

INITIAL PERMEABILITY AND DC CONDUCTIVITY OF CU – ZN FERRITE

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$Cu_{1-s}Zn_sFe_2O_4$ 800k 300k

$10^3/T$ $\log(\sigma T)$

Abstract: The initial permeability and dc conductivity as a function of temperature ranges from 300K to 800K are measured for $Cu_{1-s}Zn_sFe_2O_4$ compounds. This compound was prepared using the conventional ceramic double sintering process with various compositions.

The results show a drop at the Curie temperature. The relation of $\log(\sigma T)$ against $10^3/T$ illustrates a transition near Curie temperature. The activation energy in the ferrimagnetic region is found in general to be less than that in paramagnetic region. An attempt is also made to explain the conduction mechanism in these ferrites.

1. Introduction

The polycrystalline Cu–Zn ferrite could be considered as the most versatile ferrites, due to their high resistivity and low eddy current losses. Generally Cu–Zn ferrites were commercially used in radio frequency circuits, transformer cores, antennas and read/write heads for high-speed digital tape and in high quality filters [1,2]. The initial permeability μ_i of the ferrimagnetic materials that results from the spin rotational and domains walls motion [3,4]. It depends upon the magnetization, the ionic structure and the degree of domain walls continuity across the grain boundary layers as shown by **Globus** [5]. It is found that, μ_i varies with different conditions such as the soaking time, the sintering temperature, the time of sintering, the porosity, the defects introduced and atmosphere of firing due to the sintering process [6].

The thermal spectra of μ_i or the μ_i - T curve can be taken as a test function of homogeneity of the ionic structure of the sample [7]. The μ_i - T

curve depends strongly on the preparation conditions, since, these ferrites are in polycrystalline form [8].

In this paper, we study the initial permeability and electric conductivity of mixed Cu–Zn ferrites system from room temperature to well beyond the Curie point temperature. This would help to identify the properties of the mixed Cu–Zn compound, particularly the **Curie** point temperature which serves from industrial point of view.

2. Experimental Method

Samples of the Cu–Zn ferrites having the chemical formula $\text{Cu}_{1-s}\text{Zn}_s\text{Fe}_2\text{O}_4$ where s ranges from 0 to 1 in steps of 0.2, were prepared by usual double sintering ceramic technique, using high purity oxides, CuO, ZnO, and Fe_2O_3 . During this preparation, presintering at 750°C for 5h and powdering of the formed products was followed by final sintering at 1100°C for 5h. In addition, the furnace was cooled gradually to the room temperature in the air atmosphere. Pellets of 1cm diameter were also polished smooth to have uniform plane surfaces and silver pasted on both sides to ensure good electrical contacts. Furthermore toroidal shape of external diameter of 16mm and internal diameter of 8mm was prepared to measure the initial permeability with primary current of 30×10^{-3} A.

Electrical conductivity and initial permeability studies were carried out through the present work over a temperature range 300K to 800K.

3. Results and Discussion

In the present work, we will illustrate the experimental results that give the permeability of the prepared compounds. Figures (1a to 1d) show the change of μ_i as a function of temperature for the ferrite samples with $s \leq 0.6$. It is found that, μ_i increased with increasing temperature. It also, showed a maximum value just below the **Curie** temperature point T_C and falling abruptly close to T_C . The variation of μ_i as a function of temperature determines that the ferrite samples under investigation have different values of **Curie** temperature according to zinc increment in the compounds. This value is found to decrease relative to the zinc content in the compound. Table 1 displays the variation of T_C with different ferrite samples.

s	$(T_C)K$	$(T_1)K$	$\Delta T = T_2 - T_1$	$(T_2)K$	$(T_{av.})K$	$\Delta T / T_{av.}$
0.0	727	508	572	64	540	0.12
0.2	635	578	596	26	587	0.03
0.4	519	500	510	10	505	0.019
0.6	360	344	348	6	346	0.011

Table (1): Different values that were calculated from the figure (1a-1d).

