Electrical Properties and Conduction Mechanism of Al-Substituted Ni-Cd Spinel Ferrites

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Abstract: A series of spinel ferrites $Ni_{0.7}Cd_{0.3}Fe_{2-x}Al_xO_4$ with (x=0.4,0.6,0.8,1) were prepared by using the conventional ceramic technique to investigate their electrical properties (ac and dc conductivity) as function of frequency, temperature and composition. X- ray diffraction analysis confirmed the single phase spinel structure of the samples. The dc conductivity increases linearly with increasing temperature ensuring the semiconducting nature of samples. The temperature dependence of $ln\sigma_{dc}$ shows straight lines ensuring the Arrhenius relation of σ_{dc} and temperature. Moreover, these straight lines change slope at the transition temperature T_c-as expected- giving two regions(I, II) .The activation energy for electrical conductivity increases as the samples undergo change from ferrimagnetic state (regions I) to paramagnetic state (regions II) through the transition temperature. The ac conductivity increases with temperature. The exponents in the frequency dependant part of the electrical conductivity σ_2 (ω, T) in the power law σ_2 (ω, T)=B ω^s were found to be composition and temperature dependent, this dependence may be taken as an indication of the conduction mechanism according to literatures.
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1. Introduction

Ferrites are magnetic dielectric materials having high resistivity they are used extensively in inductors, memory cores, high frequency transformers and recording heads [1,2].

The reason that ferrites play a useful role in many magnetic applications is that the electrical conductivity is low in comparison with the magnetic metals. Al substituted Ni ferrites have high electrical resistivity and low eddy current losses, which makes them suitable for microwave devices [2].

From a literature survey [3-10] it has been understood that cadmium substitution is known to modify the electric and magnetic properties of ferrites due to its larger ionic radius. The occupancy of Cd^{+2} ions into the spinel lattice would possibly create a lattice distortion [3] and modification of all the material properties could be expected. The electronic configuration of Cd^{+2} ions with free 5s 5p orbitals permits it to form covalent bonds with oxygen ions and predispose them to occupy tetrahedral sites only [6].

In many of the observed cases [4, 5, 9] the substitution of cadmium resulted in better densification and decreasing of porosity. It is well known that high density ferrite ceramics are essential to obtain higher values of permeability which is a positive factor for magnetic core applications. It was found that among the various composition of $Ni_{1-x}Cd_xFe_2O_4$ ferrites $Ni_{0.7}Cd_{0.3}Fe_2O_4$has relatively high magnetic properties. In the present work the electrical properties of the spinel ferrite of Al substituted Ni-Cd are examined as a function of temperature, frequency and composition, where Al substitution in $Ni_{0.7}Cd_{0.3}Fe_2O_4$ spinel ferrites is expected to give interesting electrical properties as a consequence of cation redistribution in the (A) and (B) sites.

2. 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 = 0.4, 0.6, 0.8, 1) 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 powder were presintered in air in an electric furnace at 850°C for 10 hours, the grinding process was repeated before pressing the powder 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 pellets were sintered in air at 1250°C,where the furnace was raised at first to 800°C gradually in steps of 50°C per fifteen minutes to avoid cracks in the samples, then raised to 1250°C and kept at this temperature for 4 hours, the samples were left to be slowly cooled down to room temperature. The surfaces of the discs were polished well and coated with silver paste as contact materials for the electrical measurements. The X-ray diffraction studies were carried out using an X-ray diffractometer (Cu – K_α –radiation with λ= 1.5418 A°, 20MA, 35kV) and have shown the presence of a single spinel phase in all samples.

The dc electrical conductivity σ_{dc} was determined from the dc I-V characteristics for each sample at different temperatures (300-660K) using Ohm's law. AC measurements of the samples were performed using the complex impedance technique (a lock - in amplifier S R 510 Stanford research systems) (USA) at different frequencies ranging from 10^2Hz -10^5 Hz and in the temperature of 300 -660 K under vacuum to avoid moisture absorption on the surface of the sample, A block diagram of the circuit used is mentioned in a previously published work [11].

The real part (έ) of the dielectric function and the dielectric loss tangent (tan δ) were calculated according to the formulae.

$$\acute{\varepsilon} = \frac{Cd}{\varepsilon_o A}$$

$$\tan\delta = \frac{1}{tan\Phi}$$

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.

The results of the dielectric constant and loss factor of these samples were published earlier [12].

The method for calculating the ac conductivity for the samples is mentioned in a previously published work [13].

