

## Electrical Conductivity and Dielectric Properties of Copper Doped Nickel Ferrites Prepared By Double Sintering Method

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### Abstract

Ni-Cu ferrites of different compositions were prepared by a conventional double sintering ceramic technique. Electrical conductivity of Ni-Cu ferrites of various compositions have been investigated from room temperature to well beyond the Curie temperature. Composition and frequency dependent dielectric properties of mixed Ni-Cu ferrites have been measured at room temperature in the frequency range 1 to 13 MHz using a HP 4192A impedance analyser. Plots of  $\log(\sigma T)$  versus  $10^3/T$  are linear and have shown a transition near the Curie temperature. The activation energy in the ferromagnetic region is in general less than that in the paramagnetic region. Plots of dielectric constant ( $\epsilon'$ ) versus frequency have shown a normal dielectric behavior of spinel ferrites. The frequency dependence of dielectric loss tangent ( $\tan \delta$ ) is found to be abnormal, giving a peak at certain frequency for all mixed Ni-Cu ferrites. An attempt is made to explain the conduction mechanism in Ni-Cu ferrites and a qualitative explanation is given for the composition and frequency dependence of the dielectric constant and dielectric loss tangent.

**Key words:** Ni-Cu ferrites, Electrical conductivity, Dielectric properties, Activation energy, Curie temperature, Electrical resistivity,  $Fe^{2+}$  concentration.

### 1. Introduction

The copper substituted nickel ferrites find a variety of applications at radio and microwave frequencies [1, 2]. Particularly no information is available on electrical conductivity and dielectric properties of Ni-Cu ferrites prepared by a conventional double sintering ceramic technique in the literature. Moreover, there is a need for a thorough study of electrical and dielectric properties of these ferrites possessing desired application in microwave devices. The dielectric behavior of the Mn-Zn-Gd ferrites as a function of frequency and composition was reported by Ravi Kumar and Ravinder [3]. A strong correlation between conduction mechanism and the dielectric behavior of ferrites has been reported by Iwauchi [4]. The dielectric properties of Mn-Zn-Er ferrites were investigated by Ravinder and Vijaya Kumar [5]. The dielectric behavior of Ni-Zn-Gd ferrites was studied by Ravinder *et al* [6]. With a view of understanding the dielectric phenomena in mixed Ni-Cu ferrites, we have undertaken a systematic study of the electrical conductivity as a function of composition and temperature and the dielectric behavior as a function of frequency and composition.

### 2. Experimental details

Polycrystalline samples of nickel-copper ferrites having the chemical compositions  $Ni_{1-x}Cu_xFe_2O_4$ , where  $x = 0.2, 0.4, 0.6$  and  $0.8$  were prepared by the conventional double sintering ceramic technique. The samples were pre-sintered for 6 hr in air at  $800^\circ C$ . Final sintering of the specimens was carried out for 6 hr at  $1200^\circ C$ . The electrical conductivity measurements were carried out by two-probe method [7]. The dielectric measurements were made from 1-13 MHz by a HP 4192 A impedance analyser.

### 3. Results and discussion

Experimental data for the mixed Ni-Cu ferrites are given in Table-1, which includes the compositional formulae of all the ferrites under investigation and the values of electrical conductivity at room temperature. It can be seen from the table that the values of electrical conductivity are decreased with the increase of copper content from 0.2 to 0.8. This observation is in agreement with the result reported by Rezlescu *et al.* [8], who found that the resistivity of Li-Zn ferrites increased with the increase of zinc content. Among all the Ni-Cu ferrites the specimen with the composition  $Ni_{0.2}Cu_{0.8}Fe_2O_4$  exhibits highest value of electrical resistivity ( $\rho = 1.21 \times 10^7$  Ohm. cm).

Table-1: Electrical conductivity data of mixed Ni-Cu ferrites at room temperature.

Sl. No.	Ferrite composition	Electrical conductivity( $\sigma$ ) ( $\text{Ohm}^{-1}\text{Cm}^{-1}$ )	Seebeck coefficient (S) ( $\mu\text{v/K}$ )
1	$\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$	$2.82 \times 10^{-5}$	-424
2	$\text{Ni}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4$	$4.68 \times 10^{-6}$	-342
3	$\text{Ni}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$	$6.78 \times 10^{-7}$	-312
4	$\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Fe}_2\text{O}_4$	$8.26 \times 10^{-8}$	-278

The values of the Seebeck coefficient of mixed Ni-Cu ferrites at room temperature are calculated from the observed values of thermo emf, and are also included in Table-1 to facilitate the discussion. It can be seen from the table that the sign of the Seebeck coefficient is negative for all the ferrites under investigation which indicates that the predominant conduction mechanism in these ferrites is of n-type semiconductors.

