CHAPTER - V

Electrical studies $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ and $\text{CuCr}_x\text{Fe}_{2-x}\text{O}_4$ ferrite system

5.1 Introduction:

Magnetic semiconductor ferrites have a wide spread role in many technological applications due to their magnetic properties, high electrical resistivity, 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 dielectric and magnetic 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 $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ 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]. Several researchers have studied the electrical and dielectric properties of spinel ferrite [10 - 13]. Electrical switching in ferrites was reported by Yamashiro [14] in polycrystalline thermally treated bulk copper ferrite. Similar reports are presented for copper ferrite by Vaingankar [15]. The dielectric behaviour Cu – Zn, Li – Zn, Mg – Zn ferrite systems as a function of frequency was reported by many workers [16-19].

The purpose of the present work is to study the electrical and dielectric properties of zinc and chromium substituted copper ferrite as a function of temperature and frequency respectively. In the present chapter we report our results on the electrical and dielectric properties of Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ and CuCr$_x$Fe$_{2-x}$O$_4$.

### 5.2 Experimental techniques:

#### 5.2.1 D.C. electrical resistivity:

The temperature dependence of d.c. electrical resistivity of all the samples of the series Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ and CuCr$_x$Fe$_{2-x}$O$_4$ were studied by 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 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 ± 5 K. The temperature of the
furnace was controlled by digital temperature controller. A slow rate of change in temperature was maintained throughout the experiment. The measurements were carried out from room temperature to beyond Curie temperature, in the step of 10K. Fig. 5.1 shows the experimental setup of d.c. resistivity which was used in the present investigations.

The resistivity $\rho$ of all the samples was calculated from dimensions and resistance of the pellet by using the relation,

$$\rho_{dc} = \left( \frac{\pi r^2}{t} \right) R \quad \Omega \cdot \text{cm} \quad 5.1$$

where, $r$ is radius of the pellet,

t is thickness of the pellet,

$R$ is resistance of the pellet.

5.2.2 Dielectric measurement:

The measurements of dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric loss tangent ($\tan\delta$) were carried out as a function of temperature and frequency both on a LCR-Q meter (HP make, 4192). The measurements were performed on circular pellet of 10 mm diameter and 2 mm thickness using two-probe method. The measurements of frequency dependence of dielectric properties were carried out from 100 Hz to 1 MHz at room temperature.
The dielectric constant ($\varepsilon'$) was calculated using the following relation

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A}$$

where,
- $C$ is capacitance,
- $d$ is thickness of pellet,
- $\varepsilon_0$ is permittivity of the free space,
- $A$ is cross sectional area of pellet.

The dielectric loss ($\varepsilon''$) was calculated using the relation

$$\varepsilon'' = \frac{1}{2\pi \cdot 1000 \cdot \varepsilon_0} \sigma$$

where, $\sigma$ is a.c. conductivity.

The dielectric loss tangent (tan$\delta$) was calculated using the relation.

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

### 5.3 Results and discussion:

**Series I: Zinc substituted copper ferrite (CuZn$_{1-x}$Fe$_2$O$_4$):**

The d.c. electrical resistivity was studied as a function of temperature from room temperature to beyond Curie temperature using two probe method. The resistivity values measured at room temperature are given in Table 5.1. It can be seen from Table 5.1 that the values of electrical resistivity varies from $2.3 \times 10^5$–$4.5 \times 10^5$
Ωcm and increases continuously with increase in zinc content. The observations are in good agreement with the results reported by several workers [20-21]. The increase in resistivity may be due to the presence of more number of Fe$^{3+}$ ions at octahedral B-site. In the present case according to the cation distribution data Zn$^{2+}$ ions are occupied at tetrahedral A-site leading to more Fe$^{3+}$ ions at octahedral B-site. The dependence of resistivity with varying composition is shown in Fig. 5.2.

