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Compositional, temperature and frequency dependence of dielectric behaviour of zinc substituted copper- ferri-chromates

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Abstract The comprehensive study on compositional, temperature and frequency dependent dielectric properties of $Zn_xCu_{1-x}FeCrO_4$ (x = 0.0, 0.2, 0.4 and 0.6) was carried out by means of a. c. resistivity (ρ_{ac}), dielectric constant (ε') and loss tangent ($\tan\delta$) measurements in the frequency range from 100 Hz to 1 MHz at different temperatures ranging from 40 °C to 500 °C. An abnormal behaviour of ε' as a function of temperature is explained on the basis of contribution of two types of charge carriers in the polarization process. It is found that magnetic ordering does not have marked influence on the dielectric properties. The probable conduction mechanism in the present system is due to electron transition such as $Fe^{2+} \leftrightarrows Fe^{3+}$ and $Cu^{2+} \leftrightarrows Cu^{1+}$ rather than ionization or polaron hopping mechanism.

Introduction

Ferrite materials have attracted attention due to their good magneto-dielectric properties at high frequencies. Ferrites have gained technological importance by virtue of their high resistivity and negligible eddy current losses. The ferrites containing Zn and Mg have range of applications from low frequency to microwave frequency on account of their low cost and high efficiency. The world market of microwave devices is growing at the rate of 20% annually and may cross 9 billion dollars by 2005. In recent times, the polarization studies were further extended to understand and interpret the earlier theories in a microscopic manner relevant to different materials [1–6]. These theories were also extended to interpret the low frequency dielectric properties of ceramic materials that include ferrites. Thus the theory and conclusion put forward by Jonscher [7] were used to interpret the possible mechanism in this class of materials.

Though the number of research articles is available in literature covering various aspects of pure and substituted Cu-less and Cu-containing spinel ferrite systems, we have restricted ourselves to electrical and dielectric properties of Cu-based system substituted with magnetic, non-magnetic cations, as in present case. The dielectric properties by means of dielectric constant and loss tangent for Cu–Zn, Cu–Ni and Cu–Mn ferrites have been studied as a function of composition, frequency and temperature by Rezlescu et al. [3]. The dielectric behaviour of Cr-substituted $CuFe_2O_4$ as a function of frequency and temperature was studied by El Hiti et al. [8]. The observed behaviour has been explained in the light of the fact that the dielectric polarization process is similar to that of conduction and the appearance of the dispersion peak is related to the contribution of two types of charge carriers. The dielectric properties of Cu–Cd ferrites were investigated by Vaingankar et al. [9, 10].

To our knowledge no work has been reported on compositional, temperature and frequency dependent dielectric and a.c. electrical behaviour of Zn-substituted $CuFeCrO_4$. Therefore, aim of the present work is to study the mechanism of dielectric polarization and conduction, which is part of our earlier study on magnetic properties [11, 12], structural properties [13] and d. c. resistivity and thermoelectric power measurement study [14] infrared spectroscopic study [15] and elastic properties [16] of the $Zn_xCu_{1-x}FeCrO_4$ system.

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Experimental details

The powdered samples of $Zn_xCu_{1-x}FeCrO_4$ have been prepared by usual double sintering ceramic technique, with composition x = 0.0, 0.2, 0.4 and 0.6. The details regarding sample preparation and X-ray diffractometry have been given in our earlier communications [11–14].

The samples for electrical measurements were in the form of disc 10 mm in diameter and 3 mm thick and both the faces of each disc sample were polished by rubbing zero grade emery paper, washed in dilute HCl and acetone. Finally, graphite was rubbed on both flat faces of samples on which aluminum foil was also kept for good electrical contacts. The a.c. electrical measurements were carried out at Department of Physics, Sardar Patel University, Vallabh Vidyanagar using Hewlett-Packard (Model 4284 A) made precision LCR meter in the frequency range of 100 Hz–1 MHz at different temperatures ranging from 40 °C to 500 °C.

