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Dielectric behaviour and a.c. conductivity in $Cu_xFe_{3-x}O_4$ ferrite

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Abstract. **The dielectric properties (dielectric constant and loss) for the system $Cu_xFe_{3-x}O_4$ with x = 1·0, 0·8, 0·6, 0·4 and 0·2, were studied in the temperature range 300 ~ 800 K and also in the frequency range 1 kHz ~ 1 MHz. A.c. conductivity was derived from dielectric constant and loss tangent data. The conduction in this system is interpreted as due to small polaron hopping. The dielectric relaxation was observed for the compositions with tetragonal structure whereas normal behaviour was observed for cubic structure.**

Keywords. **Dielectric constant; polaron hopping.**

1. Introduction

Polycrystalline ferrites exhibiting low hysteresis loss and high resistivity at room temperature are used in microwave applications and radio electronics (Krupanicha 1976). Hence the study of magnetic and electrical properties is important and useful. The electrical conductivity and dielectric behaviour of ferrite depends on chemical compositions and preparation conditions (Patil 1981). Studies on the effect of temperature, composition and frequency on the dielectric behaviour and a.c. electrical conductivity offers valuable information about conduction phenomenon in ferrites based on localized electric charge carriers (El Hitti 1996). The d.c. electrical conductivity and thermoelectric power have already been studied for copper ferrite (Patil *et al* 1994), while a.c. electrical conductivity and dielectric behaviour are hitherto not reported. Therefore, the present paper reports the study of the effect of temperature, frequency and composition on the dielectric constant and a.c. electric conductivity of copper ferrite prepared by the ceramic method.

2. Experimental

The ferrites with general formula $Cu_xFe_{3-x}O_4$, where x varies as 1, 0·8, 0·6, 0·4 and 0·2, were prepared in the form of pellet by the standard ceramic method. In this method, AR grade CuO and Fe_2O_3 were taken in a required molar proportion, milled for couple of hours, then calcined at 700°C in air. Finally, the calcined powder was pressed in the form of pellets and sintered at 1050°C. The X-ray diffractogram of $x = 0·6$ sample is shown in figure 1. Analysis of X-ray diffraction revealed that all the samples were found to be single phase spinels and showed tetragonal structure except the sample with composition $x = 0·2$, which showed cubic structure. This result is similar to that observed earlier by Patil (1981). The surfaces of the samples were well polished and painted with silver paste for good electrical contacts.

Dielectric measurements as a function of frequency in the range 100 Hz ~ 1 MHz at room temperature and also as a function of temperature in the range 300 ~ 800 K for a few selected frequencies, viz. 1 kHz, 10 kHz, 100 kHz, 500 kHz and 1 MHz, were carried out using a LCR meter (HP-4284A model) in conjunction with a laboratory designed cell, temperature controller (± 1°C) using two-probe method. The dielectric constant was calculated by using the formula

$$e' = (C\, d)/(e_0\, A),$$

where C is capacitance of pellet in pf, d the thickness of pellet, A the cross-sectional area of the flat surface of the pellet and e_0 the constant of permittivity for free space. The a.c. conductivity ($s_{a.c.}$) is obtained from the data of dielectric constant (e') and loss tan d using the relation

$$s_{a.c.} = e' e_0 w \tan d,$$

where e_0 is the permittivity of vacuum and w the angular frequency.

3. Results and discussion

The variation of dielectric constant (e') with frequency at room temperature is shown in figure 2. From the plot it can be seen that the dielectric constant initially decreases

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rapidly with increase in frequency but beyond 1 kHz remains fairly constant for all the compositions. The dispersion in e' is large for $x = 0{\cdot}8$ sample and comparatively low for $x = 0{\cdot}4$ composition. At a given frequency, e' varies randomly with Cu content. A similar behaviour was observed for Co–Zn ferrites (Ahmed and El Hitti 1995). The dielectric behaviour for the present samples can be explained on the basis that the mechanism of polarization process in ferrites is similar to that of conduction process. The electron exchange $Fe^{3+} \Leftrightarrow Fe^{2+}$ gives local displacement of electrons in the direction of an applied electric field, which induces polarization in ferrites. In normal dielectric behaviour, the dielectric constant decreases with increasing frequency reaching a constant value, depending on the fact that beyond a certain frequency of electric field the electron exchange does not follow the alternating field (Patil *et al* 1996). The variation of loss tangent (tan d) with frequency at room temperature is shown in figure 3. The variation is similar to variation of e' with frequency.