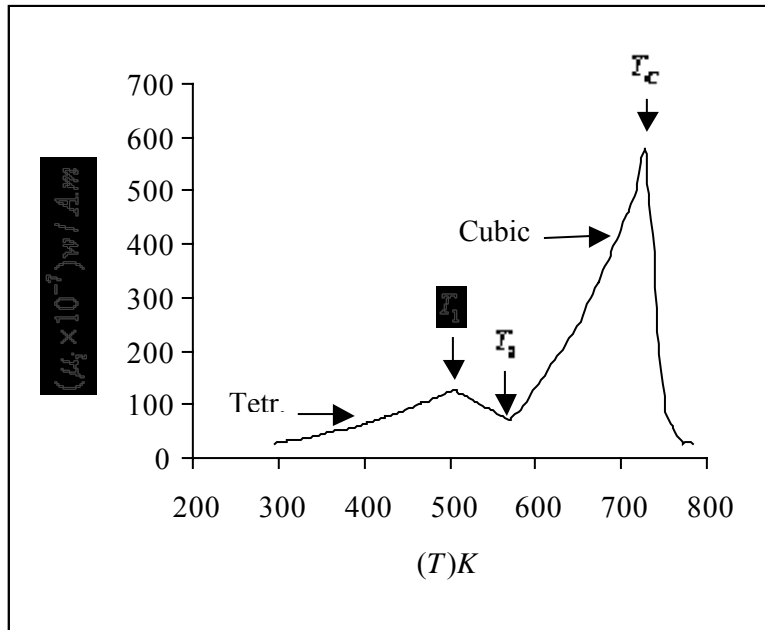


Fig. (1a): Change of the μ_i with temperature for the sample with $s = 0.0$.

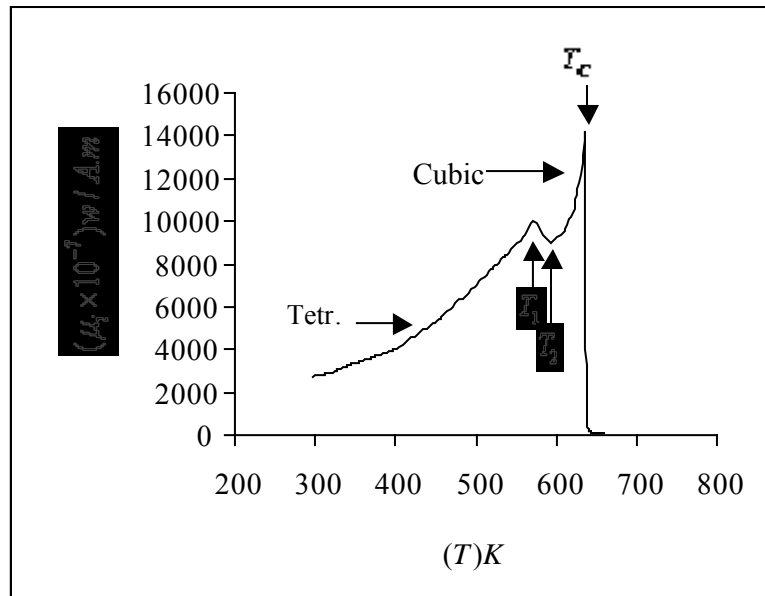


Fig. (1b): Change of the μ_i with temperature for the sample with $s = 0.2$.

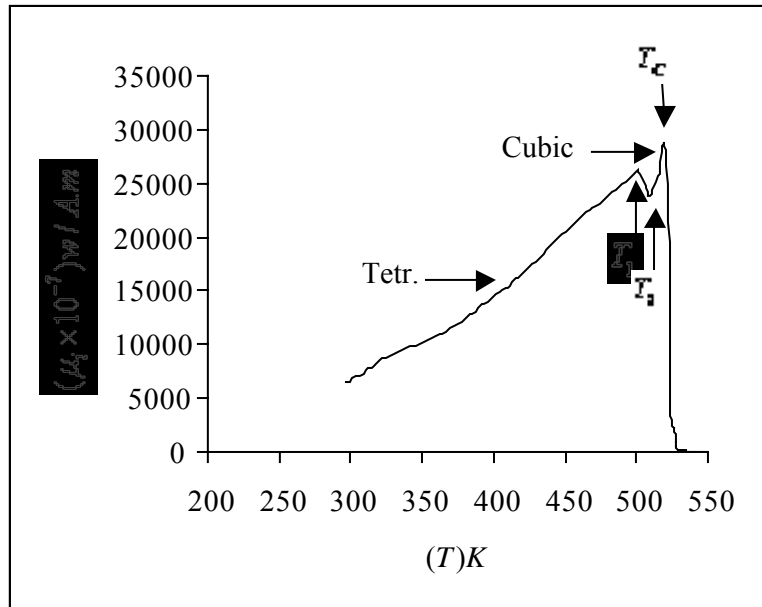


Fig. (1c): Change of the μ_i with temperature for the sample with $s = 0.4$.