Results and discussion

Compositional dependence of ε', ρ_{ac} and $\tan\delta$

The variation of dielectric constant (ε') and a.c. resistivity (ρ_{ac}) at selected temperatures (140 °C, 300 °C, 460 °C) and frequencies (10 kHz, 100 kHz, 800 kHz) as a function of Zn-content (x) are shown in Table 1. It is clear from the table that ε' and ρ_{ac} have inverse trend with each other. The a.c. resistivity initially found to increase while dielectric constant found to decrease with increase in Zn-content upto 0.4. Further, with the addition of zinc beyond 0.4, ρ_{ac} decreases while ε' found to increase. These observed variation in both ρ_{ac} and ε' can be explained as follows.

Since both the dielectric constant and electrical conductivity are basically electrical transport properties and their variation with temperature is similar, it may be assumed that the same mechanism is responsible for both the phenomena. Earlier researchers [2, 3, 17] have explained the dielectric behaviour of ferrites with the assumption that the mechanism of dielectric polarization is similar to that of conduction process. They observed that the electron exchange interaction between $Fe^{2+} \leftrightarrows Fe^{3+}$ and $Cu^{2+} \leftrightarrows Cu^{1+}$ ions results in the local displacement of electron in the direction of the externally applied field, which determines the polarization of the ferrites.

The numbers of ferrous (Fe^{2+}) ions play a dominant role in the mechanism of conduction and dielectric polarization. The presence of small amount of Fe^{2+} ions decreases resistivity. The magnitude of electron exchange interaction between Fe^{2+} and Fe^{3+} ions depends upon the concentration of Fe^{2+}/Fe^{3+} present on the crystallographically equivalent states in the lattice, i.e., on B-site. The Fe^{2+} ion concentration is a characteristic property of a given ferrite material and its value depends upon the factors viz. sintering temperature, atmosphere, annealing time, etc. Some amount of Fe^{2+} ions can also be formed due to the possible evaporation of Zn during sintering process [18]. The presence of Fe^{2+} ion which takes part in the electron exchange interaction between Fe^{2+} and Fe^{3+} ions and hence are responsible for the conduction and polarization, is minimum for the sample with x = 0.4. Thus, the highest value of ρ_{ac} and lowest value of ε' for the x = 0.4 sample

Table 1 Dielectric constant (ε') and a.c. resistivity (ρ)(Ω cm) for the $Zn_xCu_{1-x}FeCrO_4$ system

Zn-Content (x)	140 °C		300 °C		400 °C	
	$\varepsilon' \times 10^2$	$\rho \times 10^3$	$\varepsilon' \times 10^2$	$\rho \times 10^3$	$\varepsilon' \times 10^2$	$\rho \times 10^3$
10 kHz						
0.0	522.8	3.840	1900.27	0.483	3300.4	0.276
0.2	310.11	7.060	1091.23	1.043	2041.02	0.577
0.4	4.70	318.984	9.06	163.271	16.63	84.102
0.6	12.12	123.038	19.60	52.275	29.70	25.409
100 kHz						
0.0	268.69	0.980	590.12	0.120	951.00	0.100
0.2	159.48	1.580	338.82	0.381	587.73	0.194
0.4	3.40	58.407	5.32	30.005	8.88	16.144
0.6	39.94	6.674	48.14	4.409	33.41	5.043
800 kHz						
0.0	352.7	0.640	284.43	0.152	351.06	0.080
0.2	110.02	0.808	161.55	0.215	217.72	0.113
0.4	3.02	18.465	3.73	9.007	4.97	5.207
0.6	105.91	0.131	114.13	0.119	108.73	0.140

can be attributed to the less formation of Fe^{2+} ions. With further increase in Zn-content (x) beyond 0.4, ρ_{ac} goes on decreasing, which is due to increasing concentration of Fe^{3+} ions on B- site as the content of zinc increases. Since the dielectric constant is roughly inversely proportional to resistivity, dielectric constant shows an increasing trend for zinc content beyond 0.4.

The resistivity (ρ_{ac}) increases with increase in zinc content (x) for x = 0.0–0.4. This happens because the replacement of Cu^{2+} by Zn^{2+} in $Zn_xCu_{1-x}FeCrO_4$ system dilutes conduction through the octahedral site. The incorporation of Zn^{2+} ions, which do not participate in the conduction process, limits the degree of Fe^{2+} + -Cu^{2+} $\leftrightarrows$ Fe^{3+} + Cu^{1+} conduction that occurs. Thus, the efficient method of curtailing the conduction process is the replacement of the effective ion (Cu^{2+}–Cu^{1+}) by less effective ones (Zn^{2+}).