The temperature dependence of electrical conductivity of mixed Ni-Cu ferrites of various compositions has been investigated from room temperature to well beyond the Curie temperature. Plots of  $\log(\sigma T)$  versus temperature ( $10^3/T$ ) are shown in Figs. 1-4. It can be seen from the figures that the value of  $\log(\sigma T)$  increases linearly with increasing temperature up to a certain temperature  $T_c(\text{K})$  at which a change of slope has occurred. The Curie temperatures for the Ni-Cu ferrite specimens under investigation have been determined by using a gravity method [9].

The ferrite specimen is made to attach itself to a bar magnet due to the magnetic attraction and the combination is suspended inside a furnace, where temperature can be varied up to 1000 K. As the temperature of the system is increased, at a particular temperature the specimen loses its spontaneous magnetization and becomes paramagnetic. This temperature is taken as the approximate Curie point of the specimen. The temperature of the specimen is measured by a chromel-alumel thermocouple in the furnace.

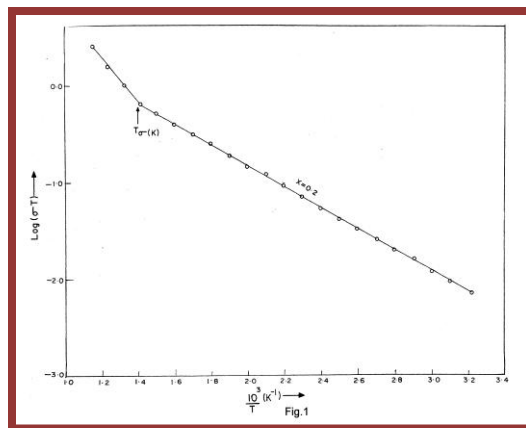


Fig.1: Plot of  $\log(\sigma T)$  versus temperature for  $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$  ferrite.

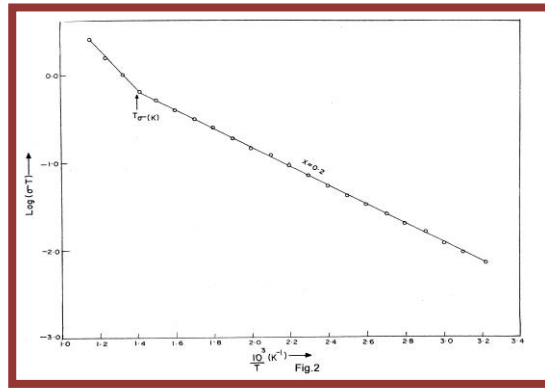


Fig.2: Plot of  $\log(\sigma T)$  versus temperature for  $\text{Ni}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4$  ferrite.

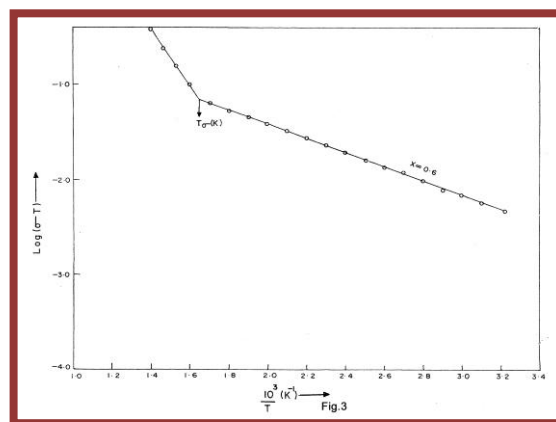


Fig.3: Plot of  $\log(\sigma T)$  versus temperature for  $\text{Ni}_{0.4}\text{Cu}_{0.6}\text{Fe}_2\text{O}_4$  ferrite.