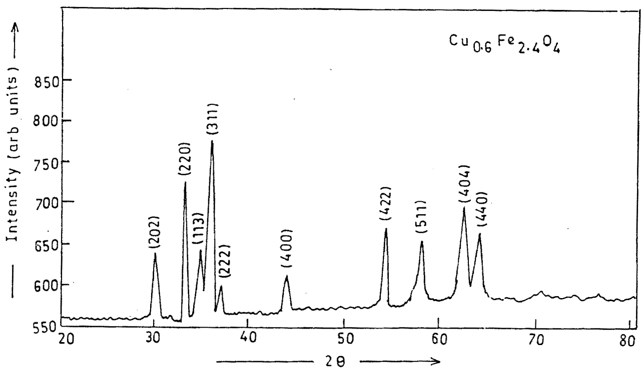

Figure 1. XRD of $Cu_{0{\cdot}6}Fe_{2{\cdot}4}O_4$.

3.1 *Temperature dependence of e¢ and tan d*

Variation of dielectric constant with temperature for the composition $x = 1$ is shown in figure 4. From the graph it is clear that the dielectric constant initially increases gradually with temperature up to 600 K but beyond 600 K a sudden increase in e' for 1 kHz frequency is noticed. Again around 750 K, a dramatic fall in e' is observed for the same frequency. The increase in e' for the same sample as observed at 10 kHz,100 kHz, 500 kHz and 1 MHz is gradual up to 750 K, after which it starts decreasing again gradually. The anomaly in variation of e' as observed at 750 K for all the frequencies is attributed to the transition of the sample from the ferrimagnetic (magnetically ordered) to the paramagnetic state (disordered state). In fact, it was reported that on passing through the transition temperature anomalies in variation of e' are observed (Smith and Wijn 1959). The transition temperature, T_c = 750 K for $x = 1$ sample was also confirmed from magnetic susceptibility and permeability measurements. The variation of e' for the samples $x = 0{\cdot}8$ and $x = 0{\cdot}6$ is different as shown in figures 5 and 6, respectively. The variation for these samples show a broad maxima in the temperature range 500 ~ 570 K. This anomaly can be ascribed to the diffused tetragonal to cubic phase transitions normally observed in Cu ferrites in the temperature range 423 ~ 573 K (Murthy *et al* 1987). Moreover, a careful observation of figures 5 and 6 reveals that the temperature of maxima increases with increase in frequency. Such an abnormal behaviour was observed earlier in Cu–Zn ferrite (Rezlescu and Rezlescu 1974). According to Rezlescu, the abnormal dielectric behaviour of some ferrites is due to a collective contribution of two types of carriers p and n to the polarization. The appearance of p-type carriers in the present system is due to reduction tendency of Cu^{2+} to Cu^{1+} ion, which means that in the present sample the two