The compositional dependence of the loss tangent (tanδ) at selected frequencies (10 kHz, 100 kHz, 800 kHz) and temperatures (140 °C, 300 °C, 400 °C) is presented in Table 2. It is clear that the loss tangent decreases as the Zn-content increases. The results can be explained on the basis of the fact that the conduction mechanism can be expressed in terms of electron hopping between Cu^{2+} $\leftrightarrows$ Cu^{1+} and Fe^{2+} $\leftrightarrows$ Fe^{2+} in the octahedral sites for *n*-type ferrites and in terms of hole hopping for *p*-type ferrites [19]. Hence, on the substitution of Zn^{2+} ions in the system according to cation distribution determined earlier by X-ray intensity calculations [13], number of Fe^{3+} ions increases but number of Cu^{2+} ions decreases on B-site. Though total number of ions between which the hopping conduction mechanism takes place remains constant, decrease in dielectric loss suggested that responsible or dominated conduction mechanism is electron exchange between Cu^{2+} and Cu^{1+} rather than Fe^{2+} and Fe^{3+} in the system.

Table 2 Loss tangent (tanδ) for $Zn_xCu_{1-x}FeCrO_4$ system

Zn-Content (x)	140 °C tanδ	300 °C tanδ	400 °C tanδ
10 kHz			
0.0	1.011	1.94	2.07
0.2	0.822	1.58	1.63
0.4	1.199	1.21	1.28
0.6	1.212	1.755	2.38
100 kHz			
0.0	0.89	1.76	1.98
0.2	0.71	1.39	1.58
0.4	0.90	1.12	1.25
0.6	0.67	0.85	1.07
800 kHz			
0.0	0.036	0.79	1.15
0.2	0.253	0.65	0.91
0.4	0.402	0.067	0.87
0.6	1.620	1.66	1.48

Temperature and frequency dependence of dielectric parameters

The temperature dependence of dielectric constant (ε') at different applied frequency for the composition with x = 0.2, 0.4 and 0.6 is shown in Fig. 1a. It is seen that absolute value of ε' decreases with increasing frequency within the temperature range studied, exhibiting normal ferrimagnetic behaviour. A more dielectric dispersion is observed at lower frequency region and it remains almost independent of applied external field at higher frequency side. The dielectric dispersion at lower frequency region is due to Maxwell–Wagner interfacial type of polarization [20, 21]. The decrease in dielectric constant with increase in frequency is due to lag of hopping frequency of electron between Cu^{2+}–Cu^{1+} and Fe^{3+}–Fe^{2+} ions against the frequency of external applied ac field. Beyond certain limit of external field electron hopping becomes independent of it. The observed peak at 370 °C for x = 0.0, 400 °C for x = 0.2, 440 °C for x = 0.4 and 454 °C for x = 0.6 cannot be correlated with ferrimagnetic to paramagnetic transition (Neel temperature or Tc) as earlier study [13] found it at 298 °C, 239 °C, 143 °C and 76 °C, respectively. This suggested that occurrence of peak is not due to magnetic transition, it may be due to structural transition or some sort of electrical transition. It is important to note that peak temperature for all the compositions is independent of frequency. In other studies [3] it has been reported that the peak temperature shifted towards higher temperature on increasing frequency. Another striking feature of these compositions is that on increasing frequency the peak intensity gets reduced. The maximum intensity has been observed at the frequency of 100 Hz and further increase in frequency reduced the peak intensity. This behaviour can be explained on the basis of resonance between the electron hopping frequency and the frequency of externally applied electric field.

The variation of dielectric constant (ε') with frequency (f) in the range 100 Hz–1 MHz, at different temperatures for the typical samples with x = 0.2, 0.4 and 0.6 is shown in Fig. 1b. The variation of ε' with frequency reveals the dispersion due to Maxwell–Wagner [20, 21] type interfacial polarization which is in agreement with Koops phenomenological theory [10]. The ε' decreases with increasing frequency reaching a constant value for all the compositions.

