Dielectric Relaxation in AL- Substituted Ni – Cd Spinel Ferrites

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The real part of dielectric constant (ε') and dielectric loss tangent ($\tan\delta$) were studied for Al.- substituted Ni – Cd spinel ferrites having the chemical formula $Ni_{0.7}Cd_{0.3}Fe_{2-x}Al_xO_4$ where [x= 0.4, 0.6, 0.8,and 1] This is carried our in the range of temperature from room temperature up to 650 K and applying frequencies from 10^2 to 10^5 Hz. The distribution of Al ions in the B and A sites has changed with changing x and was found to affect the dielectric constant ε' of the samples which have relatively high values. The frequency dependence of the dielectric constant was found to exhibit two different behaviors related to temperature values and indicating the presence of two types of charge carriers at high temperatures. The frequency dependence of $\tan\delta$ shows the existence of broad peaks at low temperature range, which indicates that there is a distribution of relaxation times rather than a single relaxation time.

Introduction:

Polycrystalline ferrites are simultaneously good magnetic dielectric materials. Their physical properties depend on several factors among of them are, method of preparation, chemical composition,sintering temperature, and distribution of cations among tetrahedral (A) and octahedral (B) sites [1]. E.Rezlescu et. al.[2] discuss their investigation of the physical properties of Ni-Zn-Me ferrites (Me= Cu^{2+},Cd^{2+}, Co $^{2+}$, Mn $^{2+}$and Mg $^{2+}$) on the basis of site occupation of the cation species in the spinel structure.

B.P.Ladgaonker et.al.[3] studied the thermoelectric power of Nd $^{3+}$substituted Zn-Mg ferrite.They reported that the substitution of Nd^{3+} ion,which perhaps resides at the B-site showing majority charge carriers of n-type.Murthy and Sobhanadri[4] deviding the ferrites into two groups,the n-type and the p-type,depending on excess and deficiency of iron ,respectively. In Al-containing ferrites ,Al ions exists in the (A) and (B) sites depending on the amount of Al in the ferrite[5] and then it well change the amount of the iron ions in the two sites. The bulk material in ferrites is assumed to be constituted of highly conduction grains separated by low conducting grain boundaries,this heterogeneous structure of ferrites may greatly affect the dielectric properties of the material[6,7]. It was found that among the various compositions of Ni_{1-x} Cd_x Fe_2O_4 ferrites $Ni_{0.7}$ $Cd_{0..3}$ Fe_2O_4 has relatively high magnetic properties [8].

In the present work the dielectric properties of the spinel ferrite of Al-substituted Ni-Cd are examined as a function of temperature, frequency and composition to investigate the effect of Al substitution in $Ni_{0.7}$ $Cd_{0..3}$ Fe_2O_4 spinel ferrites, which of course is expected to give us interesting electrical properties as a consequence of cation redistribution in the (A) and (B) sites.

Experimental details:

Polycrystalline Al substituted Ni – Cd ferrites having the chemical formula $Ni_{0.7}Cd_{0.3}Fe_{2-x}Al_xO_4$ (where x = 0.2, 0.4, 0.6, 0.8 and 1.0) were prepared by the conventional ceramic technique [9] by mixing highly pure raw materials: Fe_2O_3 , NiO, CdO and Al_2O_3 in the proper ratio to give stoichiometric compound .

The mixture was ground in an electrical grinding machine for two hours, then the fine powders were presintered in air in an electric furnace at 850°C for 10 hours , the grinding process was repeated before pressing this powders into disc- shaped pellets with diameters of about 1.5 cm in average and thickness ranging from (0.2 cm to 0.3 cm) using uniaxial press with pressure 6.5 kp/cm^2.

The pressed samples were sintered in air at 1250°C, the furnace was raised to 800 °c gradually in steps of 50 °c per fifteen minutes to avoid cracks in the samples ,then left to increase to 1250 °c and kept at this temperature for 4 hours. The samples are left to be slowly cooled down to room temperature. The X-ray diffraction study was carried out using an X-ray diffractometer (Cu-Kα- radiation with λ= 1.5418 Å, 20 mA, 35 kV) and have shown the presence of a single spinel phase in all the samples.