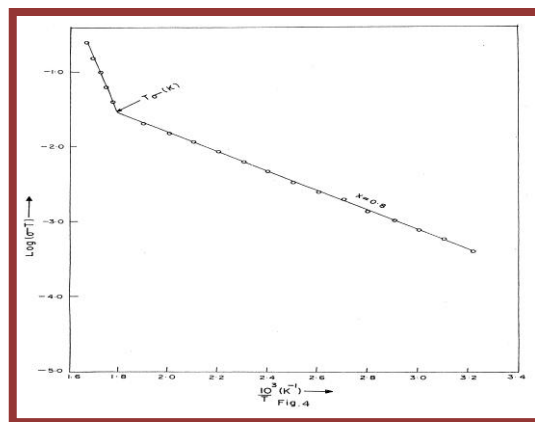


Fig.4: Plot of  $\log(\sigma T)$  versus temperature for  $\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Fe}_2\text{O}_4$  ferrite.

The transition temperatures  $T_{\sigma}(\text{K})$  are given in Table-2 along with the Curie temperatures  $T_c(\text{K})$  determined by gravity method. It can be seen from Table-2 that the transition temperature  $T_{\sigma}(\text{K})$  corresponds to the magnetic transition since it is nearer to the observed Curie temperature  $T_c(\text{K})$  for all the ferrites under investigation.

Table-2: Transition temperatures and activation energies for Ni-Cu ferrites.

Sl. No	Ferrite composition	T <sub>c</sub> (K)	T <sub>o</sub> (K)	Activation energy		ΔE=E <sub>2</sub> -E <sub>1</sub>	Resistivity(ρ) (Ohm.Cm)
				Ferri-magnetic region (E <sub>1</sub> ) eV	Para-magnetic region (E <sub>2</sub> ) eV		
1	Ni <sub>0.8</sub> Cu <sub>0.2</sub> Fe <sub>2</sub> O <sub>4</sub>	709	710	0.34	0.62	0.28	3.55x10 <sup>4</sup>
2	Ni <sub>0.6</sub> Cu <sub>0.4</sub> Fe <sub>2</sub> O <sub>4</sub>	674	672	0.29	0.58	0.29	2.14x10 <sup>5</sup>
3	Ni <sub>0.4</sub> Cu <sub>0.6</sub> Fe <sub>2</sub> O <sub>4</sub>	609	608	0.26	0.49	0.23	1.48x10 <sup>6</sup>
4	Ni <sub>0.2</sub> Cu <sub>0.8</sub> Fe <sub>2</sub> O <sub>4</sub>	558	559	0.24	0.44	0.20	1.21x10 <sup>7</sup>

Fig.5 shows the variation of Curie temperature with copper content. It can be noted from the figure that the value of T<sub>c</sub>(K) decreases with the increase of copper content. Similar kind of behavior is found in case of Ni-Cu-Zn ferrites prepared by citrate precursor method investigated by Mukesh C. Dimri *et. al* [10]. The decrease of Curie temperature with increase of copper content can be explained on the basis of the number of magnetic ions present in the two sub-lattices and their mutual interactions. As Fe<sup>3+</sup> ions are gradually replaced by copper ions, the number of magnetic ions begins to decrease at both sides, which also weakens the strength of all exchange interactions of the type Fe<sub>A</sub><sup>3+</sup>-O<sup>2-</sup>-Fe<sub>B</sub><sup>3+</sup>. Thus, the thermal energy required to offset the spin alignment decreases, thereby decreasing the Curie temperature. A similar decrease of the T<sub>c</sub>(K) with the composition was also observed by several investigators in various ferrite systems [11-13].

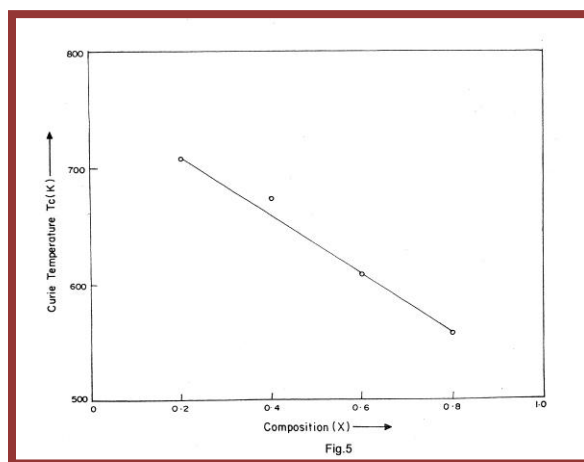


Fig.5: Variation of Curie temperature with copper content.

