DIELECTRIC STUDY OF FERRITES

(RESULTS AND DISCUSSION)

7.1 DIELECTRIC PROPERTIES

The dielectric properties of polycrystalline materials are generally determined by a combination of various factors like method of preparation, sintering temperature, grain size, additive used, the ratio of Fe^{3+} / Fe^{2+} ions, and ac conductivity [88, 150].

In present work the dielectric properties of $M_x\ Zn_{1-x}\ Fe_2O_4$ ferrites with M = Ni, Mn, Cu and x = 0.66 to 0.99 have been measured by using Capacitance bridge method. Air-dried silver epoxy electrical contacts were deposited on the flat surfaces of sintered pellets, and the dielectric constant ($\in'$) and dielectric loss tangent (tan δ) were calculated using the formula,

$$\in' = cd/\in_0 A \tag{7.1}$$

where,

'C'	is the measured capacitance
'd'	is the thickness of the sample
'A'	is the area of the capacitor's plate
'$\in_0$'	is the permittivity of free space and its value is 8.85×10^{-12} F/m.

The angle 'δ' between the vector for the amplitude of the total current and that for the amplitude of charging current is called the loss angle and is less than 90°. The tangent of this angle is the loss tangent (dissipation factor), which is used as a measure of dielectric loss and given as,

$$\tan\delta = \frac{\text{Loss current}}{\text{Charging current}} \qquad (7.2)$$

$$= \epsilon''/\epsilon' \qquad (7.3)$$

where 'ϵ' ' is the measured dielectric constant of dielectric material in the capacitor and it is the real part of complex permittivity and 'ϵ''' is the loss factor being the imaginary part of complex permittivity.

The dielectric measurements were carried out at different frequencies of 100KHz, 300KHz, 500KHz, 700KHz and 900KHz respectively. This was repeated for different temperatures from 25°C (room temperature) to 180°C.

7.1.1 The $Ni_x Zn_{1-x} Fe_2O_4$ FERRITE SYSTEM

7.1.1.1 Dependence of Dielectric Properties on Composition:

The values of Dielectric constant (ϵ') and the dielectric loss tangent ($\tan\delta$) for mixed Ni-Zn ferrites at different temperature and frequencies are given in Table 7.1. It is clear from the Table and Fig 7.1 and 7.2 that the values of ϵ' and $\tan\delta$ are found to decrease with increasing Ni content x, as Polarization in ferrites has largely been attributed to the presence of Fe^{2+} ions which give rise to heterogeneous spinal structure. Since Fe^{2+} ions are easily polarisable, the larger the number of Fe^{2+} ions the higher would be the dielectric constant [88]. It has already discussed in section 5.1.1 that the Ni ions strongly prefers the occupation of B-sites [116-119] and Fe ion partially occupies tetrahedral sites (A sites) and B sites [119,120] while Zn strongly prefers the occupation of A sites [116-119].

The electric hopping between Fe^{2+} and Fe^{3+} ions (n-type) and hole hopping between Ni^{3+} and Ni^{2+} (p-type semiconductor ferrite) on B-sties are responsible for electric conduction and dielectric polarization [103, 150-152]. As Ni ion substitution increases (at B-sites) replacing Zn ions (at A-sites), some Fe ions will be forced to migrate from B sites to A sites [150]. As a result, the number of Fe^{2+} and Fe^{3+} ions

Table 7.1 Data for Dielectric Constant ($\in'$) and dielectric loss tangent (tan δ) for ferrite system at room temperature.

x	Frequency (kHz)	Ni-Zn ferrite		Mn-Zn ferrite		Cu-Zn ferrite	
		$\in'$	tan δ	$\in'$	tan δ	$\in'$	tan δ
0.66	100	48.16	0.98	43.43	6.01	26.96	0.605
	300	35.24	0.45	40.95	4.64	24.03	0.226
	500	29.37	0.32	35.99	3.31	19.93	0.163
	700	22.7	0.3	30.40	2.93	14.65	0.159
	900	21.14	0.25	27.31	2.58	13.48	0.134
0.77	100	45.44	0.93	41.05	5.68	28.18	0.646
	300	33.71	0.43	35.92	4.60	25.09	0.240
	500	28.11	0.29	32.84	3.11	21.59	0.168
	700	20.54	0.28	29.76	2.81	16.79	0.154
	900	17.29	0.23	25.66	2.52	14.99	0.134
0.88	100	43.62	0.87	38.99	4.63	29.58	0.649
	300	31.28	0.41	32.90	2.97	27.16	0.235
	500	27.51	0.27	29.24	1.63	23.54	0.163
	700	18.06	0.26	23.17	1.15	19.31	0.141
	900	15.35	0.21	19.49	0.99	16.90	0.126
0.99	100	41.39	0.83	40.75	5.57	30.32	0.671
	300	29.93	0.34	35.13	3.65	27.89	0.243
	500	25.8	0.24	29.51	2.39	24.26	0.167
	700	22.14	0.22	23.88	1.88	21.22	0.136
	900	20.26	0.19	21.07	1.70	18.19	0.124

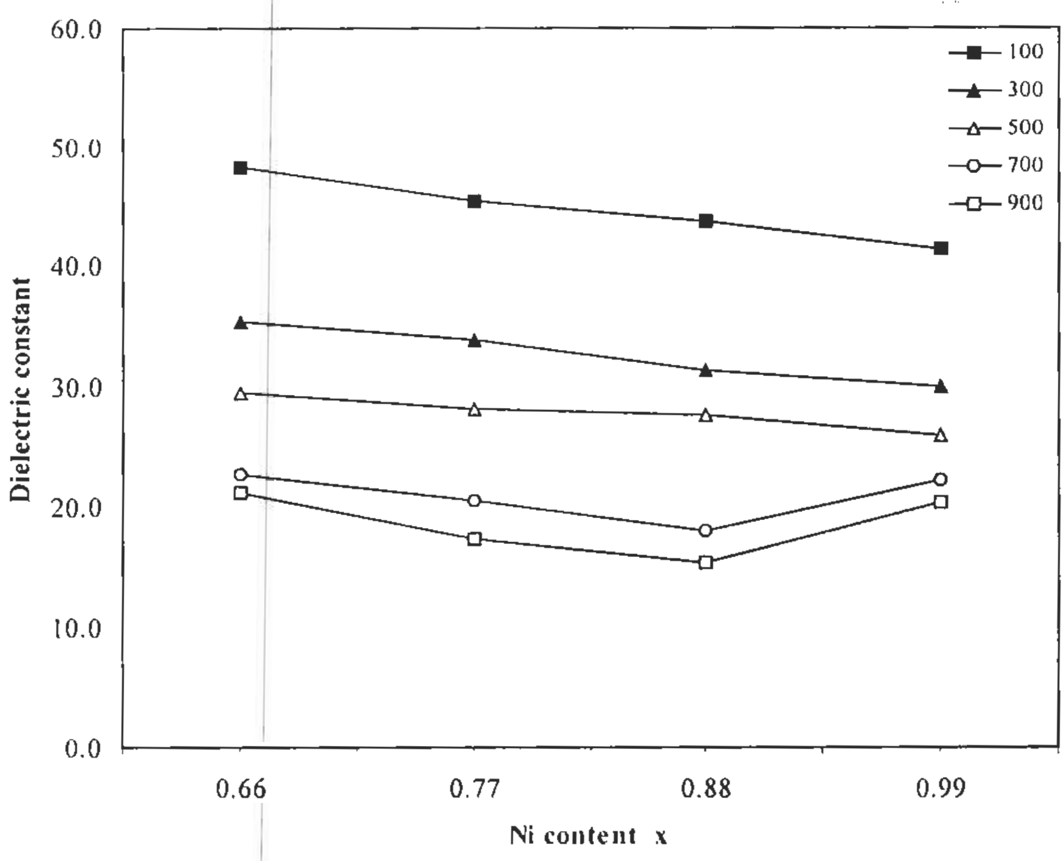

Fig. 7.1 Plot of dielectric constant (∈′) versus Ni concentration, x for Ni-Zn ferrite