AC measurements of the samples were performed at different frequencies from 10^2-10^5 Hz and temperatures of 300-660 K under vacuum to avoid moisture absorption on the surface of the sample using the complex impedance technique (a lock - in amplifier S R 510 Stanford research systems)(USA), a block diagram of the circuit used is mentioned in a previously published work[10].

The real part (ε′) of the dielectric function and the dielectric loss tangent (tanδ) were calculated according to the formulae:

$$\varepsilon' = Cd/(\varepsilon_o A) \text{ and } an\delta = 1/\tan\phi$$

where C is the capacitance due to the presence of the sample between the two electrodes of the sample holder, d is the thickness of the sample, A is its cross – sectional area, ε_o is the free space permittivity and ϕ is the phase angle between the current and the voltage across the sample.

Results and Discussion:

Dielectric Constant:

Figure (1) shows the frequency dependence of the dielectric constant (έ) of four compositions only of the five prepared samples. The dielectric constant couldn't be measured for the first composition (x= 0.2) because the sample's resistance was too law at room temperature to give a measurable dielectric behavior. From room temperature up to 500 K the data shows that ε′ decreases as the frequency increases, it can be seen that this decrease is relatively sharp at low frequencies and becomes slower at higher frequencies. This dielectric relaxation is quite expected because the charge carriers responsible for different mechanisms of polarization are expected to lag behind the field variations as the frequency increases. Moreover it is important to mention here that the high values of the dielectric constant in all samples are mainly due to interfacial polarization mechanism known to predominate in heterogeneous structures [6] where the material can be considered as composed of different regions (grains and grain boundaries for example) in which the charge carriers meet different resistances so that accumulation of charges at separating boundaries occurs and the dielectric constant value is highly raised.

Above 500K it can be noticed that the dielectric constant of the sample of (x = 0.4 and 1.0) increases with increasing frequency until reaching a peak after which it decreases with increasing frequency this peak in ε′ is shifted towards higher values of frequencies as the temperature increases. This behavior was previously reported in other ferrite compositions [11] and was interpreted as due to the presence of two types of charge carriers, which sometimes are formed at high temperatures. The shape of the curve of polarization versus frequency can be considered as the resultant of adding two oppositely directed curves each of which represents the behavior of one type of the charge carriers. Moreover the presence of two types of charge carriers in $NiAl_xFe_{2-x}O_4$ was previously suggested by M.A. Ahmed et al. [12] while investigating the temperature dependence of thermoelectric power and resistivity of those compositions. The n – type charge transfer in ferrites is due to hopping of electrons from Fe^{2+} to Fe^{3+} ions according to:

$$Fe^{3+} + e \longleftrightarrow Fe^{2+} \qquad (1)$$

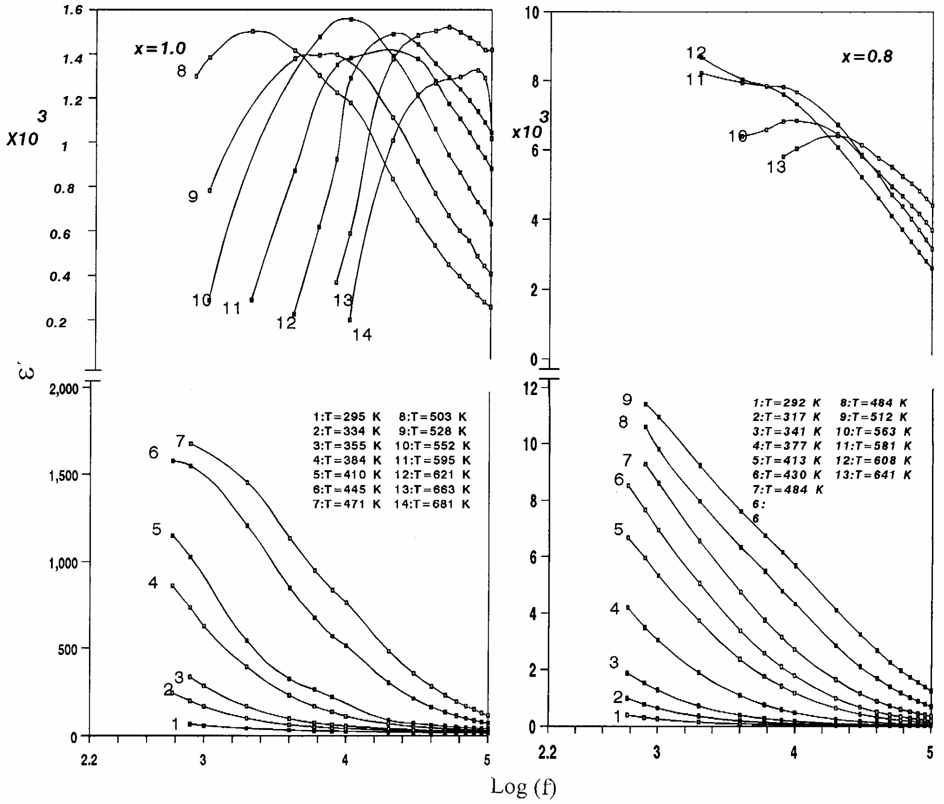

Fig. (1): Frequency dependence of the dielectric constant (ε′) as a function of temp.

while the P- type charge transfer exists in Ni ions according to [13]:

$$Ni^{2+} + h \longleftrightarrow Ni^{3+} \qquad (2)$$

For the samples of (x = 0.6 and 0.8) it can be noted that the presence of the p-type charge carriers at high temperatures isn't obviously manifested as in the samples of (x = 0.4 and 1) except for in a limited range of frequency (4 kHz to 40 kHz). This behavior may be interpreted as follows: In Al- containing ferrites, Al ions prefer the octahedral coordination until the ratio of Al substitution becomes greater than 0.6 [5] where after, Al ions may increase in

A-sites causing migration of some iron ions to the B – sites. This in general, increases the n – type transfer according to equation (1) and the behavior of n-type charge carriers predominates. The small observed humps indicating the presence of p-type charge carriers in a part of the frequency range may be attributed to the coincidence of the frequency of the applied external field with the natural frequency of the P-type charge carriers.

As the Al substitution is further increased (at $x = 1$), in this case iron content will be decreased in the sample as a whole and the n-type charge carriers are decreased also as a result of decreasing the iron content which is obviously manifested by the relative decrease of the dielectric constant values in this composition. Therefore, it can be reasonable to expect that the P-type charge carriers become again competitive with the n-type at high temperatures and result in the reappearance of the same behavior of the composition of ($x = 0.4$).

The temperature dependence of ε' at some selected frequencies for the studied samples is illustrated in Fig. (2), it is clear for all compositions that ε' increases as the temperature increases until reaching certain temperature, then it begins to decrease with increasing temperature. The formed peaks are shifted towards higher temperature as the frequency increases. It was previously reported that [14] those observed peaks may be attributed to two competitive effects, the first of which is the increase of the mobility of charge carriers with increasing temperature leading to an increase in ε' because the conductivity and polarization of the same origin, and the second opposing effect is the hindrance of the charge carriers movements due to thermal agitation. Also those peaks are attributed to the presence of two types of charge carriers as reported by Rezlescu [11].

Figure (3) shows the log of the dielectric relaxation frequency (at which the peak of ε' versus log f curve appears) as a function of 1000/T for all compositions giving straight lines verifying the relation [15]:

$$f_d = f_o \exp [-E_d / kT]$$

where f_d is the dielectric relaxation frequency f_o is pre-exponential constant and E_d is the activation energy of relaxation.
The activation energy E_d is calculated from the slopes of the lines and reported in table (1).

Table (1) values of the activation energy obtained from the relation of *l*og fd versus 1000/T shown in Fig. (3).