The existence of the kinks or transitions in the neighborhood of the Curie point has been explained by the theory given by Irkin and Turov [14]. It was shown theoretically that on passing through the Curie point a change must occur in the gradient of the straight line [15] and the magnitude of effect depends on the exchange interaction between the outer and inner electrons which alters at the Curie point. The experimental observation of the transition near the Curie point in the case of mixed Ni-Cu ferrites is thus in conformity with the theory developed by Irkin and Turov [14]. Similar transitions in the neighborhood of the Curie point have also been observed by Lanje and Kulkarni in Ca-La [16] ferrites and Ravinder in the case of Cu-Cd ferrites [17].

The activation energies in the ferrimagnetic region and paramagnetic region are calculated from the slopes of  $\log(\sigma T)$  versus  $(10^3/T)$  and presented in Table-2. The values of activation energy decrease with increase of copper content. It can be seen from the table that the activation energy in the paramagnetic region is higher than that in the ferrimagnetic region. This result is in agreement with the theory developed by Irkin and Turov [14]. Similar results have been observed in the case of Li-Ti [18] and Li-Mg [19] ferrites. The kink will be larger for cases in which there is a stronger exchange interaction between the outer and inner electrons. The size of this kink can be smaller or larger in various ferrites depending on their structural peculiarities, and also the value of electrical resistance. The earlier experiments have shown that the larger kinks are characteristic of ferrites which have small specific resistance because in these materials the activation energy is comparable with the magnitude of the energy of the spontaneous magnetization which is 'released' as a result of the magnetic transition.

The magnitude of the kink as determined by the difference between the activation energies in ferrimagnetic and paramagnetic regions ( $\Delta E$ ) is given in column-6 of Table-2. The values of resistivity for the Ni-Cu ferrites of different compositions which are under investigation are furnished in the column-7 of Table-2. An inspection of these two columns reveals that  $\Delta E$  decreases as resistivity increases. Generally, the change of slope is attributed to change in conductivity mechanism. The conduction at lower temperature (< below Curie temperature) is due to hopping of electrons between  $Fe^{2+}$  and  $Fe^{3+}$  ions, whereas at higher temperature (> above Curie temperature) it is due to polaron hopping [20-23]. The calculated activation energies in the paramagnetic region ( $E_2$ ) are greater than 0.40 eV which clearly suggest that the conduction is due to polaron hopping.

The room temperature values of the dielectric constant ( $\epsilon'$ ), dielectric loss tangent ( $\tan \delta$ ) and complex dielectric constant ( $\epsilon''$ ) of mixed Ni-Cu ferrites are given in Table-3. The values of electrical conductivity ( $\sigma$ ) and  $Fe^{2+}$  concentration were also included in the table to facilitate discussion. It can be seen from the table that the  $\epsilon'$ ,  $\tan \delta$  and  $\epsilon''$  of the mixed Ni-Cu ferrites decrease with the decrease of concentration of  $Fe^{2+}$  ions. Among all the ferrites, the specimen with the composition  $Ni_{0.8}Cu_{0.2}Fe_2O_4$  exhibits the highest value of dielectric constant, dielectric loss tangent and complex dielectric constant.

Table-3: Composition dependence of room temperature dielectric data for Ni-Cu ferrites at 1 MHz.

S. No	Ferrite composition	$\epsilon'$	Tan $\delta$	$\epsilon''$	$\sigma (\Omega^{-1}.cm^{-1})$	$Fe^{2+}$ concentration (%)
1	$Ni_{0.8}Cu_{0.2}Fe_2O_4$	428	0.96	411	$2.82 \times 10^{-5}$	0.99
2	$Ni_{0.6}Cu_{0.4}Fe_2O_4$	394	0.79	311	$4.68 \times 10^{-6}$	0.92
3	$Ni_{0.4}Cu_{0.6}Fe_2O_4$	312	0.62	193	$6.78 \times 10^{-7}$	0.84
4	$Ni_{0.2}Cu_{0.8}Fe_2O_4$	254	0.54	137	$8.26 \times 10^{-8}$	0.62

The dielectric studies of Ba-Co-Cu ferrites as a function of composition and frequency was investigated by Hongguo *et al* [24]. Ranga Mohan *et al* [25] have investigated the dielectric behavior of Ni-Zn ferrites as a function of temperature and frequency. Iwauchi [4] reported a strong correlation between the conduction mechanism and the dielectric behavior of the ferrites starting with the supposition that the mechanism of the polarization process in ferrites is similar to that of the conduction process. They observed that the electronic exchange between  $Fe^{2+} \leftrightarrow Fe^{3+}$  results in local displacement determining the polarization of the ferrites.