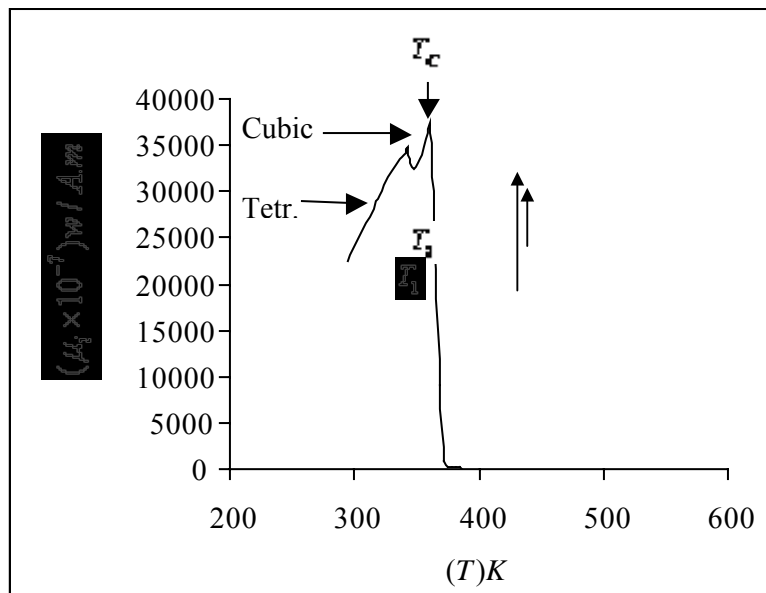


Fig. (1d): The change of the μ_i with temperature for the sample with $s = 0.6$.

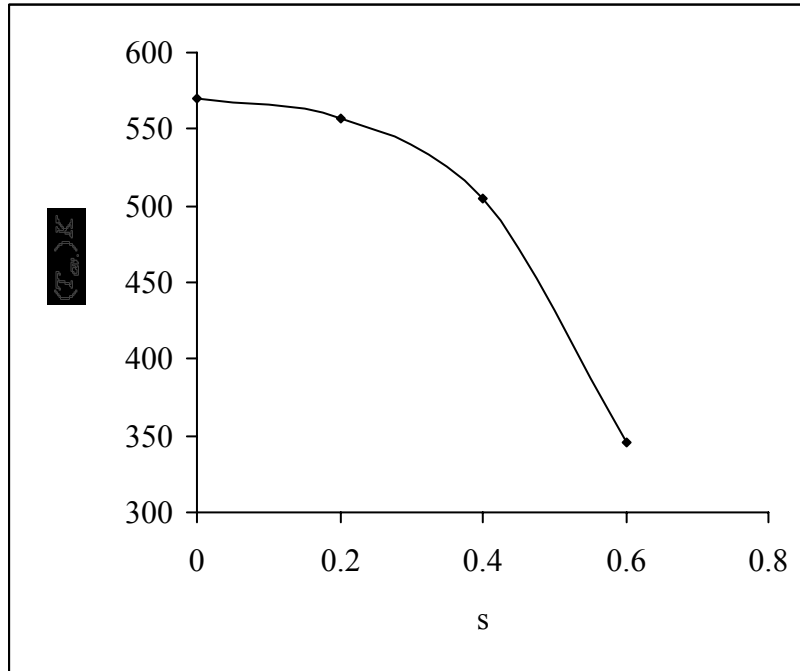


Fig. (2): Variation of $T_{av.}$ with the composition s .

In addition, figures (1a to d) illustrate that, the samples with $s \leq 0.6$ have a phase transition between T_1 and T_2 . The average temperature $T_{av.} = (T_1 + T_2)/2$ was considered as the transition temperature from tetragonal to cubic structure $T_{t \rightarrow c}$. The values of $T_{av.}$ are given in table (1), while the change of the $T_{av.}$ against the composition s is shown in figure (2). From this figure, it is noticed that, $T_{av.}$ decreases with the increase of Zn^{2+} ions.

This behavior indicated that, the samples with $s \leq 0.6$ are a mixture of tetragonal and cubic structure at room temperature. A phase transition from tetragonal to cubic structure was observed by many researchers for different ferrite systems [9]. The value of initial permeability $\mu_{i(max)}$ was found to be increased with addition of Zn^{2+} ions. Also the highest value of $\mu_{i(max)}$ obtained for the sample with $s = 0.6$. This is mainly attributed to the movement of the domain wall, which corresponds to zero point in the

anisotropy energy caused by the presence of the Fe^{2+} ions in the sample [8]. Therefore, μ_i may be considered as a function of the presence of the Fe^{2+} ions. This agrees well with the study of the IR absorption spectra analysis of our system which indicates that, the samples have some of the Fe^{2+} ions, and consequently high μ_i .