X	0.4	0.6	0.8	1
Ed (ev)	0.129	0.168	0.191	0.221

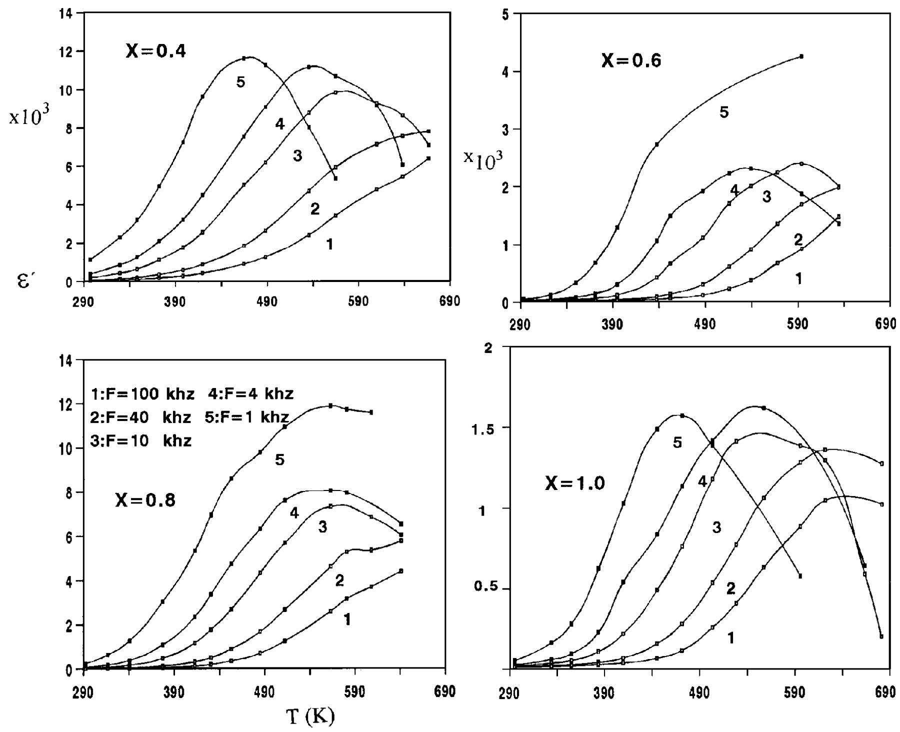

Fig. (2): Temperature dependence of the dielectric constant at different frequencies.

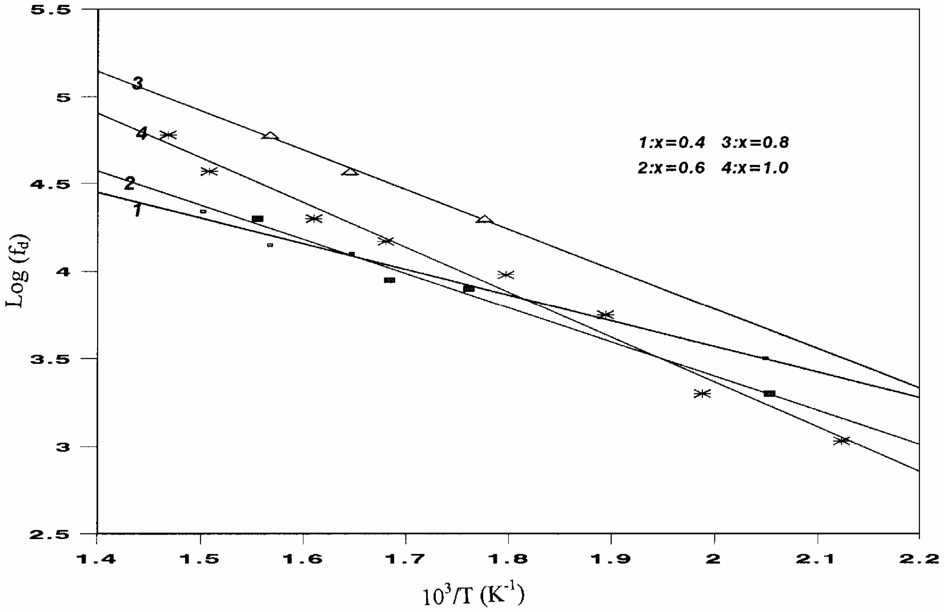

Fig. (3): The relaxation frequency as a function of temperature.