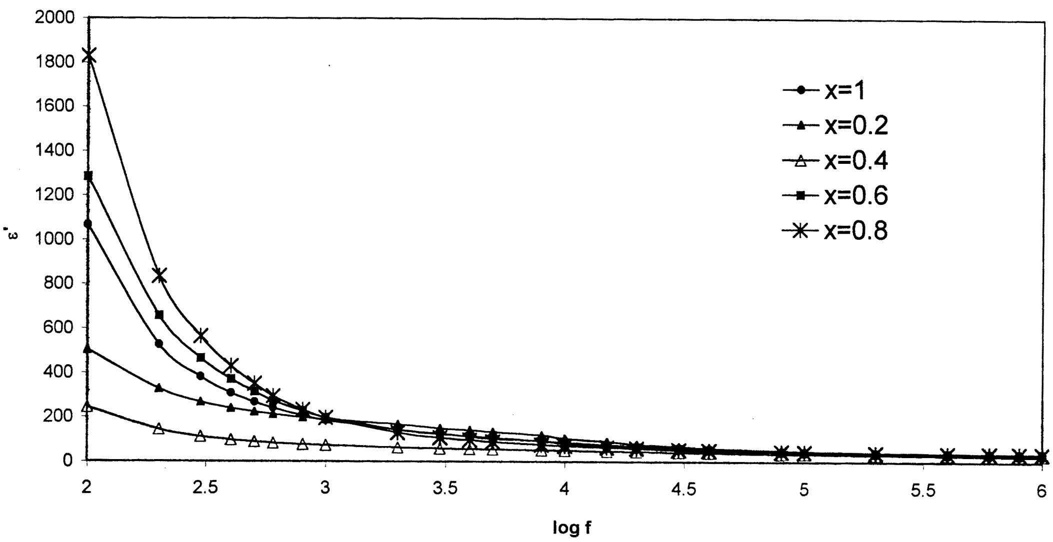

Figure 2. Variation of dielectric constant (e') with frequency (log f) for $Cu_xFe_{3-x}O_4$.

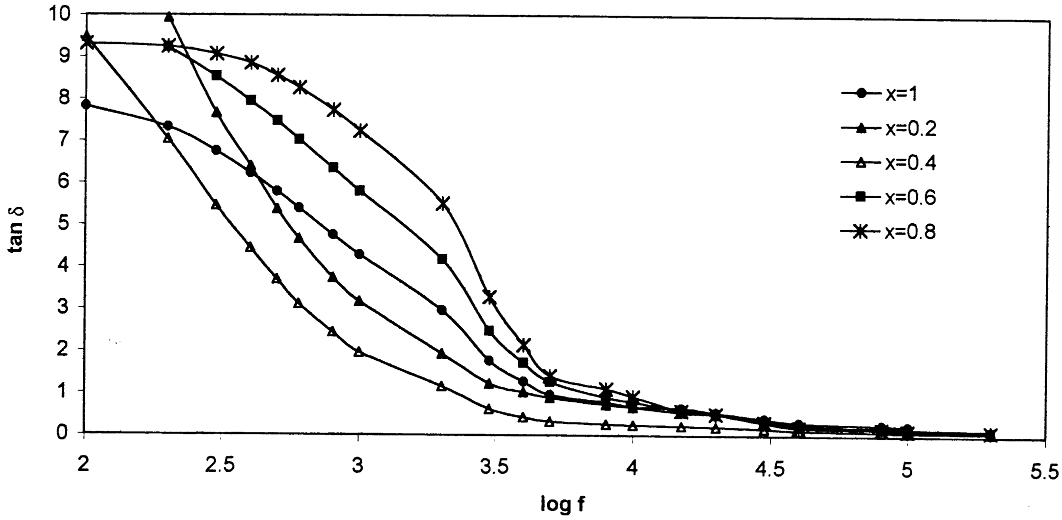

Figure 3. Variation of loss tangent (tan *d*) with frequency (log *f*) for $Cu_xFe_{3-x}O_4$.

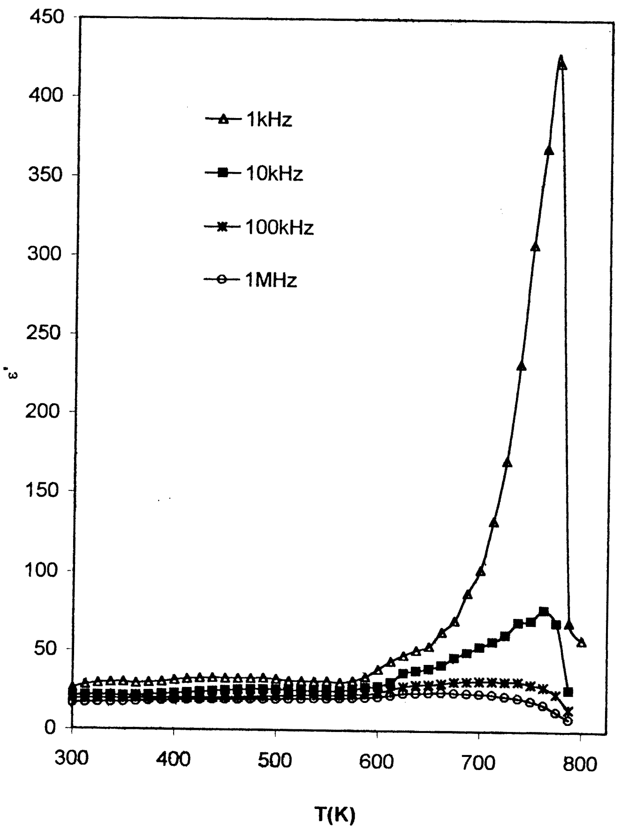

Figure 4. Variation of dielectric constant (*e*′) with temperature for *x* = 1.