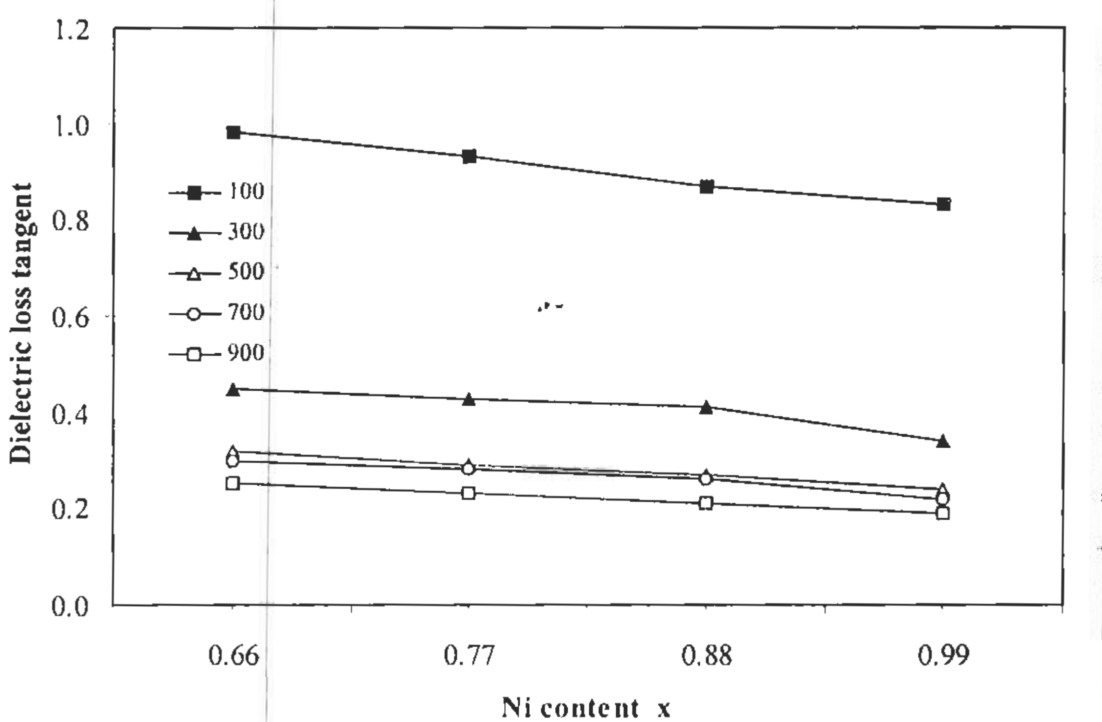

Fig. 7.2 Plot of dielectric loss (tan δ) versus Ni concentration, x for Ni-Zn ferrite

increases at A sites while the number of Zn ions decreases as Ni ions substitution increases. Therefore, the local displacements (dielectric Polarization) in the direction of external applied electric field (for electrons) decreases and those in the opposite direction (for holes) increase. This explanation provides the basis of the decrease in ∈′ and tan δ as Ni ion substitution increases.

Also with lower Zn concentration due to relatively less Zinc evaporation, the ferrite would have lesser Fe^{2+} consequently resulting low dielectric constant [103] as shown in Table 7.1.

Lower dielectric constant (∈′) and dielectric loss (tan δ) is also due to the addition of Si which is there as impurity in the starting low cost iron oxide powder (as mentioned in section 3.1. The Si additive has a great influence both on magnetic properties and dielectric properties of the sintered bodies [152]. The ceramic grain growth was suppressed by Si doping and proves effective to lower the dielectric constant and loss thus improving its applicability at high frequencies.

7.1.1.2 Variation of Dielectric Constant (∈′) and Dielectric loss tangent (tan δ) with Frequency:

The variation of the dielectric constant and dielectric loss tangent as a function of frequency for $Ni_x Zn_{1-x} Fe_2O_4$ ferrites at room temperature are shown in Fig.7.3 and Fig. 7.4. It is clear from the figures that both the dielectric constant and dielectric loss tangent decreases with increasing frequency. The decrease of dielectric constant and dielectric loss tangent with frequency is a normal dielectric behaviour of spinal ferrites [150-153] and is due to the reason that, as the frequency of the externally applied field increases gradually, though the number of ferrous ions is present in the ferrite material, 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, i.e., $Fe^{2+} \Leftrightarrow Fe^{3+}$, can not follow the alternating field [151].

The decrease of dielectric loss tangent by increasing frequency is due to the reason that there is a strong correlation between the conduction mechanism and