Figure (4) shows the frequency dependence of the dielectric constant at room temperature for the investigated compositions. This figure clarifies two important points: the first one is that there is no manifestation of the presence of P-type charge carriers at room temperature which is in agreement with our assumption in the previous discussion that p-type charges appear at relatively high temperatures. The second point is that our suggestion about the distribution of Al in A and B sites is reasonably valid, because, it can be seen from the figure that the values of ε′ at first decreases with increasing Al substitution (at x = 0.6) as a result of the entrance of Al in the B-sites causing a decrease of the iron content in those sites and consequently a decrease in the charge transfer according to equation (1) and their accumulation at different boundaries and consequently the dielectric constant value in the sample as a whole. With further increase in Al – substitution (x = 0.8), Al ions are suggested to increase slightly on A-sites causing some of the iron ions to migrate to B-sites and the charge transfer increases again as shown in the increase of the dielectric constant in the composition of (x = 0.8).

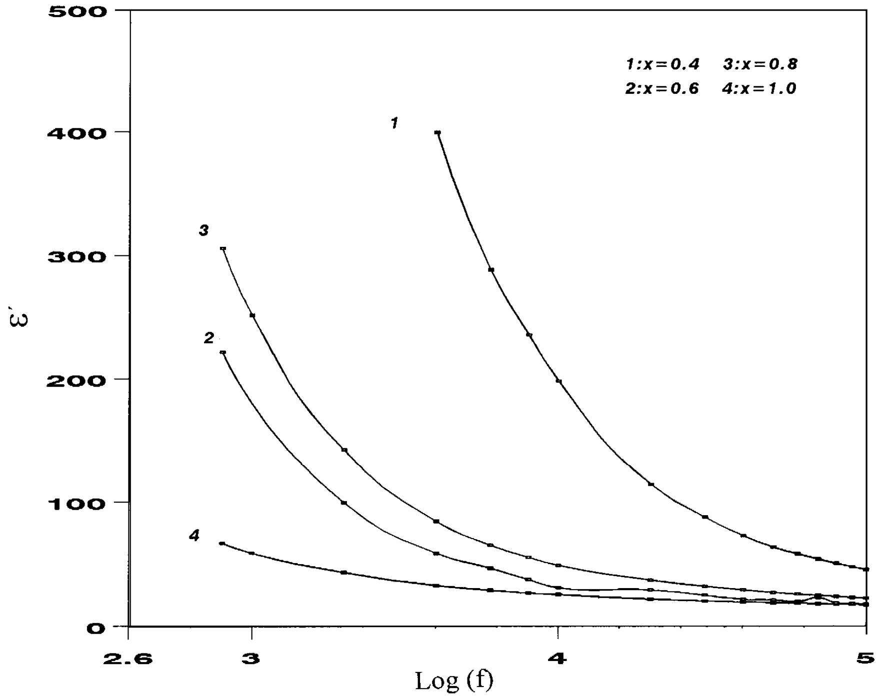

Fig. (4): Frequency dependence of the dielectric constant (ε′) at room temperature.

Finally, as the Al content increases more (at x = 1) on the expense of the iron content the dielectric constant decreases again as a result of decreasing the n-type charges in the sample as a whole.

Dielectric losses (tanδ):

Figure (5) shows a plot of the dielectric loss tangent tanδ versus log f at different temperatures for the investigated samples. We can see that tanδ decreases with increasing frequency at high temperature but as the temperature increases some shoulders or bread peaks in the relaxation spectra were appeared.