Another feature for the μ_i - T curve is the determination of the T_C for the mixed Cu-Zn spinel ferrite. As in figure (3), the T_C decreases continuously with

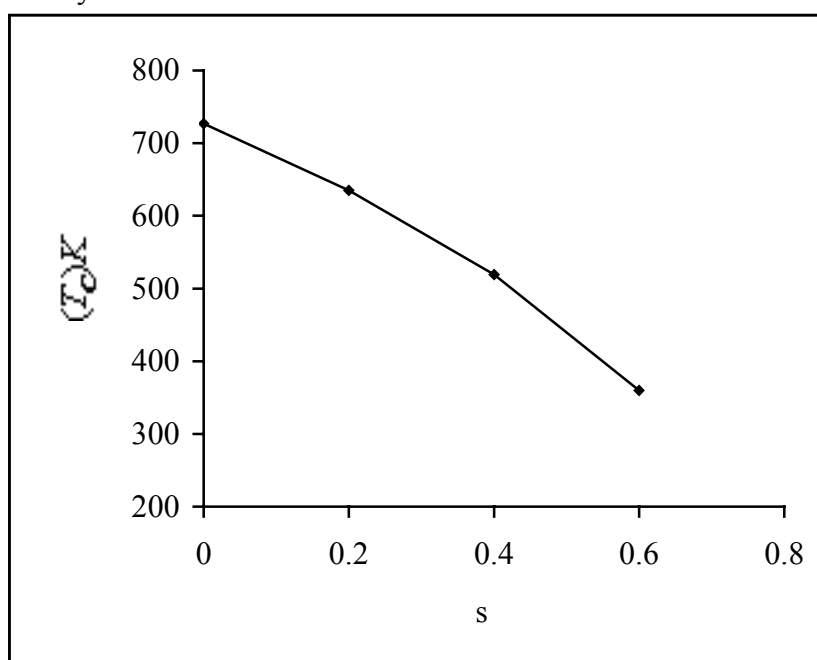


Fig. (3): Variation of T_C with the composition s.

the increase of the Zn^{2+} ions. This decrement in the T_C on the ferrimagnetic materials was, also, observed by other workers [10,11]. This is attributed to the addition of the non-magnetic Zn^{2+} ions that replaced the magnetic Fe^{3+} ions at the T_d sites, thus; the number of the Fe^{3+} ions decrease at the T_d sites. This tends to decrease the strength of tetrahedral T_d and octahedral O_h exchange interactions of the type $Fe_T^{3+} - O^{2-} - Fe_O^{3+}$, apart from decreasing number of bonds or linkages between the magnetic ions[12].

It was also found that, the T_C is reduced by 50.5 % for the samples with $s \leq 0.6$. This decrement may be related to the net magnetic moment of each sample through the change in its tendency from ferrimagnetic type to antiferromagnetic type. Another factor which affects the T_C is the existence of the Cu^{1+} ions in the samples, that is, the Cu^{1+} ions have a certain preference for the T_d sites, this fact accounts for lowering the T_C [13]. The oxidation of $Cu^{2+} \rightarrow Cu^{1+}$ ions involves movement of the copper ions from T_d to O_h sites, where the Cu^{2+} ions prefer O_h sites [14]. This tends to an increase in the T_C value, where the migration of the copper ions from T_d sites to O_h sites occurs and an inverse migration of the Fe^{3+} ions take place [15]. **Snoek** [16] found that, as the Zn^{2+} ions increase the $\mu_{i(\max)}$ shift to a lower temperature for the mixed Zn spinel ferrite, which is in good agreement with our results. On the other hand, the μ_i was not changed with temperature in the case of the samples with $s > 0.6$, because these samples are considered diamagnetic at room temperature. The same observation was found by **Sawant** [17].

The structure change from tetragonal to cubic requires an activation energy, which depends on the basis of thermodynamic theories. The magnetized state of the magnetic materials has lower entropy than the unmagnetized state, and this difference in the entropy tends to change in spin system. Therefore, the slowly cooled copper spinel ferrite has lower symmetry tetragonal maximum disorder structure at lower temperature with higher values of oxygen content, while it has a cubic structure at higher temperature [18]. If the transition is accomplished by heating a ferrimagnetic substance through its **Curie** temperature the entropy change appears as an anomaly in the heat capacity [19].