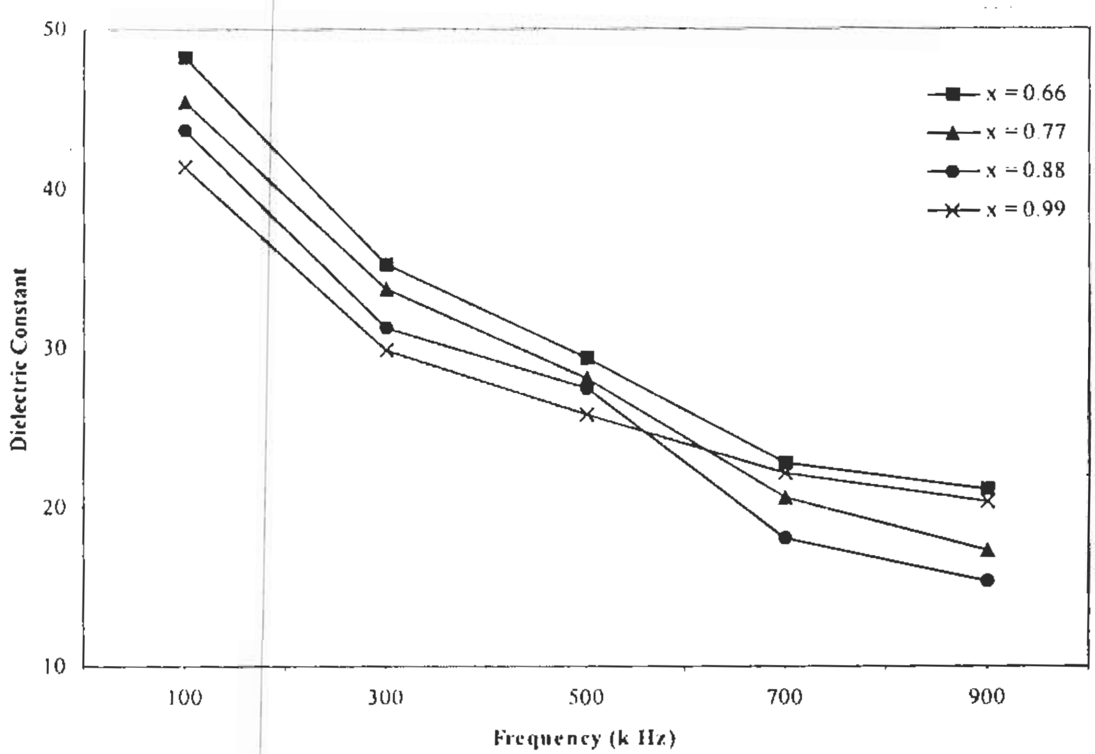

Fig. 7.3 Plot of dielectric constant (∈′) versus frequency for Ni-Zn ferrite

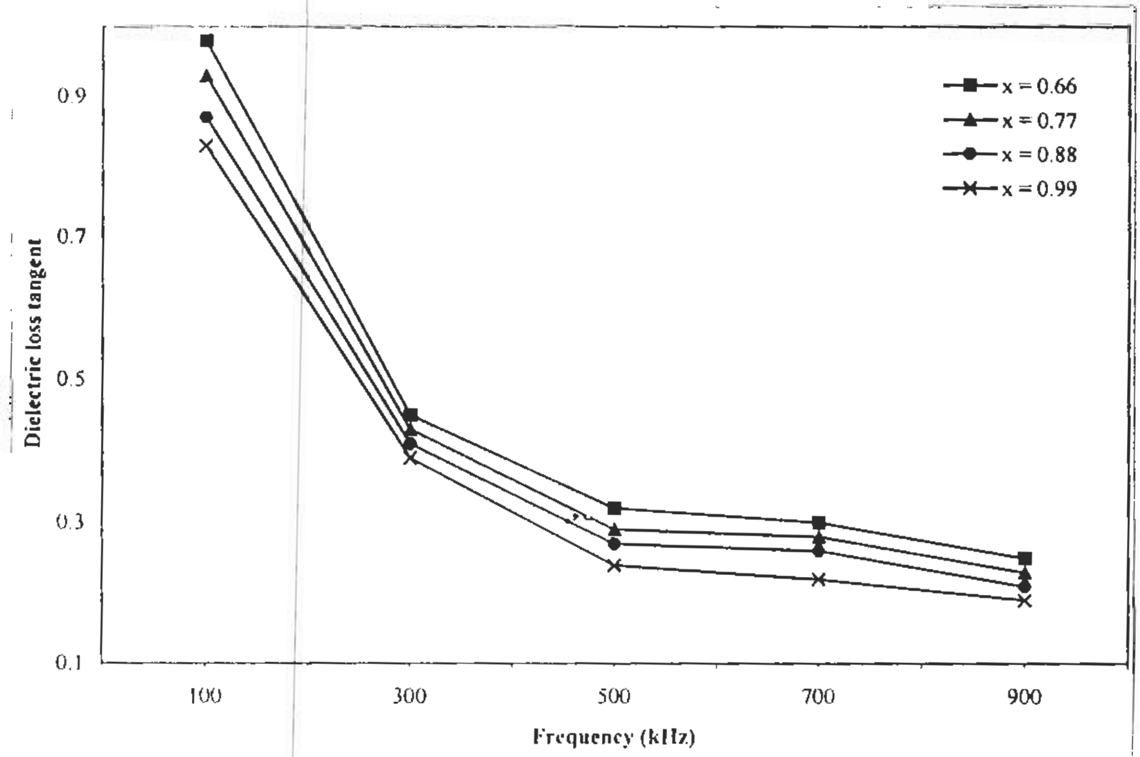

Fig. 7.4 Plot of dielectric loss (tan δ) versus frequency for Ni-Zn ferrite

dielectric behaviour of ferrites. The conduction mechanism in ferrite is considered due to hopping of electrons and holes in n and p- type respectively. AS such, when the hopping frequency is nearly equal to that of the externally applied electric field, a maximum of loss may be observed [150].

7.1.1.3 Variation of Dielectric Constant (ϵ') and Dielectric Loss tangent (tan δ) with Temperature.

The temperature dependence of ϵ' and tan δ at different frequencies are represented in Fig. 7.5 and Fig. 7.6, which shows increase in ϵ' and tan δ as the temperature T increases. A similar temperature variation of the dielectric constant and dielectric loss tangent has been reported earlier [88, 103, 150-153]. On increasing the temperature, electrical conductivity increases due to the increase in thermally activated drift mobility of electric charge carries according to hopping conduction mechanism. Therefore, the dielectric polarization increases causing a marked increase in ϵ' and tan δ as the temperature increases [150-151].

7.1.2 The $Mn_x Zn_{1-x} Fe_2O_4$ FERRITE SYSTEM

7.1.2.1 Dependence of Dielectric Properties on Composition:

It is known that Zinc ion occupy tetrahedral (A sites), while iron and manganese ions occupy both A and B sites [154], however, probability of finding manganese ions at B sites is more [8]. Both Mn and Fe ions exists in 2^+ as well as 3^+ states. To maintain the electric charge balance, a decrease in Fe^{2+} and Mn^{3+} concentration is expected [154].

It is also known that the B sites of a hexagonal ferrites play a dominate role in the phenomenon of electrical conductivity, and the conduction in these ferrites may be due to hopping of electrons in $Fe^{3+} + e \Leftrightarrow Fe^{2+}$ at B sites [52, 155]. The substitution of Mn for Fe on the B sites (octahedral sites) acts to reduce Fe^{2+} concentration through the following buffering reaction:

$$Mn^{3+} + Fe^{2+} \rightarrow Fe^{3+} + Mn^{2+}$$

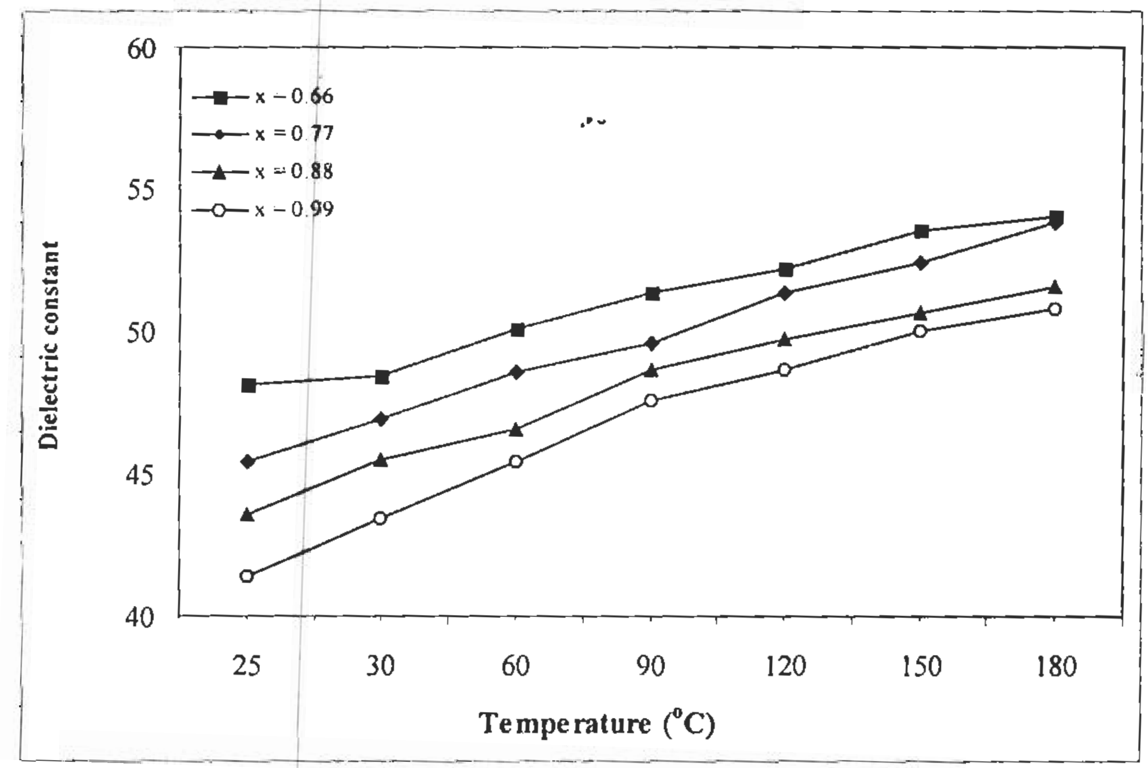

Fig. 7.5 Plot of dielectric constant (∈') versus temperature for Ni-Zn ferrite

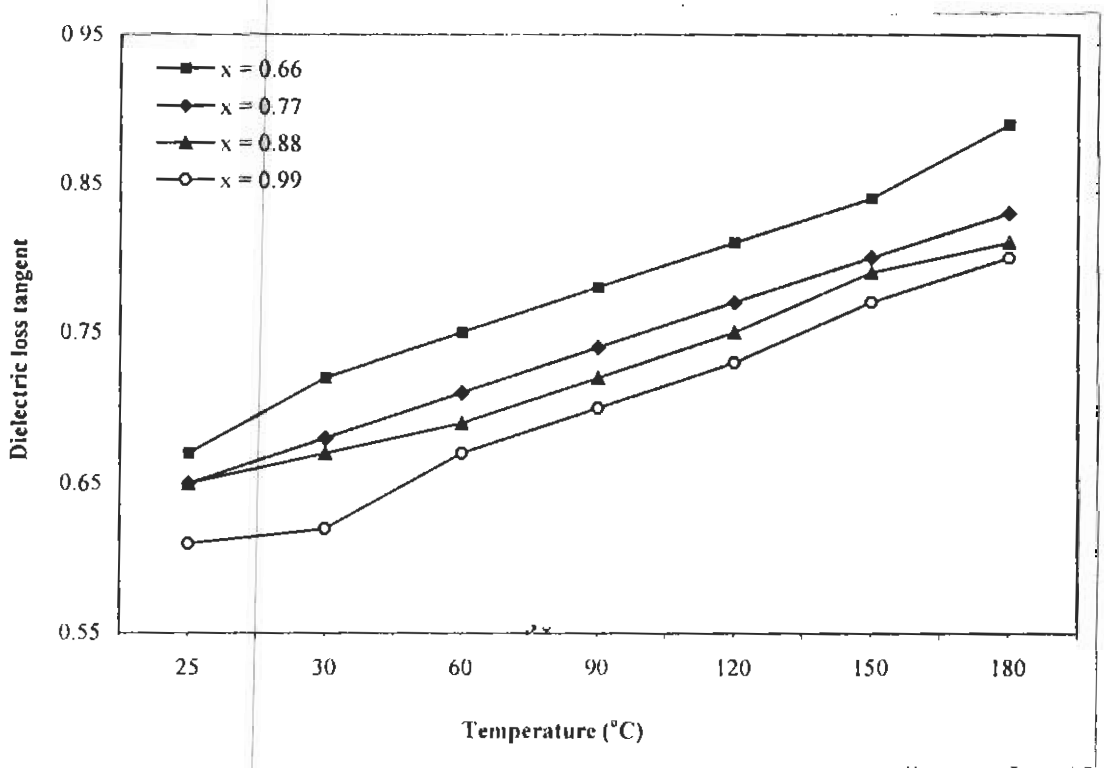

Fig.7.6 Plot of dielectric loss (tan δ) versus Ni concentration, x for Ni-Zn ferrite

Also, the hopping energy in $Mn^{3+} \leftrightarrow Mn^{2+}$ is larger than that in $Fe^{3+} \leftrightarrow Fe^{2+}$.

By increasing the replacement of Mn to Fe ions, the numbers of ferrous and ferric ions at B sites decreases.

It seems likely that the concentration of Fe^{2+} on B sites becomes very small whereas the concentration of Fe^{3+} on B site remains high. In terms of a model of electron hopping, the electron exchange is suppressed. Therefore, the dielectric conductivity and consequently the local displacement of electrons in the direction of an external AC electric field (holes in opposite direction) which determines dielectric polarization in ferrites decreases as Mn substitution increases. Consequently the dielectric constant ($\in'$) and loss tangent (tan δ) decreases as Mn increases for x = 0.66 to 0.88 as shown in Figs. 7.7 and 7.8, respectively.

But for x=0.99, Mn ions which preferably occupy A sites may force the remaining Fe ions at A sites to migrate to B sites. Hopping probabilities, therefore, between Mn^{3+} and Mn^{2+} may also become appreciable as the concentration of Mn increases. As a result, the dielectric constant starts increasing for x = 0.99.

For all the compositions of $Mn_x Zn_{1-x} Fe_2O_4$ ferrites the value of dielectric constant and dielectric loss tangent is less than as reported in the literature [52,154,155] due to the presence of Si. . These lower values may be attributed to the presence of Si impurity. As with the addition of Si. ., grain size of the ferrite was decreased and proportion of grain boundaries is assumed to be increased resulting decrease in conductivity and hence dielectric constant [152].

7.1.2.2 Variation of Dielectric Constant ($\in'$) and Dielectric loss tangent (tan δ) with Frequency:

The frequency variations of the room temperature dielectric constant ($\in'$), and dielectric loss factor (tanδ) of Mn-Zn ferrites are shown in Figs. 7.9 to 7.10

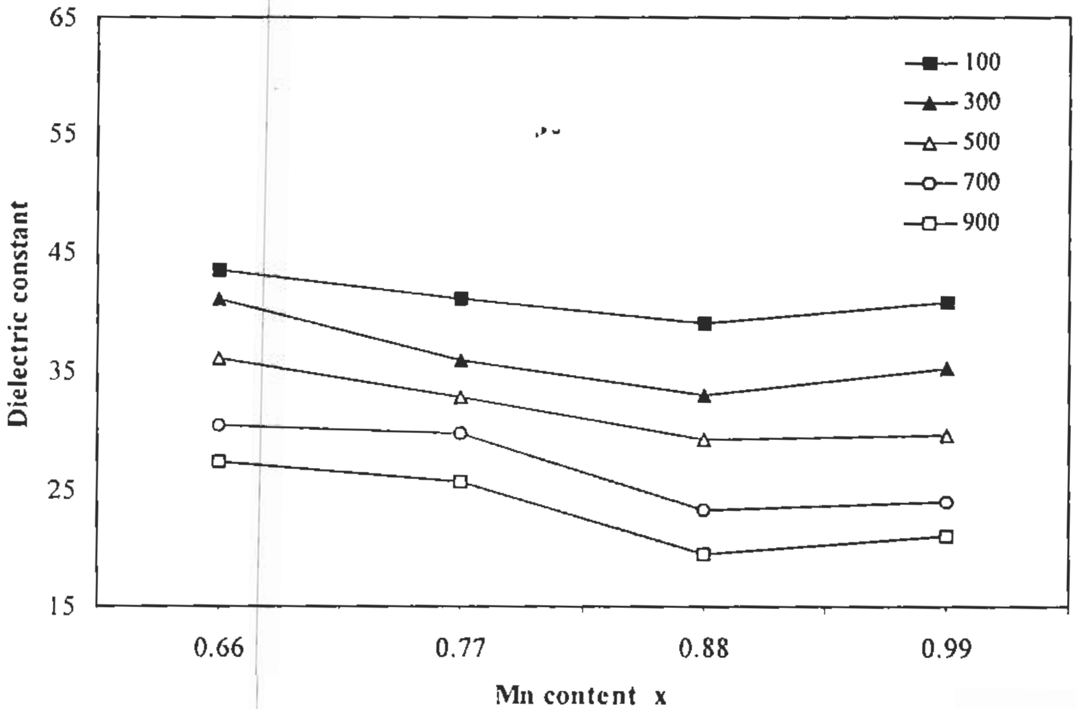

Fig. 7.7 Plot of dielectric constant (∈′) versus Mn concentration, x for Mn-Zn ferrite

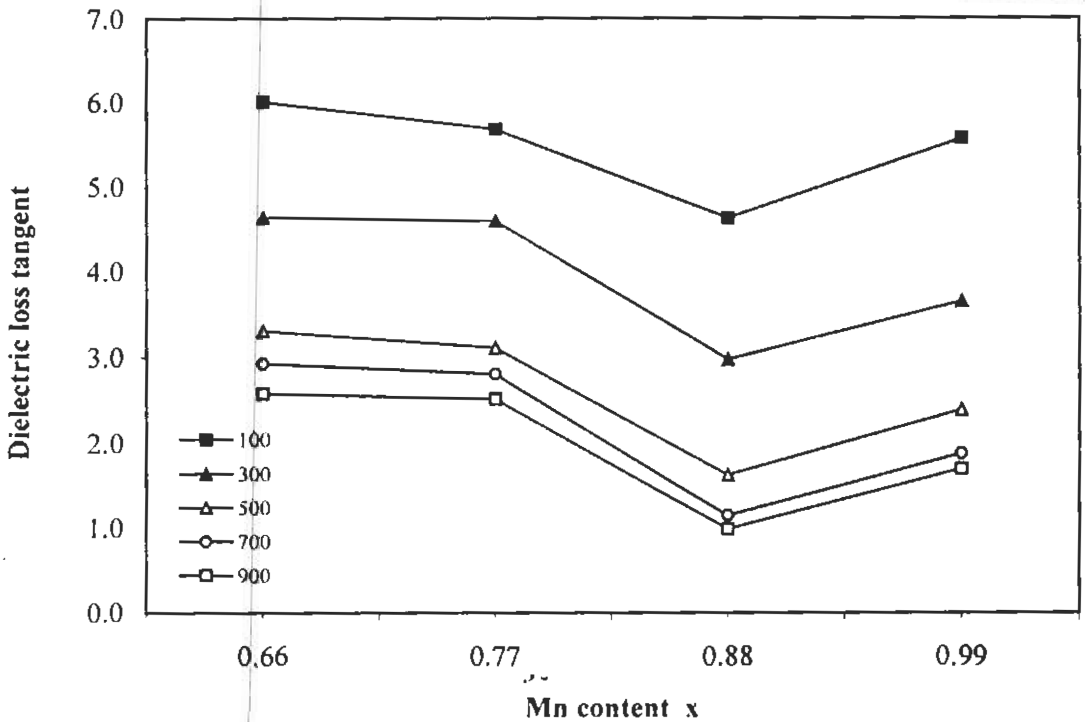

Fig. 7.8 Plot of dielectric loss (tan δ) versus Mn concentration, x for Mn-Zn ferrite