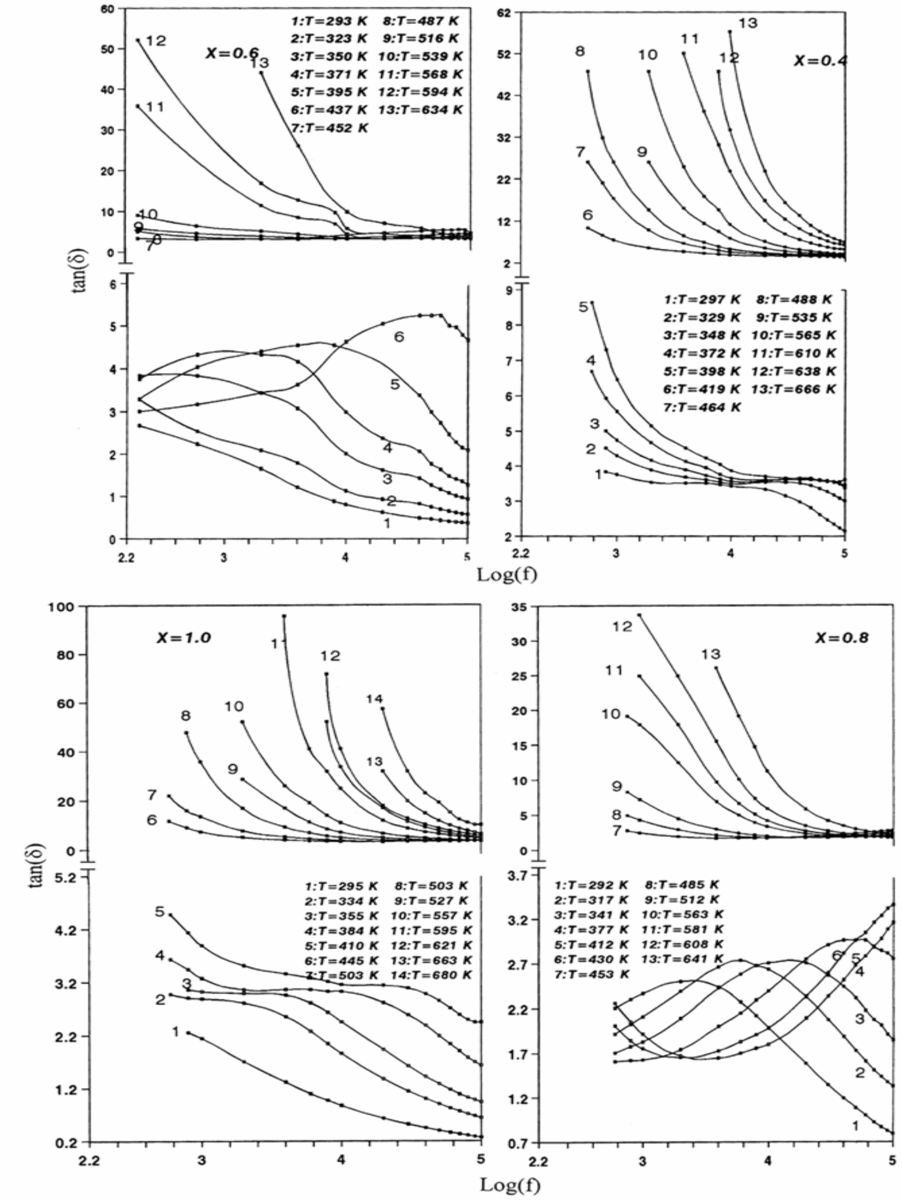

Fig. (5): Frequency dependence of the dielectric loss tangent (tanδ) as a function of temperature.

Generally, a maximum in tanδ versus frequency appears when the frequency of the hopping charge carriers coincides with the frequency of the applied alternating field [16], and the shift of this maximum towards higher frequencies as the temperature increases is often attributed to the increase of hopping frequency of the charge carriers as the temperature increases. The figure shows also that tanδ gives maxima at relatively low temperature range. The maxima shift towards higher temperature with increasing frequency. At relatively higher temperatures tanδ generally increases but it decreases with increasing frequency and the broad peaks disappear. The disappearance of those peaks may be due to their shift to higher frequencies out of the studied range A broad peak of dielectric loss tangent (tanδ) indicates the existence of a distribution of relaxation times rather than a single relaxation time [17]. This distribution of relaxation times is generally attributed to the difference in the environment surrounding different ions in a condensed material, in addition, the interactions between ions and thermal fluctuations of the lattice are not identical every where and at every time.

The frequency (f_c) taken at the middle of the broad peaks, i.e. that corresponds to the most probable relaxation time of the distribution has been determined as a function of temperature for each composition. The most probable relaxation time (τ) can be calculated approximately from the relation $\omega\tau = 1$ [18] where $\omega = 2\pi f_c$ is the angular frequency .The logarithmic representation of $\ln\tau$ versus$10^3/T$ is displayed in Fig (6) which shows a straight line for each composition implying the validity of the following equation [5].

$$\tau=\tau_o \exp [-E_D/kT]$$

where τ_o is the pre-exponential constant which equals the relaxation time at infinitely high temperature, k is the Boltzmann's constant, T is the absolute temperature and E_D is the activation energy for dielectric relaxation which is calculated for different compositions and displayed in table (2).