A similar explanation is proposed for the composition dependence of the dielectric constants of the ferrites under investigation. It can be observed from the Table-3 that the composition  $Ni_{0.8}Cu_{0.2}Fe_2O_4$  has the maximum divalent iron ion concentration among all the mixed Ni-Cu ferrites. Correspondingly the dielectric constant for this specimen has a value of 428 at 1 MHz. This high value can be explained on the basis of the fact that it has maximum number of ferrous ions whose exchange  $Fe^{2+} \leftrightarrow Fe^{3+}$  gives rise to maximum dielectric polarization. Table-3 reveals that the variation of the dielectric constant of Ni-Cu ferrites runs parallel to the variation of available ferrous ions on octahedral sites. It is significant to note that  $Ni_{0.2}Cu_{0.8}Fe_2O_4$  which has the lowest ferrous ion concentration, possesses the lower dielectric constant. It is also pertinent to mention that the variation of electrical conductivity with composition (Table-3) runs parallel to the variation of ferrous ion concentration. Thus, it

is the number of ferrous ions on the octahedral sites that play a predominant role in the processes of conduction as well as dielectric polarization. This result is in agreement with the assumption made by Rabinkin and Novikova [26].

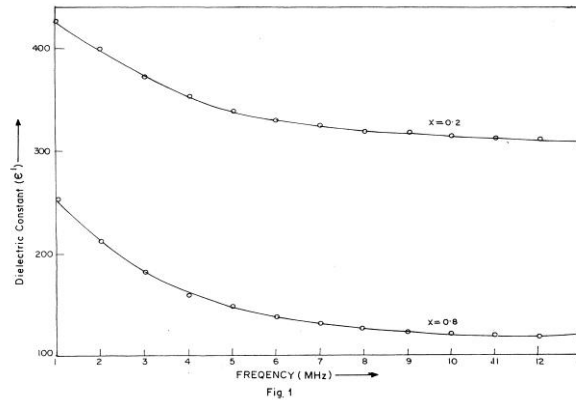


Fig.6: Plot of dielectric constant ( $\epsilon'$ ) versus frequency for  $\text{Ni}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$  (where  $x=0.2$  and  $0.8$ ).

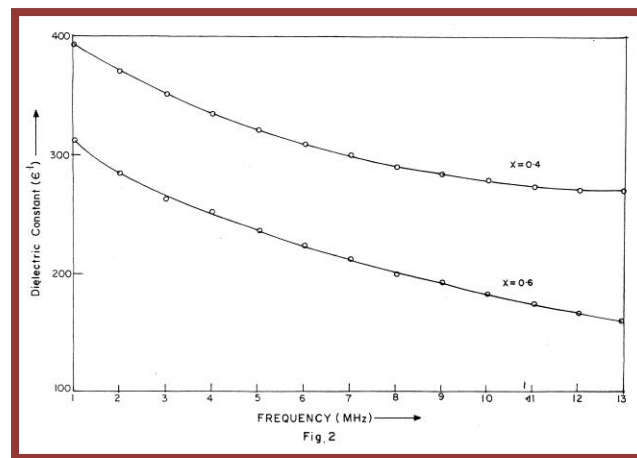


Fig.7: Plot of dielectric constant ( $\epsilon'$ ) versus frequency for  $\text{Ni}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$  (where  $x=0.4$  and  $0.6$ ).

The variation of dielectric constant as a function of frequency for mixed Ni-Cu ferrites for different compositions is shown in Figs. 6 and 7. It can be seen from the figures that the value of dielectric constant decreases continuously with increasing frequency. The decrease of dielectric constant with increase of frequency of the applied electric field can also be explained on the basis of Koop's theory, which assumes that the ferrites are made up of well conducting grains separated by a thin layer of poorly conducting grain boundaries [9, 27-29]. The dispersion of dielectric constant is maximum for  $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$ . The decrease of dielectric constant with increase of frequency as observed in the case of mixed Ni-Cu ferrites is a normal dielectric behavior. This normal dielectric behavior was also observed by several investigators [30-33]. The normal dielectric behavior of spinel ferrites was explained by Rezlescu and Rezlescu [34]. Following their work, the dependence of the dispersion of the dielectric constant on composition can be explained. The observation that  $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$  shows a maximum dielectric dispersion among all the mixed Ni-Cu ferrites may be explained on the basis of the available ferrous ions on octahedral sites. In the case of  $\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$  the ferrous ion content is higher than that in other mixed Ni-Cu ferrites. As a consequence, it is possible for these ions to be polarized to the maximum possible extent. Further, as the frequency of the externally applied electric field increases gradually, and though the same number of ferrous ions is present in the ferrites material, the dielectric constant ( $\epsilon'$ ) decreases from 428 at 1 MHz to 330 at 13 MHz. This reduction occurs because beyond a certain frequency of the externally applied electric field the electronic exchange between ferrous and ferric ions i.e.  $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$  can not follow the alternating field. The variation of the dispersion of  $\epsilon'$  with composition can also be explained on the same lines as above.