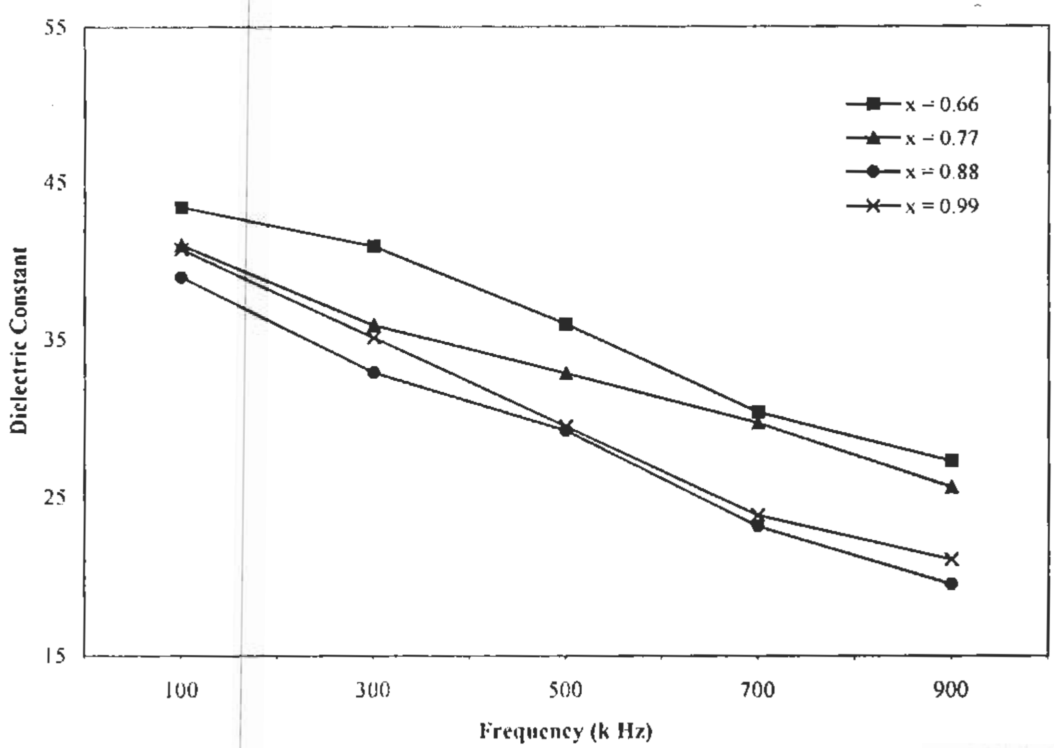

Fig. 7.9 Plot of dielectric constant (∈′) versus frequency for Mn-Zn ferrite

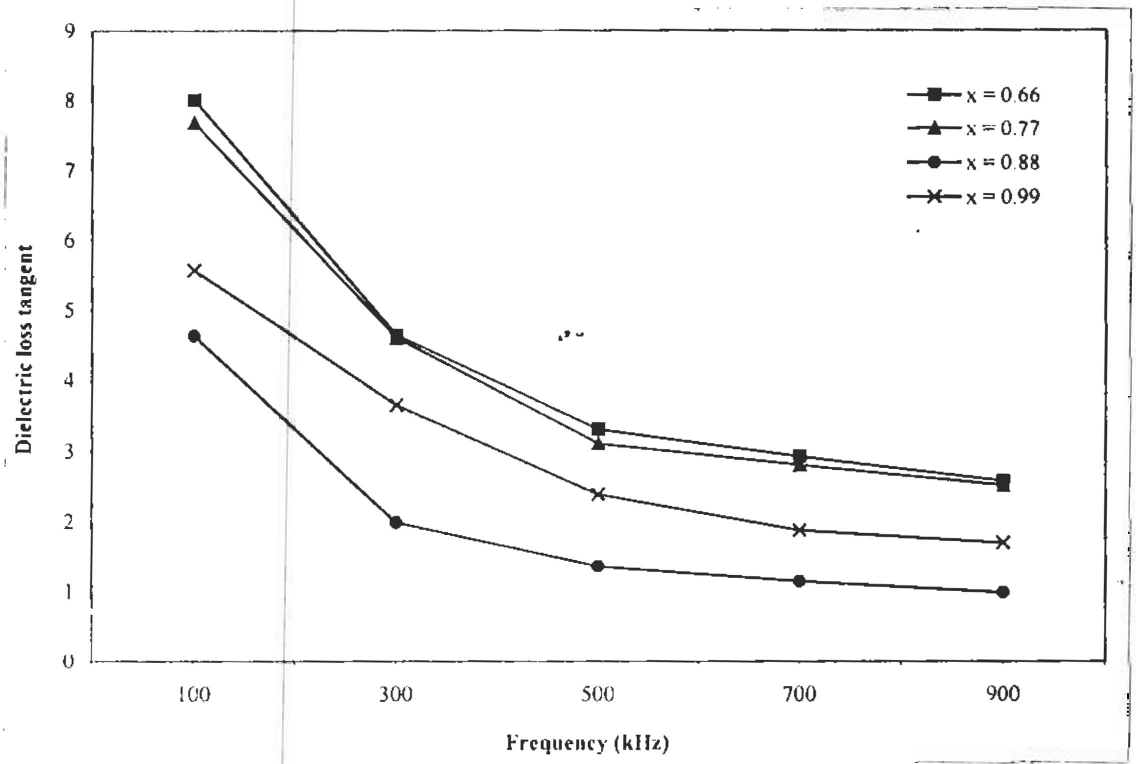

Fig. 7.10 Plot of dielectric loss (tan δ) versus frequency for Mn-Zn ferrite

respectively. A decrease in dielectric constant and dielectric loss factor with frequency is observed for all compositions. This is the normal dielectric behaviour in ferrites [88,150-155] and can be attributed to the fact that the electron exchange between Fe^{2+} and Fe^{3+} ions and hole transfer between Mn^{3+} and Mn^{2+} cannot follow the alternating electric field beyond a critical frequency [155].

7.1.2.3 Variation of Dielectric Constant ($\in'$) and Dielectric Loss tangent (tan δ) with Temperature.

The temperature variation of dielectric constant $\in'$ was studied in the temperature range from room temperature to 180°C at fixed frequencies of 100, 300, 500, 700 and 900 KHz, and results are plotted in Figs. 7.11 and 7.12 respectively. As can be seen from the figures, the dielectric constant and loss tangent increases by increasing temperature. This is the normal dielectric behaviour for ferrites due to the increase in numbers of electric charge carriers and there drift motilities, which are thermally activated as, described by Bao [156] in his work for different composition.

7.1.3 The$Cu_xZn_{1-x}Fe_2O_4$ FERRITE SYSTEM

7.1.3.1 Dependence of Dielectric Properties on Composition:

The composition dependence of $\in'$ and dissipation factor (tan δ) as shown in Figs. 7.13 and 7.14, can be explained by using the assumption that the mechanism of dielectric polarization is similar to that of conduction process [156]. It has been concluded that the electron exchange between Fe^{2+} and Fe^{3+} results in the local displacement of charges in the direction of an electric field, which is responsible for polarization in ferrites [157,158]. The magnitude of exchange depends on the concentration of Fe^{2+} / Fe^{3+} ion pairs present on B site [159]. For the present ferrite Cu^{2+} ions are the majority ions and the probability of formation of Cu^{+} ions increases [160]. Hence, the exchange mechanism between Cu^{2+} and Cu^{+} will be more probable. Therefore, the electron exchange of $Cu^{2+} <=> Cu^{+}$ is responsible for conduction and the polarization, as the incorporation of Cu may increase the concentration of Fe^{3+} / Fe^{3+} ion pairs due to the presence of oxidation from Cu+ to Cu^{2+}, as also discussed by