Table (2): values of the activation energy obtained from the relation of *l*n T versus 1/T shown in Fig. (6).

X	0.4	0.6	0.8	1
E_d (ev)	0.259	0.581	0.336	0.387

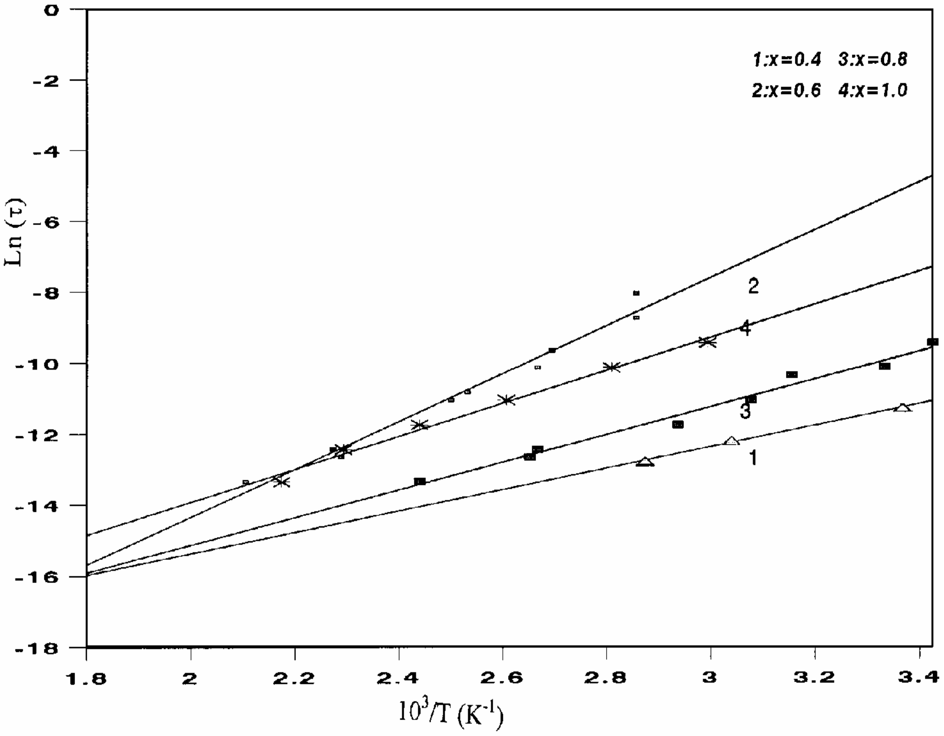

Fig. (6): Dielectric relaxation as a function of temperature at different Al content.

Figure (7) shows the temperature dependence of tanδ at some selected frequencies for the investigated samples. This figure clarifies the previous observation of Fig (5)(tanδ - log f), that is, tanδ values show maxima at relatively low temperature range, this maxima shifts towards higher temperature with increasing frequency. Those observed maxima in tanδ (T) curves suggest an activated hopping process with an activation energy w governed by [19]:

$$F = F_o \mathrm{Exp}\ (-w/kT)$$

where F-relaxation frequency, F_o is the pre-exponential constant k, is Boltzmann’s constant and T is the absolute temperature. Similar behavior of tanδ (T) in the same temperature range was reported by street et. al. [20].