types of conduction exist, i.e. $Cu^{2+} \Leftrightarrow Cu^{1+}$ resulting in *p*-type conduction and $Fe^{2+} \Leftrightarrow Fe^{3+}$ in *n*-type conduction. It is well known that the local displacements of *p*-type carriers take part in the polarization in an opposite direction to that of external field. In addition, since the mobility of *p*-type carrier is lower than that of *n*-type carrier, their contribution to polarization decreases more rapidly at lower frequency. Therefore, the position of peak depends on the majority of *p*-type or *n*-type carriers in the sample. In the present samples the composition *x* = 1 only shows *p*-type behaviour and the remaining samples show *n*-type behaviour. It is obvious, as the iron content is increased resulting in more $Fe^{2+} \Leftrightarrow Fe^{3+}$ transitions. Therefore, the increase in *n*-type carrier with increasing Fe content results in shift of peak temperature towards higher temperature side with increase in frequency. The activation energies for the samples *x* = 0·6 and *x* = 0·8 are calculated from relaxation time measurements and these values are 0·20 and 0·18, respectively, which are comparable for transition of $Fe^{3+} \Leftrightarrow Fe^{2+}$. Figure 6 shows another maxima around 600 K for the frequencies 100 KHz, 500 KHz and 1 MHz. The two peaks are well resolved only for 100 KHz frequency. The higher temperature peak may be due to the space charges getting depleted resulting in a peak at a particular temperature (Mahesh Kumar *et al* 1998). The space charge polarization in ferrites is well established. The samples *x* = 0·4 and *x* = 0·2 (not shown in figures) show a gradual increase in *e*′ with temperature without any anomalies.

3.2 *Temperature dependence of a.c. conductivity*

The plots of a.c. conductivity with temperature are shown in figures 7 and 8 for compositions *x* = 0·8 and 0·6. It is clear from the figures that the conductivity is found to be high for higher frequency at a given temperature, thus confirming small polaron hopping in the present samples (Adler 1968; Appel 1968; Austin and Mott 1969). An observation of figure 7 reveals that at high temperature the frequency dependence of $s_{a.c.}$ decreases. It has been reported that frequency dependence of $s_{a.c.}$ is large in ferri-