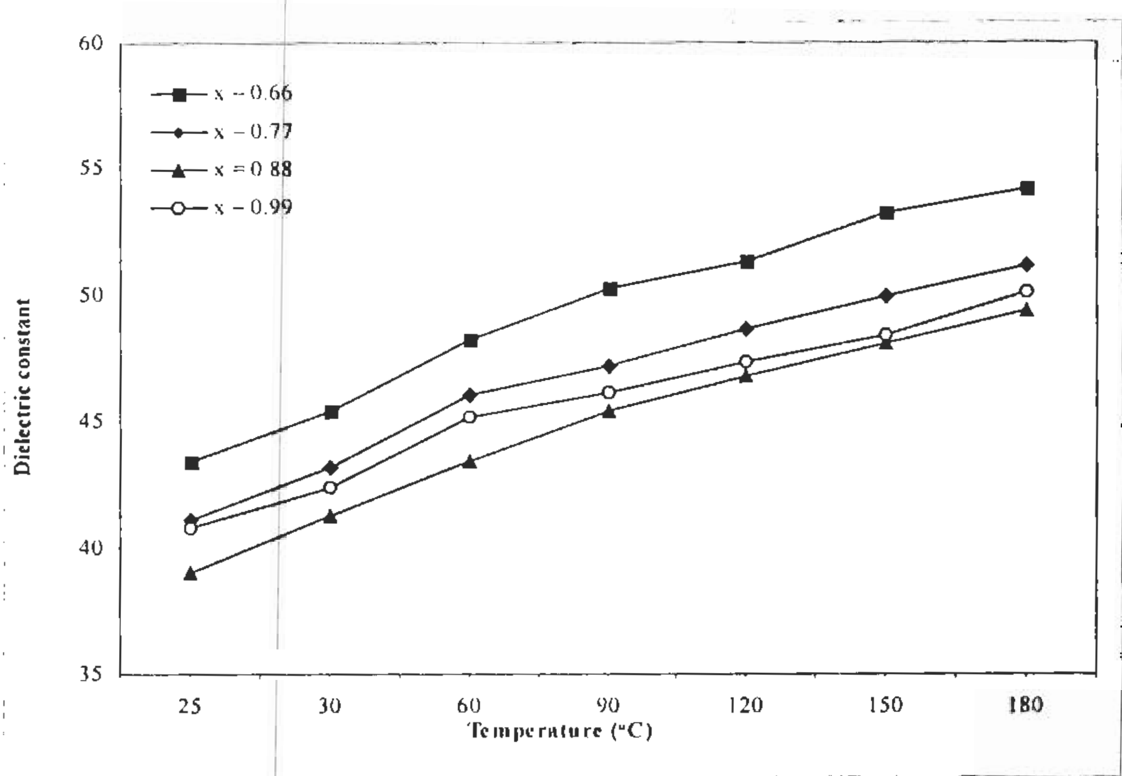

Fig. 7.11 Plot of dielectric constant (∈′) versus temperature for Mn-Zn ferrite

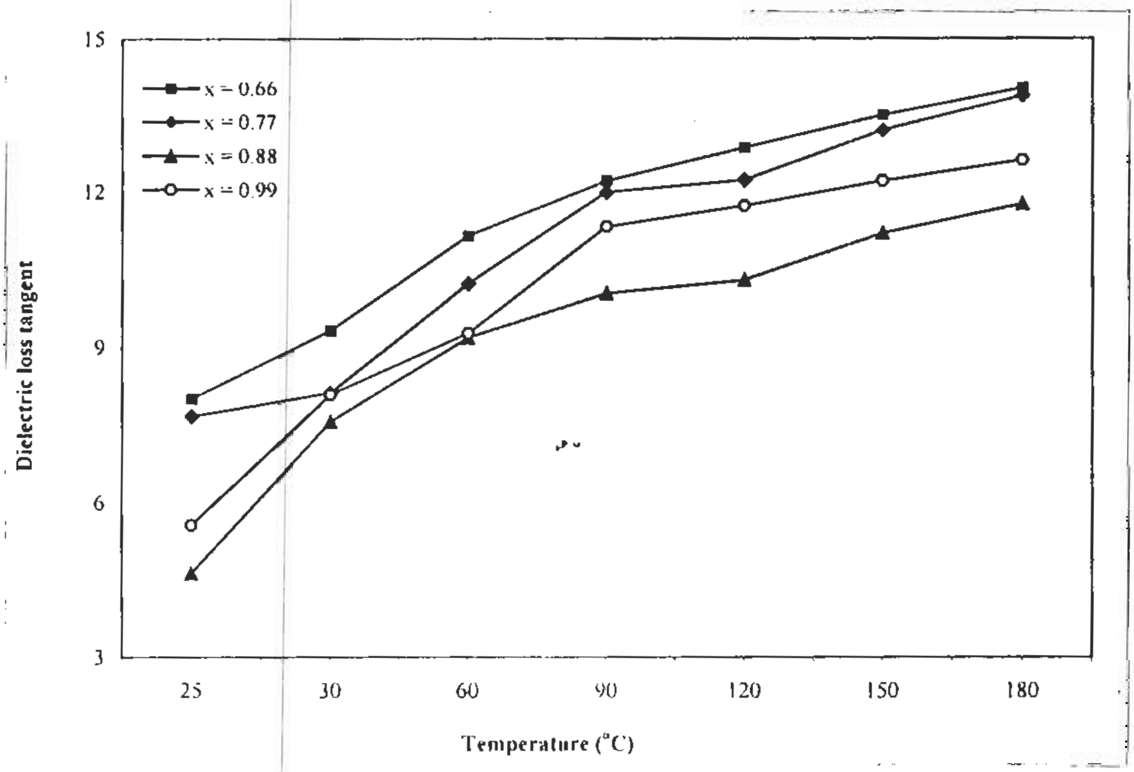

Fig. 7. 12 Plot of dielectric loss (tan δ) versus temperature for Mn-Zn ferrite

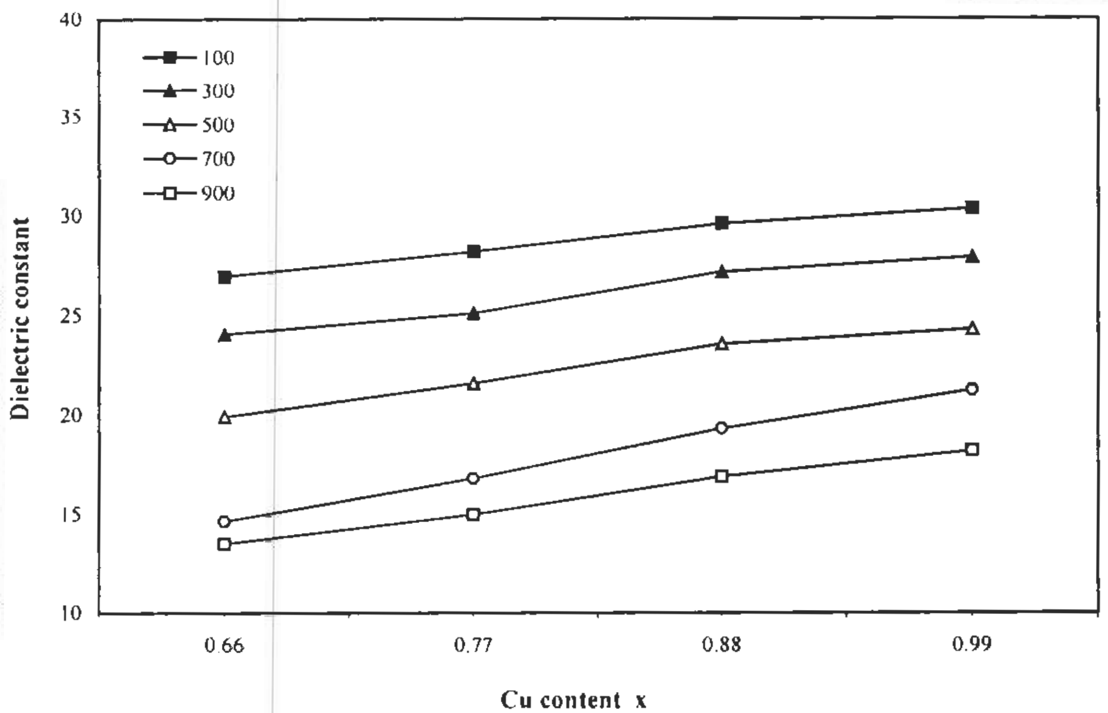

Fig. 7. 13 Plot of dielectric constant (∈') versus Cu concentration, x for Cu-Zn ferrite