3. Results and Discussion

3.1- The dc electrical conductivity

Fig. (1) illustrates the variation of the $ln\sigma_{dc}$ with temperature for the studied samples in the temperature range (293 – 650 K). The conductivity of these ferrites is observed to increase with arising temperature according to the Arrherius relation .

$\sigma = \sigma_o e^{E/kT}$, where E is the activation energy for conduction, k is Boltzmann constant, and T is the absolute temperature. It can be observed that all samples exhibit semiconducting behavior. There are two distinct regions with different slopes for each sample characterized by a certain transition temperature T_C.

Each region is characterized by certain activation energy E_1 for the low temperature region and E_2 for the high temperature region. Therefore change in slope is expected to happen at the Curie temperature due to these two different activation energies [14]. Some previously published data [15, 16] had confirmed almost the same Curie points by using magnetic measurements. It can be seen that, the activation energy E_p in the high-temperature region (paramagnetic region) is higher than the activation energy E_f in the low-temperature region (ferrimagnetic region). In agreement with literature since it is known that the transition from the ordered ferrimagnetic state to the disordered paramagnetic state is associated with an increase in the activation energy.

Table (1): shows the composition dependence of activation energies (E_f,E_p), dc conductivity (σ_{dc}) and Curie temperature (T_C)for the different samples.

X values	E_p.ev	$E_f$ev	T_c K
0.4	0.39	0.282	419
0.6	0.491	0.362	437
0.8	0.463	0.311	412
1.0	0.754	0.404	430

Fig (2 a, b) shows the behavior of the dc electrical conductivity (σ_{dc})asa function of composition (x) at two different values of temperature (room, and 373 ˚K). It can be noticed that, the conductivity decreases sharply between (x = 0.4) and (x = 0.6) then increases slightly at (x = 0.8) then decrease again at (x= 1). This can be explained as follows:

The presence of two types of charge carriers in $NiAl_xFe_{2-x}O_4$ was previously suggested by Ahmed *et al*. [17] 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

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

while the p-type charge transfer exists in Ni ions according to

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

In Al- containing ferrites, Al^{+3} ions prefer the octahedral coordination until the ratio of Al substitution becomes greater than 0.6 [6] where after, Al ions may increase in A- sites causing migration of some iron ions to B- sites. This increases the n- type transfer according to equation (1) and the behavior of n- type charge carrier predominates. 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 which is obviously manifested by the relative decrease in σ_{ac} for the sample (x=1).

3.2- AC conductivity behavior

Fig. (3 a-d) shows the log-log plot of the real part of ac electrical conductivity σ'ac against frequency at different temperature for all studied samples. It is observed that σ' increases as the temperature increase and also with increasing frequency. The dispersion in ac conductivity

decreases as the temperature increases Notice that σ'_{ac} approximately becomes frequency independent at high temperature for the samples with (x = 0.4 and x = 1).

Fig. (4 a-d) shows the temperature dependence of lnσ'_{ac} at five different frequencies (f = 1, 4, 10, 40, 100 kHz) for all samples. It shows obviously that the general behavior of ac conductivity with temperature is a semiconducting behavior where the conductivity increases with increasing temperature. It can be also seen that at relatively high temperature, the ac conductivity is approximately frequency independent. As the temperature decreases the ac conductivity becomes frequency dependent where its values increase with increasing frequency. A similar behavior of σ'_{ac} with frequency and temperature were observed for Ti-substituted Li-ferrites and Co-Cu hexagonal ferrites. This behavior could be explained on the basis of Maxwell-Wagner theory [19] and Koops [20] phenomenological theory. According to this model, a ferrite sample with heterogeneous structure can be regarded as a system consisting of well-conducting grains having thickness d_2, conductivity σ_2 and permittivity ε_2 separated by poorly conducting layers (grain boundaries) having thickness d_1, conductivity $\sigma_1$and permittivity ε_1. The real part of ac conductivity $\sigma'_{ac}$of such a system can be written as $\sigma' = \sigma_\infty + \frac{\sigma_o - \sigma_\infty}{1+\omega^2\tau^2}$ where $\sigma_\infty$is the conductivity at high frequency($\omega\rightarrow\infty$), $\sigma_0$is the conductivity at low frequency ($\omega\rightarrow 0$), τ is the relaxation time and ω is the angular frequency of the applied ac electric field.

According to this theory it can be concluded that at low frequencies the conductivity is mainly due to the grain boundaries while at high frequencies the conductivity is due to the grains.

