis reveals that there exist two strong IR bands corresponding to metal oxygen stretching at the A and B sites respectively. The electrical properties such as dc resistivity and complex dielectric were investigated. Experimental data reveals an anomalous increase of dielectric constant with substitution of  $\text{Cu}^{2+}$  while the dc resistivity decreases. The variation of dielectric constant with frequency (20Hz-2MHz) shows dispersion whereas the variation of dielectric loss with frequency shows a resonance peak. Magnetic property such as magnetization was also measured and is found to increase with increasing substitution of  $\text{Cu}^{2+}$ . Possible mechanism responsible for the above results is being discussed.

**Keywords:** Citrate precursor; XRD; dielectric constant; dielectric loss; DC resistivity

## INTRODUCTION

Lithium based ferrites are well studied material. However, investigation is still continuing throughout the world for their unique and versatile applications based on the properties which can be tailored by changing the preparation method, substitution, sintering etc [1-3]. They have been found to be used as an important component in microwave devices, memory core, recording heads etc due to their various properties like high resistivity, high dielectric constant, high initial permeability, high saturation magnetization etc [4-6]. There are various methods such as solid state reaction, wet chemical method. Among the wet chemical method citrate

precursor method is preferred due to its low temperature requirements, simple, easy and economic. As was learnt from the study of different workers the different properties of spinel ferrites arise from the incorporation of cations into their lattice giving interesting changes. Several authors reported that the substitution of  $\text{Cu}^{2+}$  after a particular concentration migrate to tetrahedral (A) site after studying the magnetic properties [7-8]. Therefore it might be interesting to investigate the structural, electrical and magnetic properties altogether and find the correlation exhibited between the different parameters.

As such, a detailed investigation on the structural, electrical and magnetic properties of  $\text{Cu}^{2+}$  substitution in lithium ferrite was carried out.

## EXPERIMENT

$\text{Li}_{0.5-0.5x}\text{Cu}_x\text{Fe}_{2.5-0.5x}\text{O}_4$  where  $0.1 \leq x \leq 0.3$  in step of 0.05 were synthesized by the citrate precursor method. The precursor used were Lithium nitrate  $\text{LiNO}_3$  (Merck, India), Copper (II) nitrate trihydrates  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Merck, India), Iron (III) nitrate monohydrates  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck, India), and citric acid nonahydrates  $\text{C}_6\text{H}_8\text{O}_7$  (Merck, India). The preparation method had been explained elsewhere [9]. These synthesized powders were then mixed with polyvinyl alcohol (PVA) as a binder and pressed to form pellets (10mm diameter) by applying a pressure of  $10 \text{ ton cm}^{-2}$  and further given heat treatment at a temperature of  $900^\circ\text{C}$ . The phase identification and structure analysis of the sintered samples were performed using Philips X-ray diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5406\text{\AA}$ ) and FTIR spectra (Perkin Elmer FTIR spectrometer). From the XRD data the lattice constant, density, and the crystallite size (Debye-Scherrer relation) of each composition was determined. Measurement on the complex dielectric constant  $\epsilon = \epsilon' - j\epsilon''$  where real part  $\epsilon'$  is the dielectric constant and imaginary part  $\epsilon''$  is the dielectric loss is carried out. The capacitance and loss factor was measured by using Agilent E4980 Precession LCR meter in the frequency range of 20Hz-2MHz. Then the

dielectric constant  $\epsilon'$  was calculated using the formula

$$\epsilon' = \frac{Cd}{\epsilon_0 A} \quad (1)$$

where d is the thickness of the sample  $\epsilon_0$  is the absolute permittivity of free space and A is the area of the sample. The electrical resistivity of the samples was also determined.

Sintered torroids samples wounded with 70 turns 30SWG enameled copper wire was used to investigate the saturation magnetization of all the samples.