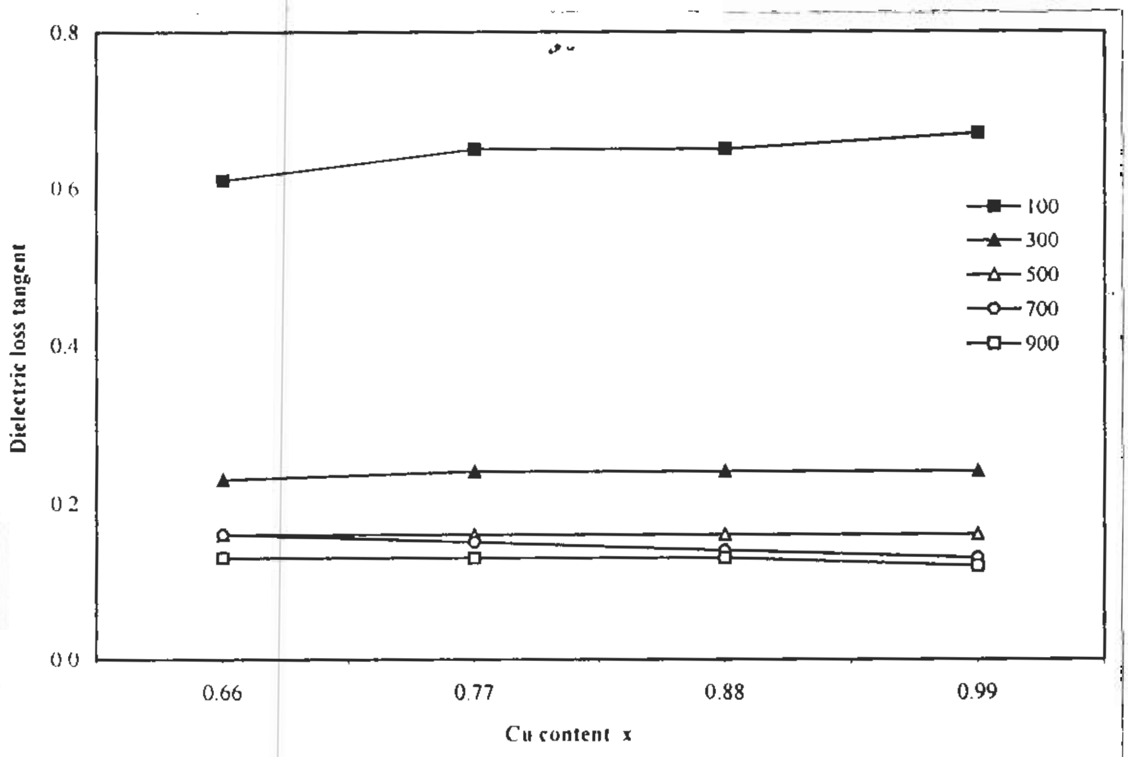

Fig. 7. 14 Plot of dielectric loss (tan δ) versus Cu concentration, x for Cu-Zn ferrite

Zhenxing [160] for different composition. Accordingly, the conductivity and dielectric constants increases by increasing Cu content. But the addition of Si could decrease the dielectric constant (as also in present work) and promote the quality factor at higher frequencies [152].

7.1.3.2 Variation of Dielectric Constant ($\in'$) and Dielectric loss tangent (tan δ) with Frequency:

The effect of frequency on each of the dielectric constant and dielectric loss factor is illustrated in Figs. 7.15 and 7.16, respectively. Both $\in'$ and tan δ decreases as the frequency increases, which is a normal dielectric behaviour in ferrites [52, 150-153,155]. This decrease in $\in'$ and tan δ takes place when the jumping frequency of electric charge carriers cannot follow the alternation of applied AC electric field beyond a certain critical frequency as described by Abdeen [150] for different composition of ferrites.

7.1.3.3 Variation of Dielectric Constant ($\in'$) and Dielectric Loss tangent (tan δ) with Temperature.

The dielectric constant ($\in'$) and dielectric loss tangent (tan δ) were found to depend on the variation of external factors such as temperature. The dependence of $\in'$ and tan δ on temperature, of the investigated system are shown in Figs. 7.17 and 7.18, respectively for x = 0.66 to 0.99. It has been found that both $\in'$ and tan δ show appreciable increase when the temperature is increased such a temperature dependence of $\in'$ and tan δ may be due to polarization effect.

Different authors [66, 160-161] assumed that the mechanism of dielectric polarization is similar to that of conduction and concluded that the electron exchange interaction results in a local displacement of the electron in the direction of an electric field, which determine the polarization of the ferrites.

The space charge polarization is governed by the numbers of space charge carriers with the rise in temperature the numbers of carriers increase resulting in an enhanced built up space charge polarization and hence increase in dielectric properties [161-163].

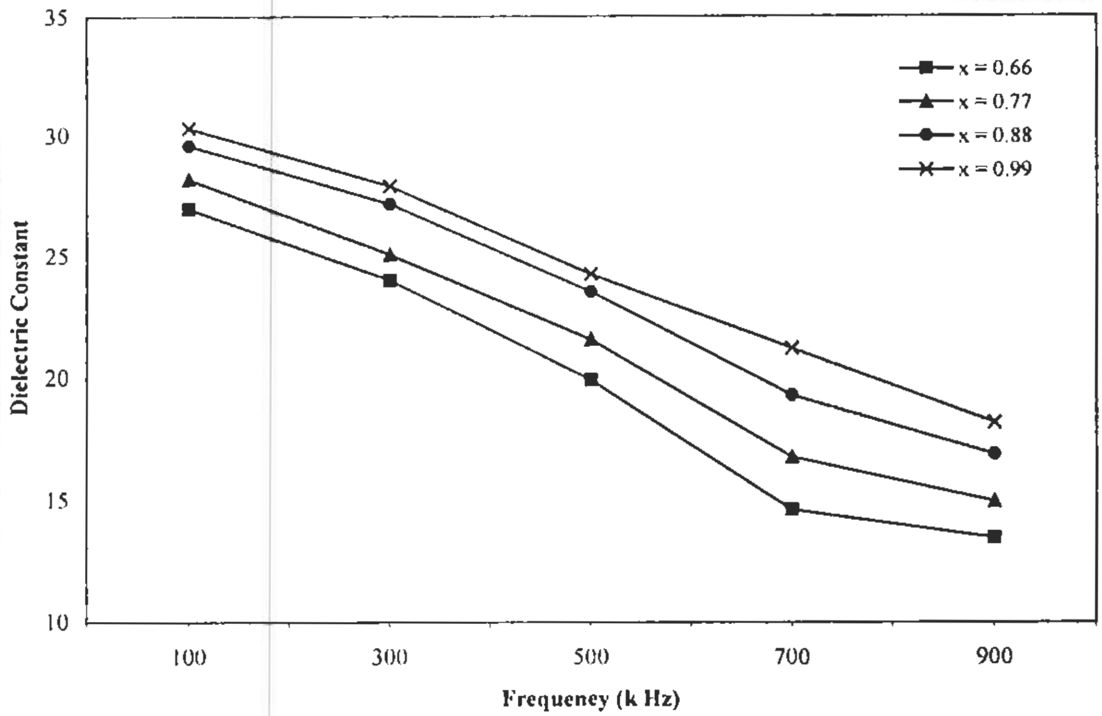

Fig. 7. 15 Plot of dielectric constant ($\in'$) versus frequency for Cu-Zn ferrite