According to Rabinkin and Novikova [17], the polarization in ferrites is through a mechanism similar to the conduction process. By electron exchange between

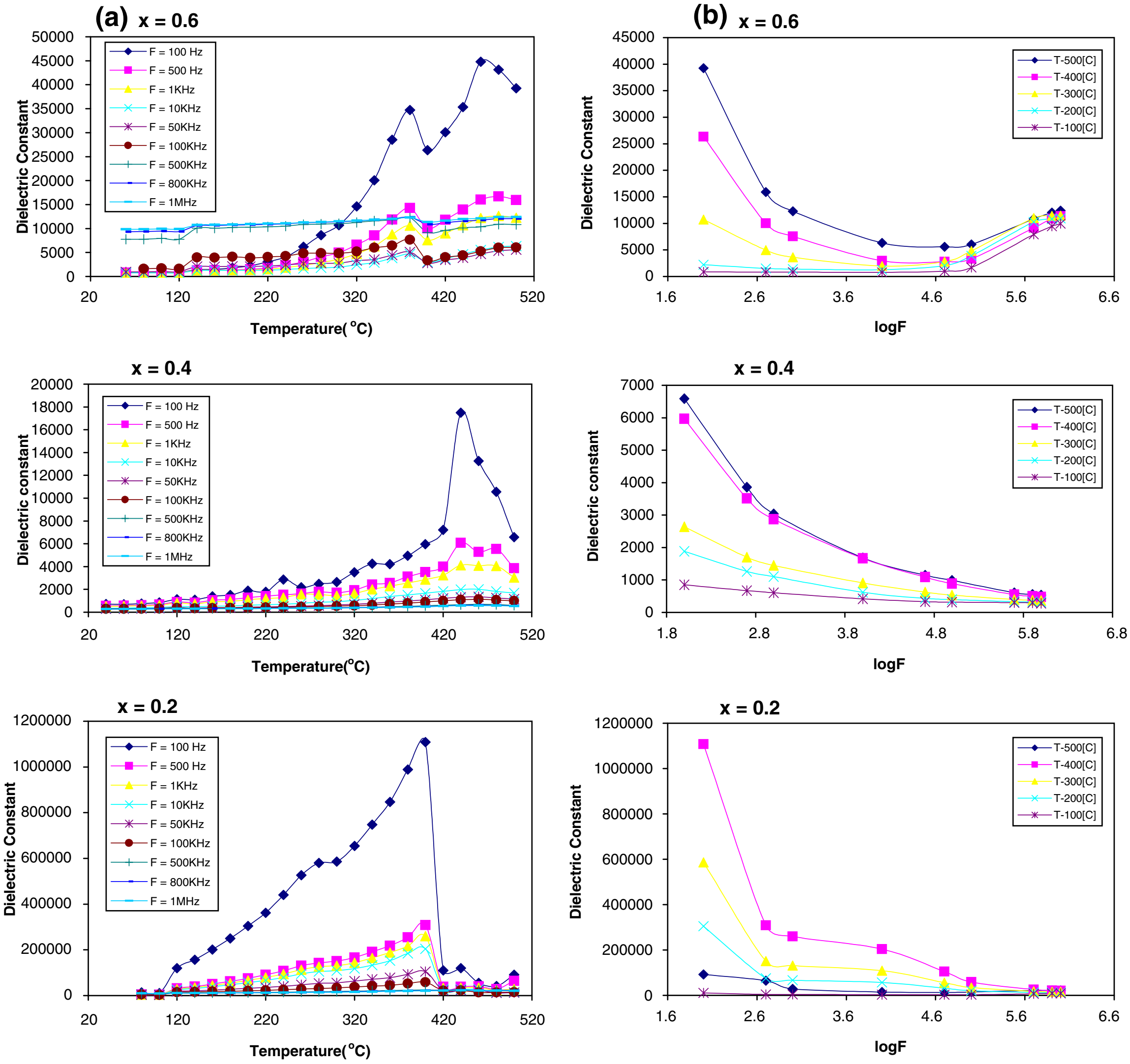

Fig. 1 (**a**) Temperature dependence of dielectric constant for the compositions with x = 0.2, 0.4 and 0.6. 1 (**b**) Frequency dependence of dielectric constant for the compositions with x = 0.2,0.4 and 0.6

Fe^{2+}–Fe^{3+} and Cu^{1+}–Cu^{2+} one obtains local displacement of electrons in the direction of the applied field and these electrons determine the polarization. The polarization decreases with increase in frequency and then reaches a constant value due to the fact that beyond a certain frequency of external field the electron exchange can not follow the alternating field.