## RESULT AND DISCUSSION

Fig. 1 shows the XRD pattern of  $\text{Li}_{0.5-0.5x}\text{Cu}_x\text{Fe}_{2.5-0.5x}\text{O}_4$  confirming the spinel phase structure of the prepared sample. The observation shows peak corresponding to the lattice planes of (220), (311), (400), (422), (511), (440) etc. All the peaks could be indexed to the standard pattern reported by the Joint Committee on Powder Diffraction Standards. No extra peak due to impurities is observed.

The XRD parameters like lattice constant, X-ray density and crystallite size were tabulated in Table 1. Lattice expansion occurs if the doping ion has larger radii than the displaced ion. In the present investigation,  $\text{Cu}^{2+}$  ions of ionic radius  $0.71\text{\AA}$  substitute  $\text{Li}^{1+}$  (0.78) and  $\text{Fe}^{3+}$  (0.067) respectively [10-11].

However no observable effect is seen in the variation of lattice constant with increasing substitution. The lattice constant of all samples being calculated using the formula

$$a = d_{hkl}(h^2 + k^2 + l^2)^{1/2} \quad (2)$$

where 'd' is the lattice spacing, hkl are miller indices and 'a' is the lattice constant.

An increasing trend in density (theoretical and experimental) was observed with increase in  $\text{Cu}^{2+}$  concentration. This can be explained on the basis that atomic weight of  $\text{Cu}^{2+}$  (63.55 amu) is greater than atomic weight of  $\text{Li}^{1+}$  (6.94 amu) and  $\text{Fe}^{3+}$  (55.84 amu).

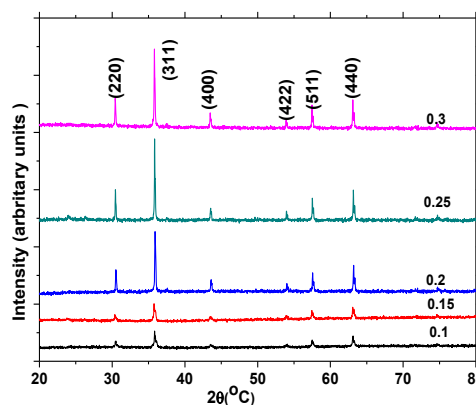


Figure 1: XRD pattern of  $\text{Li}_{0.5-0.5x}\text{Cu}_x\text{Fe}_{2.5-0.5x}\text{O}_4$  samples .

Table 1. Lattice Constant, x-ray density, experimental density, crystallite size, dielectric Constant dc resistivity and saturation magnetiation of  $\text{Li}_{0.5-0.5x}\text{Cu}_x\text{Fe}_{2.5-0.5x}\text{O}_4$ .

Conc. (x)	Lattice const. $\text{\AA}$	Theo. Density ( $\text{g/cm}^3$ )	Expt. Density ( $\text{g/cm}^3$ )	Crystallite Size (nm)	Dielectric constant $\times 10^2$	DC resistivity ( $\text{ohm-cm}) \times 10^6$	Sat. Mag. (Gauss)
0.1	8.31	4.863	3.690	43	16.63	9.2	498
0.15	8.30	4.913	3.949	47	23.33	9.1	523
0.2	8.29	4.972	3.359	50	25.39	7.3	680
0.25	8.29	5.011	3.979	53	173.44	6.1	816
0.3	8.29	5.060	4.095	55	504.00	2.0	1339

The increase in density with  $\text{Cu}^{2+}$  substitution may be attributed to the acceleration of cation inter diffusion due to  $\text{Cu}^{2+}$  ions and increase in reactivity of the fine ferrite grains which coalesce to form bigger grains. On the one hand the crystallite sizes increases with increasing  $\text{Cu}^{2+}$  concentration. The crystallite size was estimated from XRD analysis using Debye Scherer formula [12] which is given as,