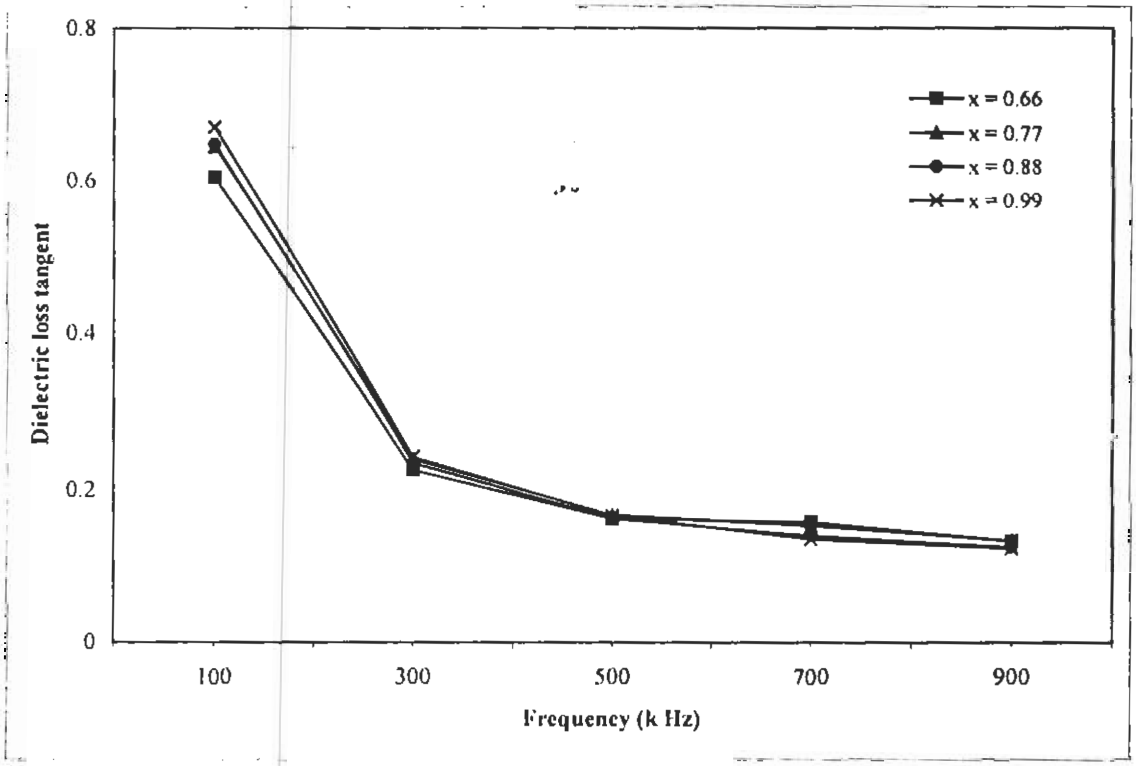

Fig. 7. 16 Plot of dielectric loss (tan δ) versus frequency for Cu-Zn ferrite

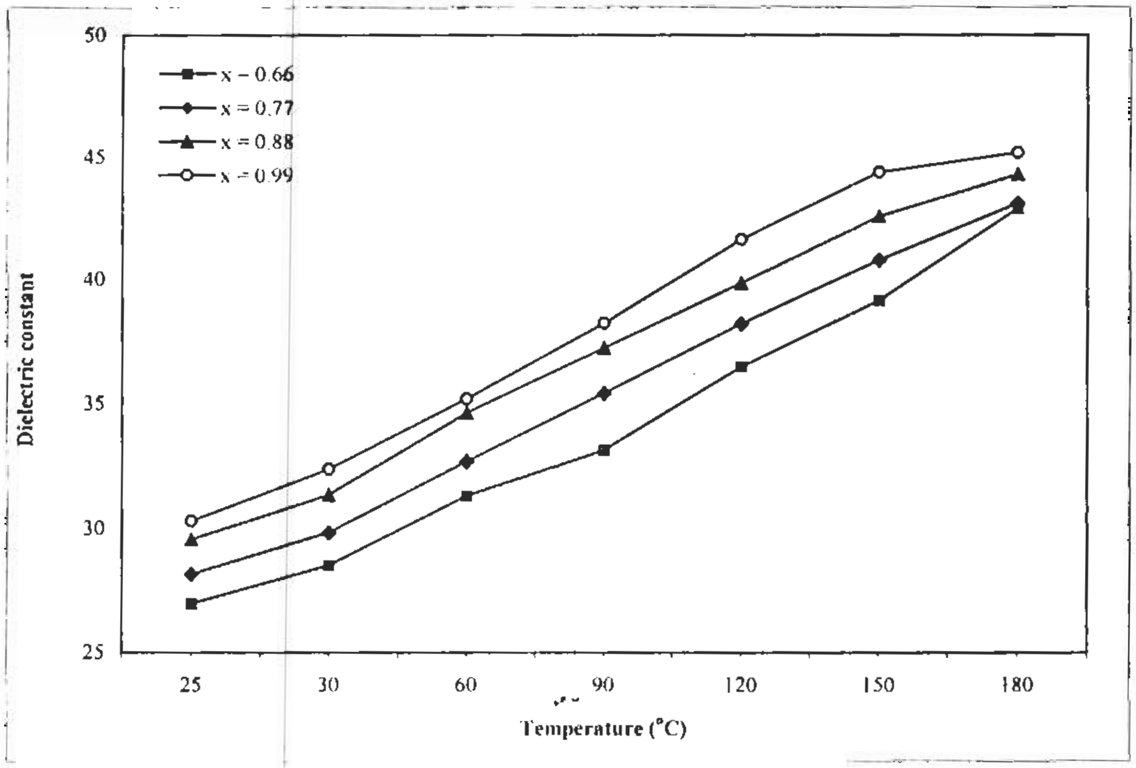

Fig. 7. 17 Plot of dielectric constant (∈′) versus temperature for Cu-Zn ferrite

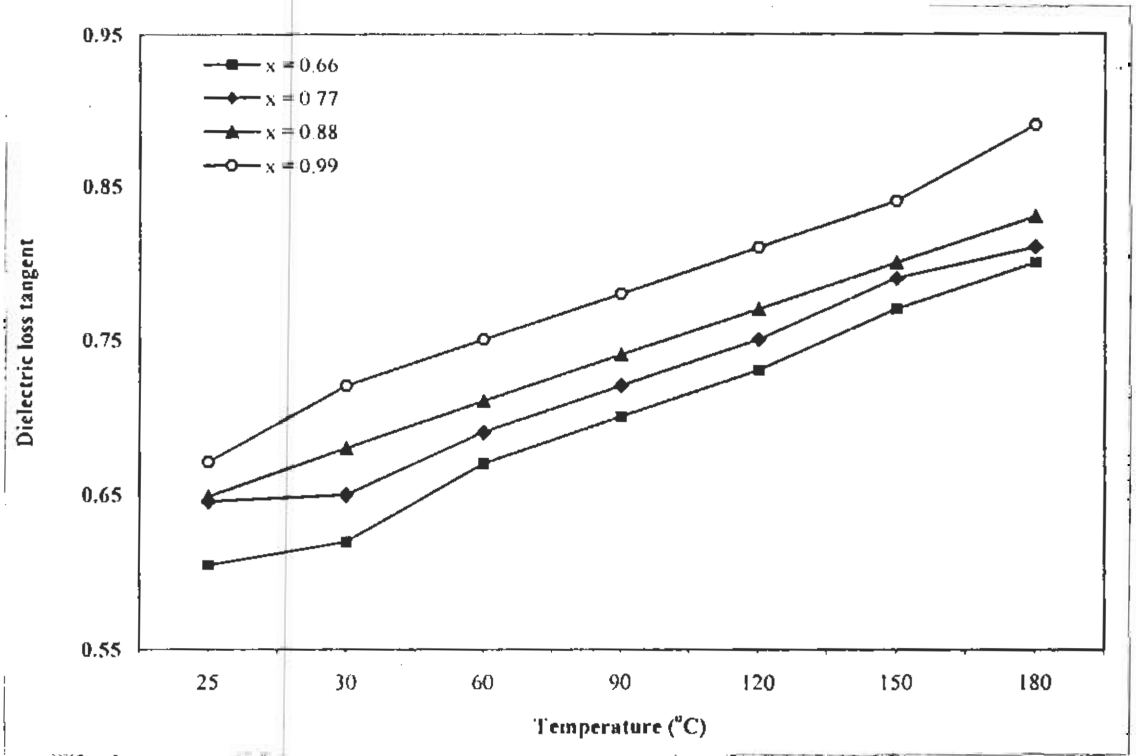

Fig. 7. 18 Plot of dielectric loss (tan δ) versus temperature for Cu-Zn ferrite