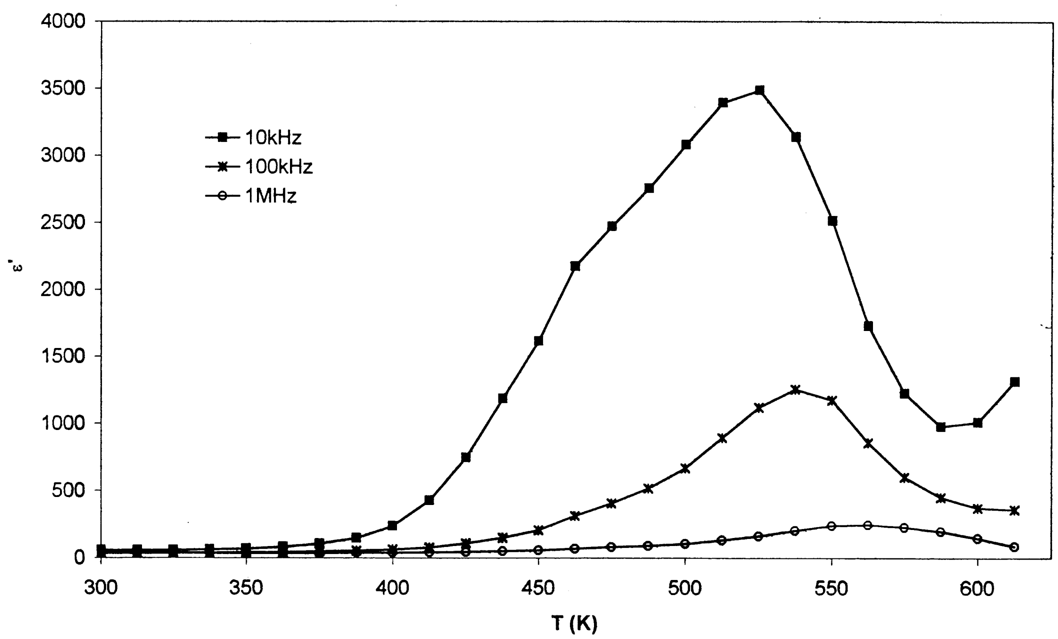

Figure 5. Variation of dielectric constant (e') with temperature for $x = 0{\cdot}8$.

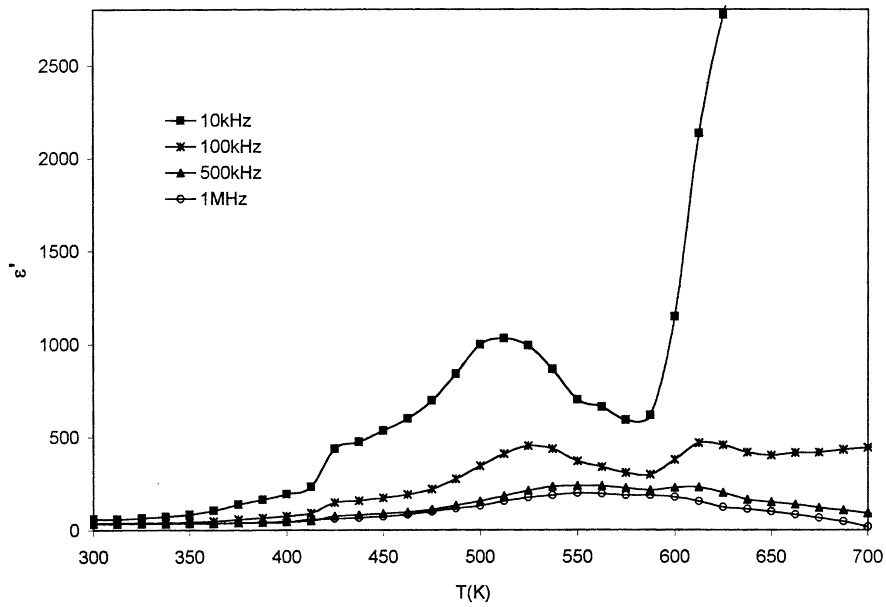

Figure 6. Variation of dielectric constant (e') with temperature for $x = 0{\cdot}6$.

magnetic or in lower temperature region (El Hitti 1996). This is also true in $x = 0{\cdot}6$ sample (figure 8), but an abrupt jump in $s_{a.c.}$ around 430 K is observed for 100 kHz, 500 kHz and 1 MHz frequency. A similar jump in e' for the same sample in e' versus temperature plots at same temperature was observed in figure 6. This marked abrupt changes are similar to abrupt changes in semiconducting properties like d.c. resistivity and thermoelectric power as observed by Noriyuki *et al* (1978). They have ascribed the changes to variation in tetragonality (c/a) and metallic ratio (cation distribution) which are very sensitive to preparative conditions.

4. Conclusions

Dielectric constant and loss decrease rapidly with increasing frequency, then reaches a constant value. Temperature dependence of dielectric constant has abnormally