The real part of ac conductivity can be expressed generally by the following relation

$$\sigma'_{ac} = \sigma_{dc}(T) + \sigma_2(\omega, T) \quad (1)$$

where σ_{dc}(T) is the electrical conductivity due to the free charges (frequency independent part = σ_{dc}), the second term $\sigma_2(\omega, T)$ is frequency and temperature dependent which can attributed to the hopping of charge carriers between localized electric states. This term could be written as:

$$\sigma_2(\omega, T) = A\,\omega^s \quad (2)$$

Where $\omega = 2\pi f$ is the angular frequency of the applied ac electric field, A is a constant having the units of conductivity when s = 0, and having the units of conductivity and time when s = 1. The parameter s is a dimensionless parameter and it increases with temperature $\sigma_2(\omega, T)$ were calculated as the difference between σ'_{ac} and σ_{dc} (T) according to the equation (1). The frequency parameter s was calculated in accordance with the above equation.

Fig. (5) shows the behavior of s with the temperature for all samples. It is well known that the dependence of s on temperature and frequency is an indicator of the conduction mechanism [22,23]. A small polaron tunneling model [23] predicts a decrease of s with decreasing temperature. On the other hand, if overlapping large polaronare formed, s decreases with increasing temperature up to a certain temperature and then increases with further increasing of temperature. For quantum mechanical tunneling [24] s is independent on temperature, while classical barrier hopping [25, 26] shows a decrease in s with increasing temperature. Fig. (5 a-d) illustrates the relation between the value of the exponent s for the measured samples and temperature. For the samples with x=0.6, 0.8 and 1.0 we can see that the overlopping large polaron may be suggested but for x=0.0 small polaron tunneling model may be suggested.

Conclusion

- The results of the dc conductivity $\sigma_{dc}$of the samples show that the conductivity decreases sharply between x=0.4 and x=0.6 so we can conclude that with increasing Al^{3+} ions in the composition $Ni_{0.7}Cd_{0.3}Fe_2O_4$ the dc conductivity decreases sharply.
- The general behavior of ac conductivity with temperature is a semiconducting behavior.
- The variation of the exponent s with temperature suggests that the overlapping large polaron may be the predominate conduction mechanism for these Al substituted ferrites.

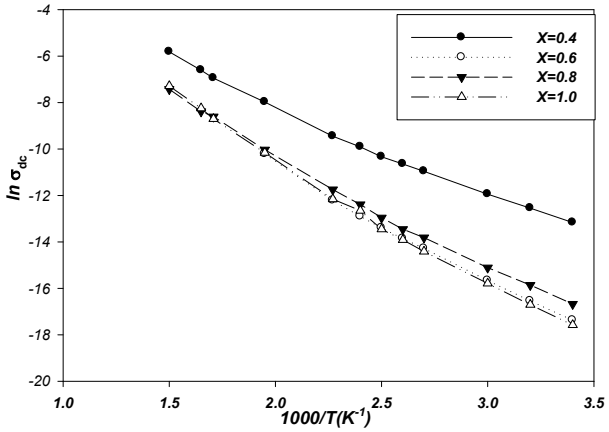

Fig (1) the variation of lnσ_{dc}vs. 10^3/ T(K^{-1}) for the samples $Ni_{0.7}Cd_{0.3}Fe_{2-x}Al_xO_4$.

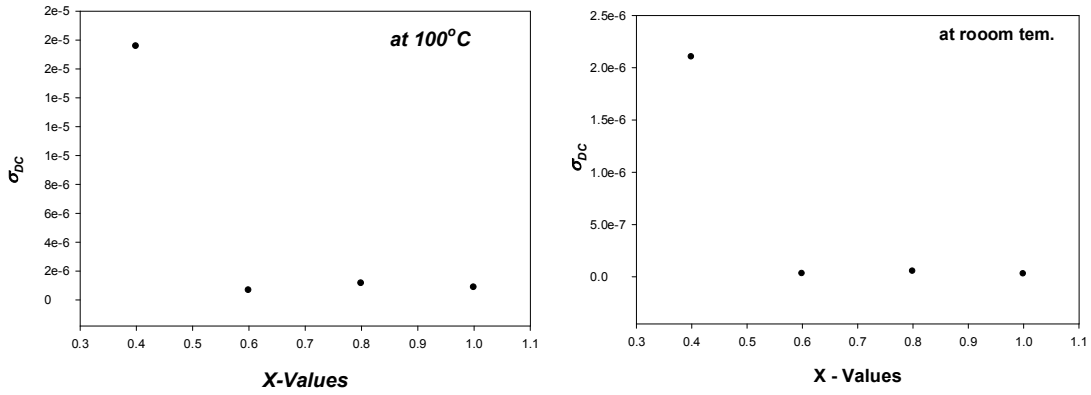

Fig (2) the variation of dc electrical conductivity as a function of composition (x) at 100˚C and room temperature