The variation of resistivity as a function of temperature is also studied. Fig. 5.3 (a and b) shows the variation of log$p$ versus $1000/T$ for all the composition x. It can be seen from Fig. 5.3 (a and b) that d.c. resistivity decreases with the increase of temperature, indicating the semi-conducting nature of the ferrite system. The resistivity - temperature behaviour obeys the relation [22],

$$\rho = \rho_0 \exp \left( -\frac{\Delta E}{kT} \right) \quad 5.5$$

where, $\rho$ is the resistivity at absolute temperature $T$, $\Delta E$ 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 above equation and the resistivity plots the activation energy in ferrimagnetic and paramagnetic region was calculated and the values of activation energies are tabulated in Table 5.2. It is well known that the electron and polaron hoping between Fe$^{2+}$/Fe$^{3+}$, Cu$^{2+}$/Cu$^{1+}$ ions, with the
activation energy 0.2 eV is responsible for conduction in mixed ferrite [23]. The lower activation energy in the ferrimagnetic region is attributed to the magnetic ordering due to the decrease in concentration of current carriers [24].

The electrical conductivity in ferrites can be explained on the basis of the Verway de Bore Mechanism [25], i.e. exchange of electrons between ions of the same element that are present in more than one valance state distributed randomly over equivalent crystallographic lattice states i.e. Fe\(^{3+}\)↔Fe\(^{2+}\).

The substitution of Zn\(^{2+}\) ions reduces Fe\(^{3+}\) ions at tetrahedral A-site by (1-x) and increases Zn\(^{2+}\) ions by x. The substitution of Zn\(^{2+}\) ions reduces Fe\(^{3+}\) ions at tetrahedral A-site by (1-x) and increases Zn\(^{2+}\) ions by x. The presence of Cu\(^{2+}\) ions at octahedral B-site reduces concentration of Fe\(^{3+}\) ions at octahedral B-site. This may results in reduction of Fe\(^{2+}\) ions that may be formed during preparation, therefore, the electron exchange between the iron-iron ions at B-site is reduced and hence the resistivity increases. The present values of activation energy suggest that the hopping of smaller polaron is responsible for the conduction in the present samples.

5.4 Dielectric properties:

Fig. 5.4 shows the variation of the dielectric constant \(\varepsilon'\) with frequency at room temperature for all the compositions. It can be seen from the Fig 5.4 that the values of the dielectric constant are \(\sim 152\sim\).
found to decrease continuously with increasing frequency for all the samples under investigation. The decrease in dielectric behaviour of Cu-Zn ferrites is a normal dielectric behaviour of spinel ferrites. This normal dielectric behaviour was also observed by several workers [26-28]. The normal dielectric behaviour of spinel ferrites was explained by Rezlescu [29]. It can be seen from the Fig. 5.4 that the dispersion in dielectric constant is analogous to Maxwell-Wagner interfacial polarization [30-31], in agreement with Koops’ phenomenological theory. Maximum dispersion of the dielectric constant is observed for $x = 1$. This maximum dielectric dispersion may be explained on the basis of available ferrous ions at octahedral B-sites. In the present series of $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ for $x = 1$, maximum ferrous ions are available at octahedral B site. Therefore, it is possible for these ions to be polarized to a maximum possible extent. Further, as the frequency of the externally applied field increases gradually, the dielectric constant decreases. The reduction occurs because beyond a certain frequency of the externally applied electric field the electronic exchange between ferrous and ferric ions do not follow the alternating field. The compositional dependence of dielectric constant at different mid frequency region is shown in Fig. 5.5. It can be seen from figure that the dielectric constant decreases with zinc concentration for all the frequency under investigation.

Similar behaviour was also observed for dielectric loss also. The variation of dielectric loss ($\varepsilon''$) versus logF is shown in Fig. 5.6.
It is observed from this figure that like dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) also decreases.