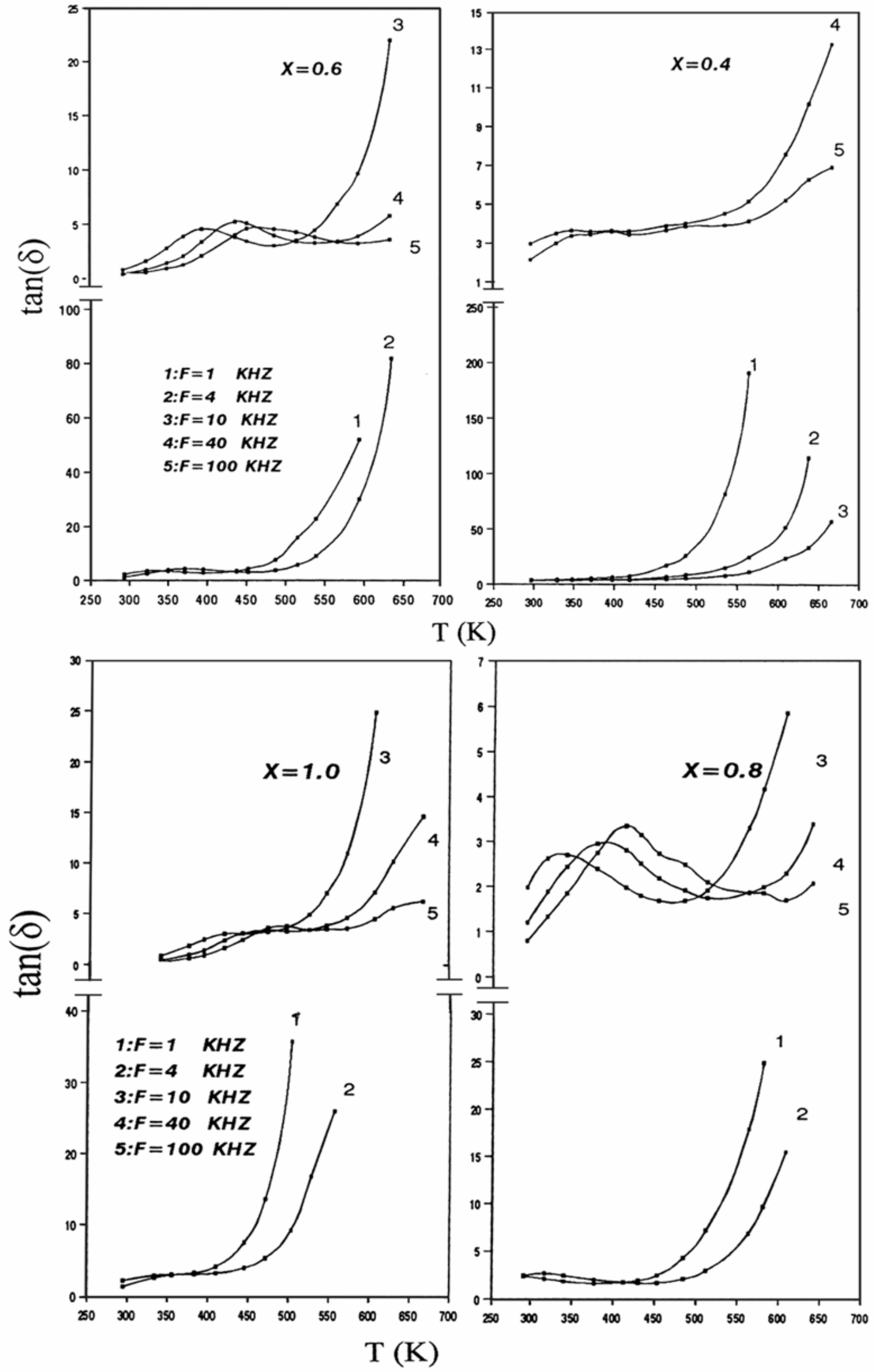

Fig. (7): Temperature dependence of dielectric loss tangnet at different frequencies at different Al content.

Conclution:

The effect of Al substitution on the dielectric properties of Ni-Cd ferrites was investigated in this study and the results are summarized as follows:

1. The amount of the Al ions in the four different prepared compositions affect the cation distribution in the (A) and (B) sites which affect the dielectric constant έ of the samples.
2. The value of the dielectric constant for the samples is found to be high due to interfacial polarization mechanism.
3. The shape of the relation between the dielectric constant and temperature demonstrate the presence of two types of charge carriers at high temperature.
4. The frequency dependence of dielectric loss tangent (tan δ) shows the existence of broad peaks at low temperature range, which indicates the existence of a distribution of relaxation times rather than a single relaxation time.

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