The large values of ε' at lower frequency are due to the predominance of the species like Fe^{2+}, Cu^{1+} ions, interfacial dislocation pile ups, oxygen vacancies, grain boundary defects etc. [20, 21]. While the decrease in ε' with frequency is obvious because of the fact that only species contributing to polarisability is bound to show lagging behind the applied field at higher frequencies.

Koops [10] gave the phenomenological theory for the dielectric dispersion in ferrites at low frequencies. Koops was among the first to study the frequency dependence of dielectric constant and dispersion of ferrites. He interpreted the results by considering the dielectric as an inhomogeneous medium of a Maxwell–Wagner type. In the present system the dispersion in ε' with frequency can be attributed to the Maxwell–Wagner type interfacial polarization.

The observed abnormal behaviour of temperature dependence of dielectric constant at different frequency can be explained in the light of the Rezlescu model [3]. According to this model in the ferrites containing copper, just like present system under investigation, an exchange $Cu^{1+} \leftrightarrows Cu^{2+}$ exists. There is an amount of Cu^{1+} ions, which causes an important modification of the electrical and magnetic properties of ferrites [22, 23]. It is known that the copper ferrites exhibit *p*-type electrical conduction, obtained by removing holes. The appearance of *p*-carriers can be ascribed to the reduction tendency of the $Cu^{1+} \leftrightarrows Cu^{2+}$ ions at about 900–950 °C during the sintering process [24]. They assumed that for the formation of each pair of Cu^{1+} ions an oxygen atom is eliminated, an equivalent quantity of metal ions must occupy the interstitial sites. The simple presence of Cu^{1+} ions does not explain the *p*-conduction since they act as *n*-carriers. But by assuming that the interstitial cations act as acceptor centers, the *p*-carriers may be identified as holes on oxygen ion sites. They also supposed that the local displacements of *p*-carriers in the direction of the external electric field take part in the polarization.

The abnormal dielectric behaviour of the ferrites containing copper is due to the collective contribution of the two types of carriers, *p*- and *n*-, to the polarization. The contribution of the *p*-type carriers is lower than that obtained by the electronic exchange and it has opposite sign. In addition, since the mobility of *p*-type carriers is lower than that of *n*-type carriers, their contribution to polarization will decrease more rapidly. By summing up the contributions of both types of carriers to the polarization, one can expect the behaviour of the dielectric constant as a function of frequency as shown in Fig. 2.

The abnormal behaviour of the temperature dependence of ε' (Fig. 1a) is probably due to the same reason. The contributions of the two types of carriers, *n*- and *p*- to polarization depend on temperature. Since the influence of temperature on the electronic exchange $Fe^{2+} \leftrightarrows Fe^{3+}$ and $Cu^{2+} \leftrightarrows Cu^{1+}$ is more pronounced than that on the displacements of *p*-carriers, ε' will increase rapidly with increasing temperature. But, above certain temperature, which naturally depends on the copper content, the *p*-transitions become important and thus ε' will begin to decrease as a result of the two contributions with opposite signs. It is interesting to note that the maximum of the $\varepsilon'(T)$ curve does not shift with increasing frequency (Fig. 1a), this suggested that the hopping of carriers are not affected by the external frequency.