The variation of dielectric loss tangent with frequency is shown in Fig 5.7 for all the samples under investigation. Similar to dielectric constant, dielectric loss tangent also decreases exponentially showing maxima at a particular frequency. According to Iwauchi [32] there is a strong correlation between conduction mechanism and dielectric behaviour of ferrites. The conduction mechanism in ‘n’ type ferrites is considered as due to hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ and the hopping of holes between Cu$^{2+}$ and Cu$^{1+}$ ions in ‘p’ type ferrites. When the hopping frequency is nearly equal to that of the externally applied electric field a maximum loss may be observed. The condition of observing a maximum in the dielectric losses of a dielectric material is given by $\omega \tau = 1$; where, $\omega = 2\pi f_{\text{max}}$ and $\tau$ is the relaxation time. The relaxation time $\tau$ is related to the jumping probability per unit time, $p$, given by equation $\tau = 1/2p$ or $f_{\text{max}} \propto p$. This equation shows that $f_{\text{max}}$ is proportional to the jumping or hopping probability. Now a decrease of $f_{\text{max}}$ with increasing zinc content indicates that the hopping or jumping probability per unit time is decrease continuously.
The d. c. electrical resistivity measurements of chromium substituted copper ferrite (CuCr$_x$Fe$_{2-x}$O$_4$) spinel ferrite system were carried out in the temperature range 300-800 K using two probe technique. The d. c. resistivity was calculated by measuring the values of resistance ‘R’. Table 5.3 gives the values of d. c. resistivity as a function of composition. It can be seen from Table 5.3 that resistivity increases with chromium content $x$.

Fig. 5.8 shows the variation of resistivity as a function of chromium concentration $x$. In the present study Fe$^{3+}$ ions are replaced by Cr$^{3+}$ ions. The substitutional ions (Cr$^{3+}$) have strong preference to octahedral B-site which leads to Fe$^{3+}$ ions at B-site. These chromium ions do not participate in the conduction process but it limits the degree of Fe$^{2+}$↔Fe$^{3+}$ conduction by blocking of Fe$^{2+}$ to Fe$^{3+}$ ions [34]. This results in increase in resistivity with increasing chromium concentration.

To understand the d. c. electrical behaviour of the samples, the variation of logarithm of resistivity versus reciprocal of temperature has been studied. Fig. 5.9 (a and b) displays the plot of logarithm of resistivity versus reciprocal of temperature. The plots exhibit a break near Curie temperature dividing the curve in two regions namely ferrimagnetic and paramagnetic region. Similar behaviour was also reported in chromium substituted nickel zinc ferrite [35] and other well know ferrites [36, 37]. These plots obey Arrhenius relation indicating semiconducting behaviour.
of the samples. Using Arrhenius relation and resistivity plots, activation energy of all the samples has been obtained and the values are presented in Table 5.4. It can be seen from table that activation energy in paramagnetic region is more as compared to the values of activation energy in ferrimagnetic region.

**Frequency dependence of dielectric properties:**

Fig. 5.10 and 5.11 show the variation of dielectric constant and dielectric loss as a function of frequency. The frequency dependence of dielectric constant for CuCr$_x$Fe$_{2-x}$O$_4$ is in very good agreement with the well known spinel ferrites [38] for which dielectric constant decreases continuously with increase in frequency. It can be seen from figures 5.10 and 5.11 that 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 [30-31] in agreement with Koops’ phenomenological theory [39]. The dielectric behaviour 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 $\text{Fe}^3 \leftrightarrow \text{Fe}^2 + e^-$ 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 can not follow the alternating field. Therefore, dielectric constant of material may decreases substantially as frequency increases.

The variation of dielectric loss tangent with frequency at room temperature for all the samples of CuCr$_x$Fe$_{2-x}$O$_4$ is shown in Fig. 5.12. It is observed from Fig. 5.12 that, dielectric loss tangent decreases exponentially with increase of frequency and attains constant value at higher frequency. According to Iwaiuchi [32] 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.

5.5 Conclusions:

The experimental data of electrical properties leads to conclude the following:
• The electrical resistivity measurements show that the resistivity increases with composition for both zinc and chromium substituted copper ferrite.

• The electrical resistivity decreases with increase in temperature as can be seen from logarithm of resistivity versus temperature plots for both zinc and chromium substituted copper ferrite.

• The conduction mechanism can be explained on the basis of hopping 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 $\varepsilon'$, dielectric loss $\varepsilon''$ and dielectric loss tangent $\tan\delta$ decreases with the rise in frequency. At lower frequencies it is observed that the dielectric properties are high in case of chromium substituted copper ferrite as compared to zinc substituted copper ferrite.
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