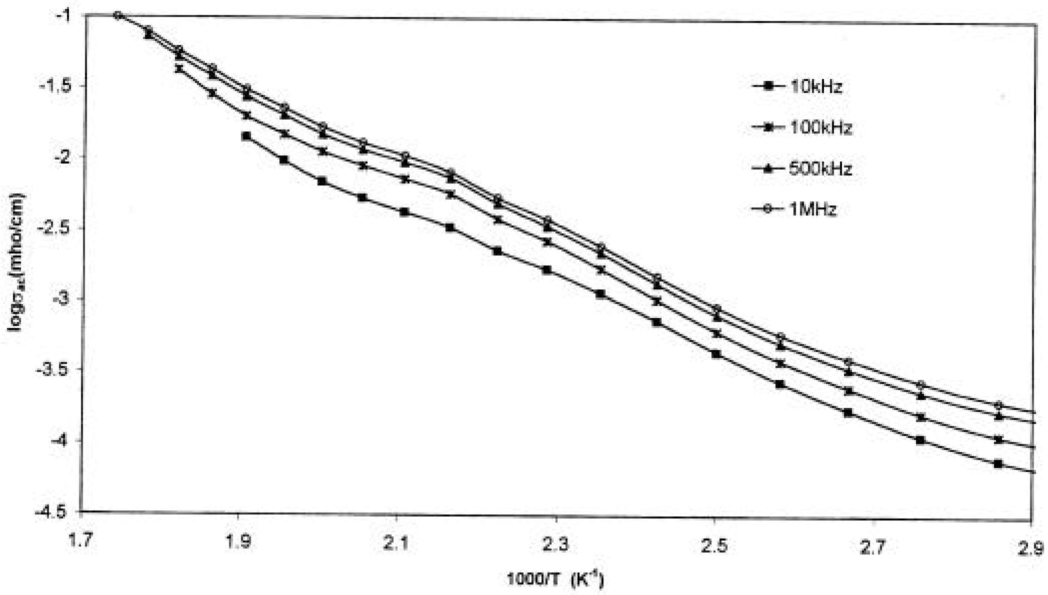

Figure 7. Variation of a.c. conductivity ($s_{a.c.}$) with temperature for $x = 0{\cdot}8$.

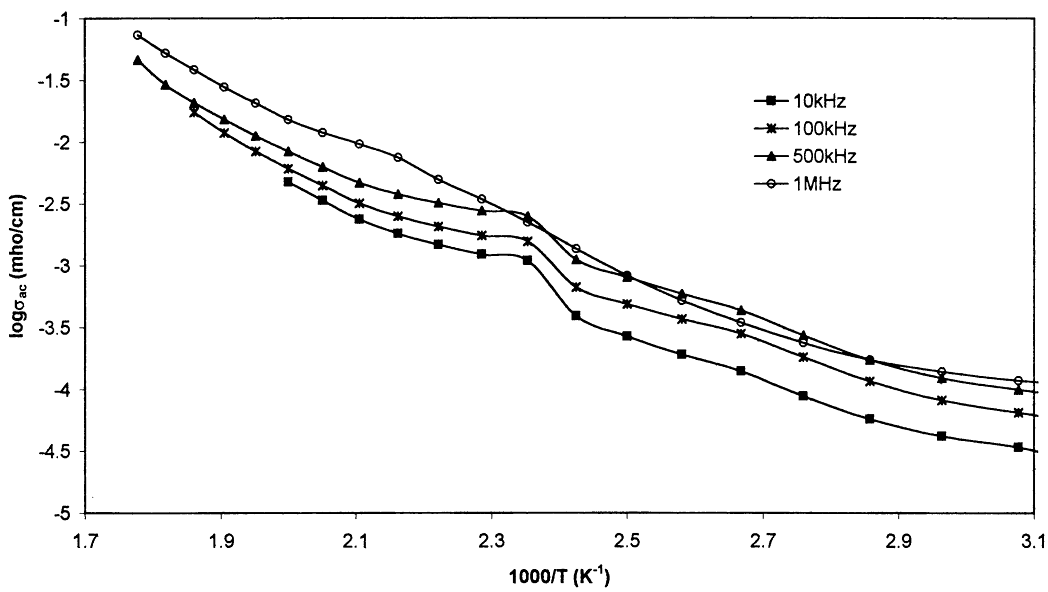

Figure 8. Variation of a.c. conductivity ($s_{a.c.}$) with temperature for $x = 0{\cdot}6$.

high value at curie temperature in $CuFe_2O_4$. The dielectric relaxation is observed and the relaxation frequency shifts towards higher frequency as the temperature increases in non-stoichiometric Cu ferrites ($x = 0{\cdot}8$ and $0{\cdot}6$). The a.c. conductivity is found to be high for higher frequency and shows a trend expected for small polaron hopping.

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