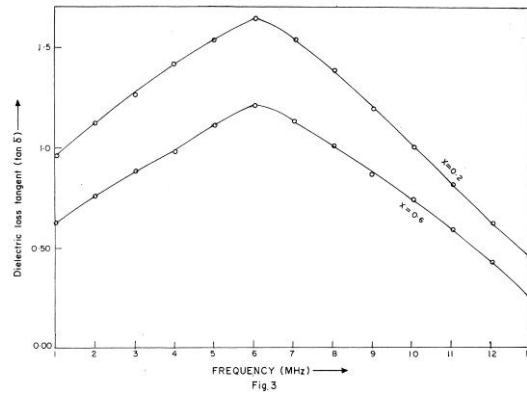


Fig.8: Plot of dielectric loss tangent ( $\tan \delta$ ) versus frequency for  $Ni_{1-x}Cu_xFe_2O_4$  (where,  $x=0.2$  and  $0.6$ ).

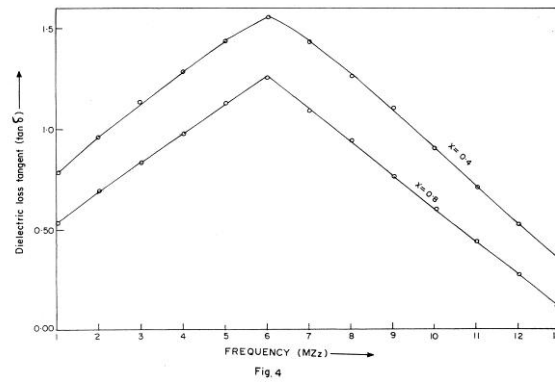


Fig.9: Plot of dielectric loss tangent ( $\tan \delta$ ) versus frequency for  $Ni_{1-x}Cu_xFe_2O_4$  (where  $x=0.4$  and  $0.8$ ).

The variation of  $\tan \delta$  with frequency for Ni-Cu ferrites is shown in Figs. 8 and 9. It can be seen from the figures that for all Ni-Cu ferrites,  $\tan \delta$  shows a maximum at a frequency of 6 MHz. A qualitative explanation can be given for the occurrence of the maximum in the  $\tan \delta$  versus frequency curves in the case of mixed Ni-Cu ferrites. As pointed out by Iwauchi [4], there is a strong correlation between the conduction mechanism and the dielectric behavior of ferrites. The conduction mechanism in n-type ferrites is considered as due to hopping of electrons between  $Fe^{2+}$  and  $Fe^{3+}$ . As such, when the hopping is nearly equal to that of the externally applied electric field, a maximum of loss tangent may be observed. Thus, it is possible for all Ni-Cu ferrites the hopping frequencies are of the appropriate magnitude to observe a loss maximum at 6 MHz.

**Conclusions**

Among all the Ni-Cu ferrites the specimen with the composition  $Ni_{0.2}Cu_{0.8}Fe_2O_4$  exhibits highest value of electrical resistivity ( $\rho=1.21 \times 10^7$  Ohm. cm). The sign of the Seebeck coefficient is negative for all the ferrites under investigation which indicates that the predominant conduction mechanism in these ferrites is of n-type semiconductors. The value of  $T_c(K)$  decreases with the increase of copper content. Among all the ferrites, the specimen with the composition  $Ni_{0.8}Cu_{0.2}Fe_2O_4$  exhibits the highest value of dielectric constant, dielectric loss tangent and complex dielectric constant. For all Ni-Cu ferrites,  $\tan \delta$  shows a maximum at a frequency of 6 MHz.

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