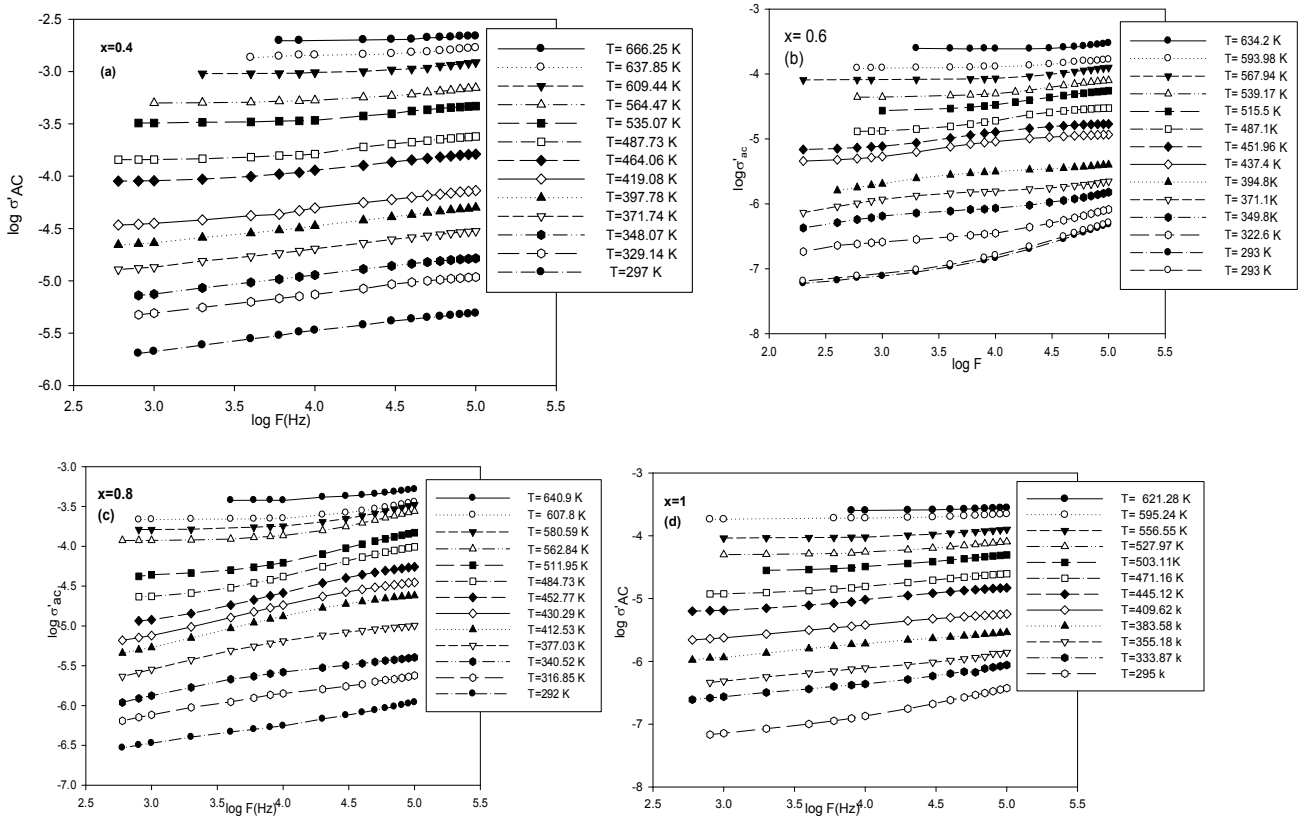

Fig. (3 a-d) the variation of *log* σ_{ac} with the frequency as log f at different temperature for all studied samples.