$$D_{\text{cryst}} = \frac{0.89\lambda}{\beta \cos\theta} \quad (3)$$

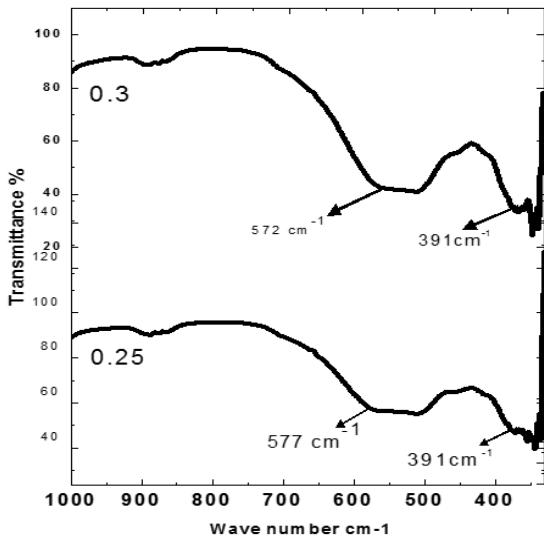
where  $\lambda$  is the wavelength of incident  $\text{CuK}\alpha$  radiation of XRD,

$\beta$  is full width at half maximum and  $\theta$  is the diffraction angle.

Fig. 2 depicts a typical FTIR spectra of  $x=0.25$  and  $x=0.3$  recorded in the wave number range of  $400\text{cm}^{-1} - 1000\text{cm}^{-1}$  at room temperature.

It was observed that IR spectra showed two strong absorption bands ( $\lambda_1$  and  $\lambda_2$ ) appearing in the wave number range of  $350-600\text{cm}^{-1}$ . These bands are the characteristics bands of spinel ferrites which are in good agreement with literature [13-14]. These bands are attributed to the metal-oxygen stretching at the tetrahedral and octahedral sites respectively. Strong band  $\lambda_1$

(580-610  $\text{cm}^{-1}$ ) was caused by  $\text{Fe}^{3+}\text{-O}^{2-}$  stretching at tetrahedral sites with higher force constant and lower bond length.

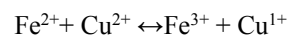


**Figure 2:** FTIR spectra of  $\text{Li}_{0.5-0.5x}\text{Cu}_x\text{Fe}_{2.5-0.5x}\text{O}_4$  with  $x=0.25$  and  $0.3$ .

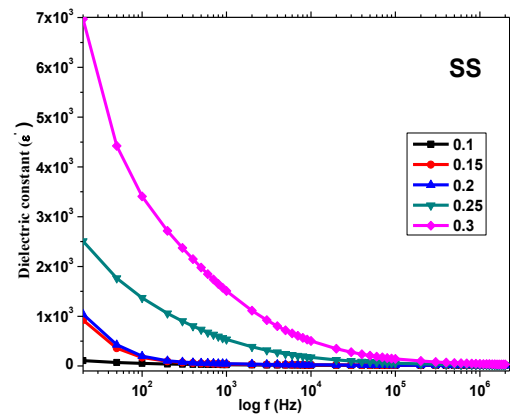
Another band  $\lambda_2$  (391-400 $\text{cm}^{-1}$ ) was caused by the  $\text{Fe}^{3+}\text{-O}^{2-}$  stretching band at the octahedral sites with low force constant and higher bond length. Since the distance between the  $\text{Fe}^{3+}$  and  $\text{O}^{2-}$  at the tetrahedral and octahedral sites is different, the bands position was found to be different for different composition. The values of  $\lambda_1$  is higher than that of  $\lambda_2$  which indicates that the normal mode of vibration of the tetrahedral sites is higher than that of the corresponding octahedral sites. This is attributed to the fact that the bond length of tetrahedral sites (1.89 $\text{\AA}$ ) is shorter than those of octahedral sites (1.99  $\text{\AA}$ ).