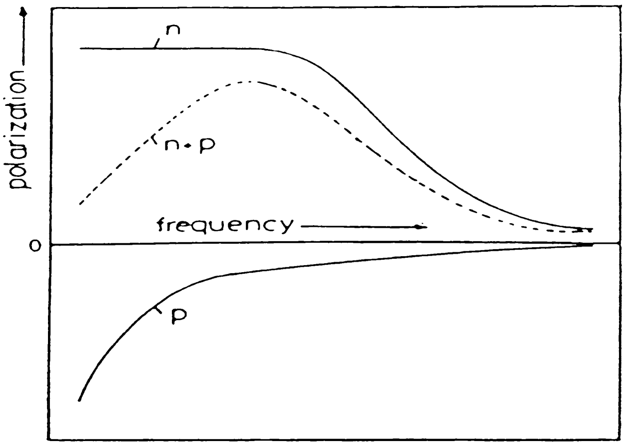

Fig. 2 Contributions of *n*- and *p*-carries to polarization (Rezlescu model)

Figure 3a correlates the a. c. resistivity in terms of $\log_{10}\rho_{ac}$ and the reciprocal of the absolute temperature for different frequencies. The general feature of the figures is the appearance of the phase transition at about ≈400 ± 50 °C. The figures also show that the resistivity of the samples is decreased by increasing both applied frequency and measuring temperature. The change of slope at Curie temperature is a general observation in ferrites, but in present case the temperature at which change in slope takes place is not corresponding to Curie temperature. Furthermore, no shifting of Curie temperature has been observed on increasing frequency as in the case of Co–Zn ferrites [25]. The values of the activation energy was calculated from the experimental data at different frequency for straight line portion of the curves using Arrhenius relation,

$$\rho = \rho_o \exp(\Delta E/kT)$$

where ΔE is the activation energy in eV, which according to Verway and De Boer [26] is the energy needed to release an electron from the ion for jumping to the neighboring ion and participate in conduction processes, ρ_o is a constant, k is the Boltzmann's constant.

The activation energies calculated at different frequencies for all the compositions is of the order of ~0.2 eV, is greater than the ionization energy 0.1 eV of donors or accepter but smaller than the polaron-hopping energy 0.5 eV. This is suggests that the conduction phenomenon in the present system is due to electron transition such as $Fe^{3+} \leftrightarrows Fe^{2+}$,$Cu^{2+} \leftrightarrows Cu^{1+}$.

In ferrite samples under investigation, the surface resistivity is lower than that of the bulk of the material due to the following reasons: The Zn-ions have been evaporated from the surface layer at high sintering temperature and as a result, ferrous ions (Fe^{2+}) have been formed and occupy the B-sites. During heating, some of Fe^{2+} ions have been transformed to Fe^{3+} ions and generate electrons, which participate in conduction mechanism [27]. The simultaneous presence Fe^{2+} and Fe^{3+} ions on equivalent lattice sites (B-sites), may cause the low surface resistivity. The large number of electrons that are generated during the transformation process of valences of both Fe^{2+} and Cu^{2+} to Fe^{2+} and Cu^{1+} respectively will raise the conduction state of the system. This means that the resistivity of the system will decrease with increasing temperature due to generation of such electrons.

Figure 3b shows the variation of ac resistivity ($\log_{10}\rho_{ac}$) with frequency measured at different temperatures. All the samples show decrease in ρ_{ac} with the increase in frequency from 100 Hz to 1 MHz, which is the normal