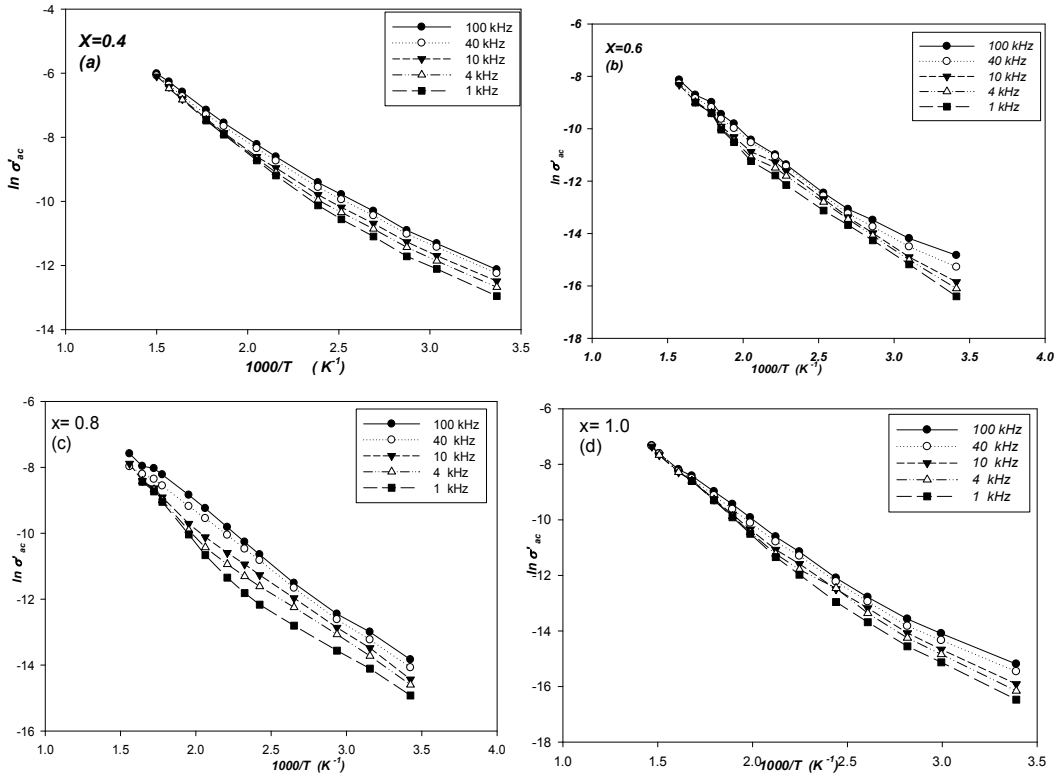

Fig. (4 a-d) Temperature dependence of $\ln\sigma'_{ac}$ at five different frequencies (f = 1, 4, 10, 40, 100 kHz) for all samples.

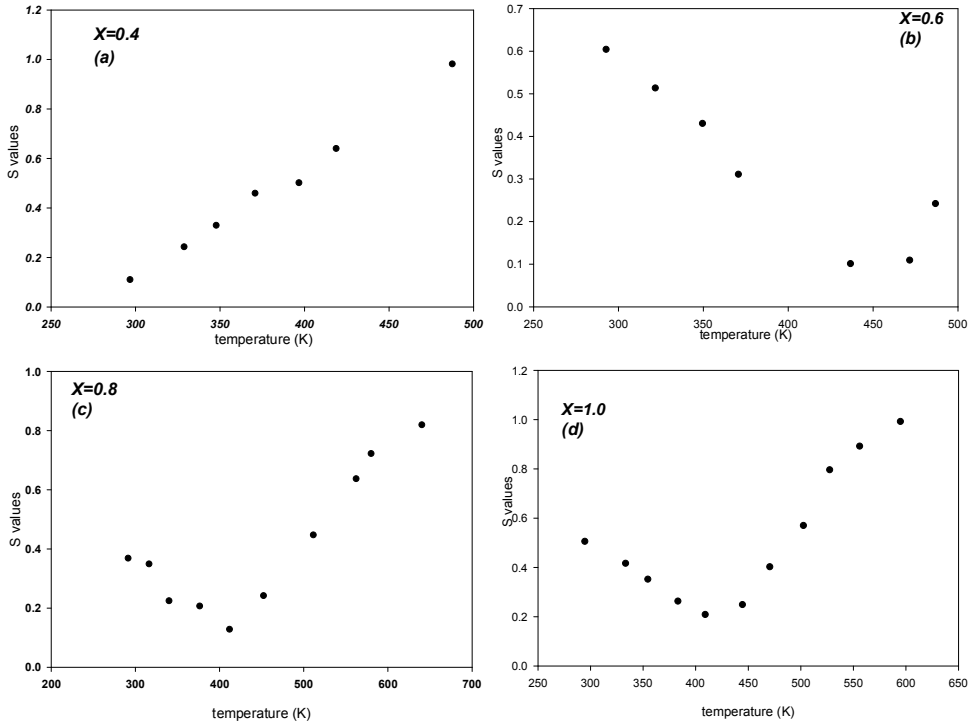

Fig. (5 a-d) Temperature dependence of the exponent s for different compositions of $Ni_{0.7}Cd_{0.3}Fe_{2-x}Al_xO_4$.

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