Investigation on the electrical studies such as dielectric constant ( $\epsilon'$ ), dielectric loss ( $\tan\delta$ ), and rt dc resistivity was carried out. Compositional variation of room temperature dielectric constant measured at 10 KHz for all the samples were studied (Table 1.). This variation was explained on the basis of space charge polarization and Koop's two layer model [15-16]. According to this model ferrite is assumed to be consisted of well conducting grain surrounded by poor conducting grain boundaries. There are four primary mechanisms contributing to the polarization which further relate to the dielectric properties of the material. They are electronic polarization, atomic polarization, dipole polarization and interfacial or space charge polarization. The former two mechanism contribute polarization at the higher frequency ( $10^{12}\text{-}10^{15}\text{Hz}$ ) whereas the latter two mechanism to that of the lower frequencies ( $<10^{12}\text{Hz}$ ). Polarization in ferrites is similar to that of electrical conduction mechanism. The electrical conduction in ferrite was explained by Verwey mechanism of electron hopping between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  at the octahedral sites [17]. The main mode of conduction in ferrites is BB hopping. The electron reaches the grain boundary by hopping motion of electron and pile up due to its higher resistivity thereby producing the space charge

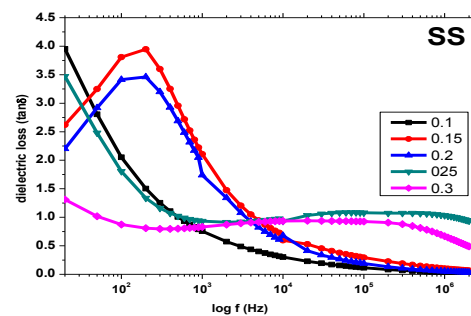
polarization. In the present series of samples the substitution with  $\text{Cu}^{2+}$  produces a change in the polarization which can be understood by considering the cationic distribution formula  $(\text{Fe})[\text{Li}_{0.5-0.5x}\text{Cu}_x\text{Fe}_{1.5-0.5x}]\text{O}_4$  [18]. As  $\text{Cu}^{2+}$  concentration is increased, there is a decrease in  $\text{Fe}^{3+}$  ion at the B sites. Thus a decrease in  $\text{Fe}^{3+}$  at the B-sites decreases the hopping motion of electron. This in turn decreases the piling up of electrons at the grain boundary and hence impedes the building up of space charge polarization. Therefore the value of dielectric constant is expected to decrease with increasing  $\text{Cu}^{2+}$  concentration. However, it shows an increasing trend with the increase in  $\text{Cu}^{2+}$  substitution. The anomalous increase might have resulted from the fact that  $\text{Cu}^{2+}$  migrate to tetrahedral (A) site in the present study. Another reason may be due to the contribution to conduction from  $\text{Cu}^{2+}$  ion during the exchange process



The variation of dc resistivity versus  $\text{Cu}^{2+}$  content is shown in Table 1. The increased variation of resistivity with  $\text{Cu}^{2+}$  content tally with that of dielectric constant as dc resistivity is inversely proportional to dielectric constant.



**Figure 3:** Variation of Dielectric Constant with Frequency for  $\text{Li}_{0.5-0.5x}\text{Cu}_x\text{Fe}_{2.5-0.5x}\text{O}_4$

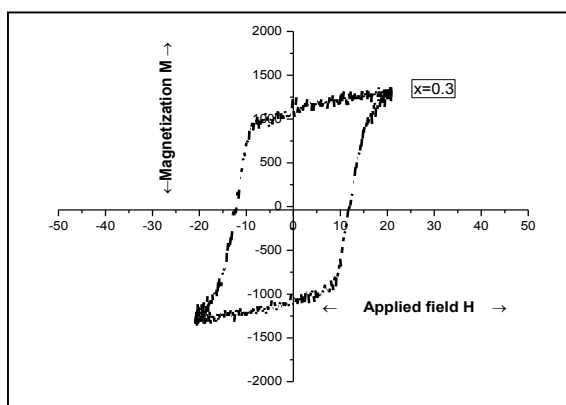


**Figure 4:** Variation of Dielectric loss with Frequency for  $\text{Li}_{0.5-0.5x}\text{Cu}_x\text{Fe}_{2.5-0.5x}\text{O}_4$

Variation of dielectric constant as a function of frequency of the applied field for all the samples was investigated and is shown in Fig. 3. Dispersion is observed for all the samples

which is a normal behavior of ferrite materials. The observed decrease in dielectric constant with the increase in frequency of all the samples was explained in term of space charge polarization and Koop's two layer model. At low frequency of the applied field, the grain boundary having the higher resistivity hinders the hopping motion of electrons creating space charge polarization, leading to a high dielectric constant. As the frequency of the applied field increased, the resistivity of grain boundary decreases and the electronic exchange is not able to follow the alternating field and the electron reverse the direction of motion thereby decreasing the probability of electron reaching the grain boundary. This leads to decrease in the value of dielectric constant. At still higher frequency, the probability of creating space charge polarization is small and become almost independent of frequency [15, 18].