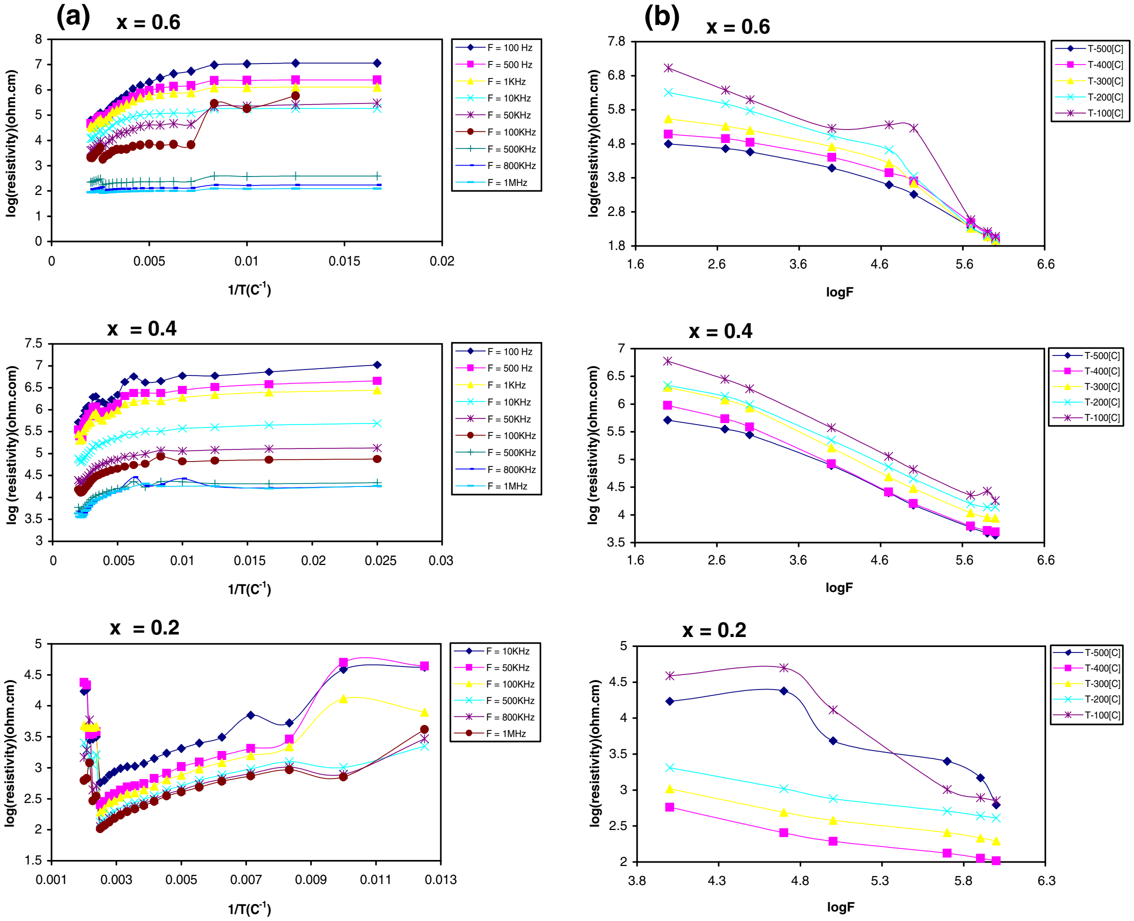

Fig. 3 (**a**) Temperature dependence of a. c. resistivity for the compositions with x = 0.2, 0.4 and 0.6. 3 (**b**) Frequency dependence of a. c. resistivity for the compositions with x = 0.2, 0.4 and 0.6

behaviour of ferrites. The ρ_{ac} remains constant and becomes negligibly small at high frequencies above 10^5 Hz. It is also clear from these figures that the dispersion is more at low-frequency side with different magnitude, which could be due to the difference in the concentration of Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu^{1+} ions in the different samples.

The conduction mechanism in the ferrites can be explained on the basis of hopping of charge carriers between Fe^{3+}–Fe^{2+} and Cu^{2+}–Cu^{1+} ions on octahedral sites. The increase in frequency of the applied field enhances the hopping of charge carriers resulting in an increase in the conduction process thereby decreasing the resistivity. At high frequency ρ_{ac} becomes negligibly small and remains constant because the hopping frequency no longer follows the external applied field and lags behind it.

Conclusions

The results of this comprehensive study on compositional, temperature and frequency dependence of dielectric parameters of $Zn_xCu_{1-x}FeCrO_4$ spinel ferrite system can be summarized as follows:

(i) The ferrites containing copper exhibit an abnormal behaviour of the dielectric constant ε' as a function of temperature and this can be explained on the basis of contribution of two types of carriers *n*- and *p*- in the polarization process.

(ii) The occurrence of peak at the temperature other than Neel temperature in ε' versus T curves indicates that magnetic ordering does not have marked influence on the dielectric properties of the present system.

(iii) The conduction phenomenon in the present system is due to electron transition such as $Fe^{2+} \leftrightarrows Fe^{3+}$ and Cu^{2+}–Cu^{1+} rather than ionization or polaron-hopping mechanism.

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