Fig.4 shows the variation of dielectric loss tangent with the frequency of the applied field for all the samples. Dielectric loss refers to the relative expenditure of energy to obtain a given amount of charge storage in the material. The maximum energy that can be stored at certain frequency is when hopping frequency of electrons between ferrous and ferric ions at the B-sites match to that of the applied field and thus it appears as a resonance peak. In the present study such resonance peak is observed and shifting of peaks occurs. Reason for shift in the peaks towards the lower frequency can be explained on the basis of Debye's relaxation theory. Accordingly, a dielectric loss peak occurred when the frequency of the applied field is equal to that of the hopping frequency satisfying condition  $\omega\tau = 1$  where  $\omega = 2\pi f_{max}$ . The relaxation time being related to the hopping probability per unit time P as  $f_{max} = (1/\pi)P$ . As the probability of hopping of electron decreased with the increase in  $Cu^{2+}$  concentration there is a decrease in frequency and hence peak should shift towards the lower frequency [19-20]. However, a systematic trend in shifting was not observed supporting the anomalous increased in dielectric constant which might have arisen from either  $Cu^{2+}$  migrating to A site or  $Cu^{2+}$  itself taking part in the exchange process. However a detailed and thorough investigation needs to be further carried out.



**Figure 5:** Hysteresis loop of  $Li_{0.5-0.5x} Cu_x Fe_{2.5-0.5x} O_4$  for  $x=0.3$

Fig. 5 shows a typical hysteresis loop for  $x=0.3$ . The saturation magnetization shows an increasing trend with the increase in  $Cu^{2+}$  content (table 1). The magnetization in ferrites is generally explained by Neel's molecular field model and cationic distribution [9]. According to Neel's model A-B super exchange interaction is dominant over the other A-A and B-B exchange interaction and the saturation magnetization is given by the vector sum of the magnetic moment of individual A and B sub lattice i.e.  $M_s = M_B - M_A$ , where  $M_A$  is the magnetic moment of magnetic ion at the A-sites and  $M_B$  is the magnetic moment of a magnetic ion at the B-sites respectively. According to the cationic distribution  $(Fe) [Li_{0.5-0.5x} Cu_x Fe_{1.5-0.5x}] O_4$ , it is known that  $Li^{1+}$  and  $Cu^{2+}$  tend to occupy at the octahedral sites. Since  $Li^{1+}$  is a non magnetic material, it does not contribute to the magnetization so the overall magnetization is contributed by less magnetic ion  $Cu^{2+}$  and strong magnetic ion  $Fe^{3+}$  ion at B sites having the magnetic moment per ion of  $1\mu_B$  and  $5\mu_B$  respectively. Therefore the net saturation magnetization is given by  $M_s = 2.5 - 1.5x$  and thus it is expected to decrease but was not observed experimentally. However reverse trend observed support to some extent the migration of  $Cu^{2+}$  to A site within the range of  $Cu^{2+}$  concentration taken in the present study. It also supports the behavior of the variation of dielectric constant.

## CONCLUSION

$Cu^{2+}$  substitution in basic lithium ferrite greatly affect the properties. Increase addition of  $Cu^{2+}$  show an increasing trend in the densification and crystallite size. The dielectric constant shows an anomalous increase with increasing  $Cu^{2+}$  concentration which was also supported by the shifting in resonance peak in the variation of dielectric loss with frequency and the increase value of saturation magnetization. The possible reason might be the migration of  $Cu^{2+}$  to A site or  $Cu^{2+}$  itself taking part in the exchange process. However, a detailed and thorough investigation needs to be further carried out. The variation of dielectric constant with frequency for all samples shows dispersion.

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