Since, the spontaneous magnetization decreases with increasing temperature, it gives a positive contribution to the heat capacity. As temperature rises the degree of order in the magnetic spin system decreases, and the entropy is associated with the magnetization increases. In thermodynamic systems the entropy change ΔS is defined by [20]

$$\Delta S = C_H \frac{\Delta T}{T} \quad (1)$$

where C_H is the specific heat of the whole system at constant applied magnetic field H . The variation of $(\Delta T/T_{av.}$ i.e. $\Delta S/C_H)$ with the

composition s for the samples with $s \leq 0.6$ is shown in figure (4). Owing to thermodynamic relation [20]

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \quad (2)$$

and making use of equations (1) and (2) we find that, the variation of temperature is given by

$$\Delta T = -\left(\frac{T}{C_H}\right)\left(\frac{\partial M}{\partial T}\right)\Delta H \quad (3)$$

According to the **Weiss** field theory, the change of magnetization (M) with the applied magnetic field and temperature is given by:

$$\left(\frac{\partial M}{\partial H}\right) = -\left(\frac{T}{WM}\right)\left(\frac{\partial M}{\partial T}\right) \quad (4)$$

From equations (3) and (4), ΔT may be expressed as [20]

$$\Delta T = \left(\frac{WM}{C_H}\right)\Delta M = \frac{1}{2}\left(\frac{W}{C_H}\right)(\Delta M)^2 \quad (5)$$

where W is the **Weiss** field constant which assumed to be independent of M and T , but can be calculated from the experimental values of ΔM and ΔT .

From equation (5), ΔT is related to $(\Delta M)^2$ by :

$$\Delta T \propto (\Delta M)^2 \quad (6)$$

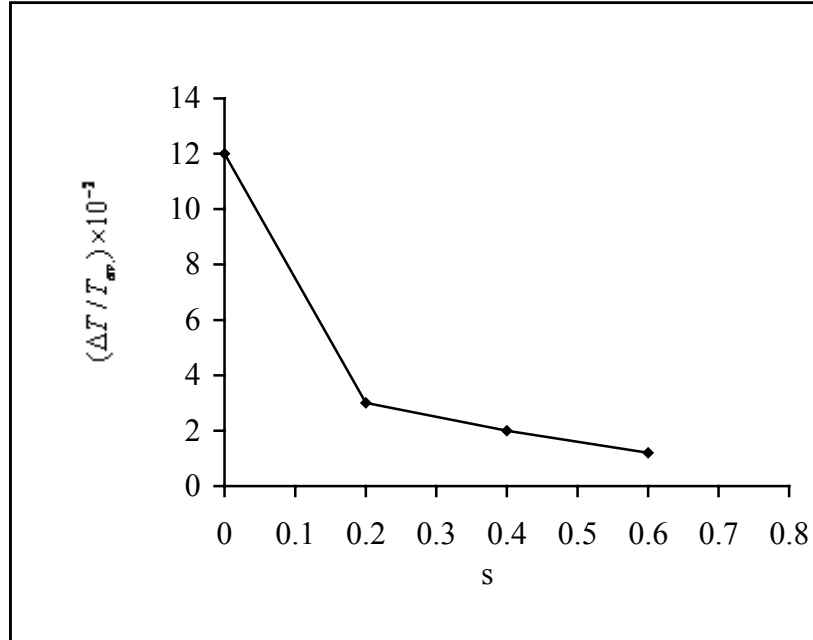


Fig. (4): Variation of $\Delta T / T_{av}$ with the composition s for the samples with $s \leq 0.6$.

Since, μ_i is directly proportional to the square of the saturation magnetization and inversely to the magnetic anisotropy energy, both quantities vary with temperature, thus, μ_i has a complicated function of temperature [20]. Therefore, the change of the initial permeability $\Delta\mu_i$ is directly proportional to the square of the change of the magnetization $(\Delta M)^2$, thus; ΔT is directly proportional to $\Delta\mu_i$

$$\Delta T \propto \Delta\mu_i \quad (7)$$

As shown in figure (4), ΔT decreases with the increasing of the composition s. It is also found that, the lowest value of ΔT corresponds to $s = 0.6$, which has the highest magnetization (see figures 1a,b,c,d).

3.2 DC Resistivity

The DC resistivity ρ_{DC} for the ferrite system $\text{Cu}_{1-s}\text{Zn}_s\text{Fe}_2\text{O}_4$ was calculated in a range of temperature (300 K to 773 K). The variation of $\ln \rho_{DC}$ against $(10^3 / T)$ is depicted in figure (5a to 5f). It is noticed that, $\ln \rho_{DC}$ continuously decreases with the increase in temperature. This agrees well with the results observed in the mixed Cu-Zn spinel ferrite [21]

accordingly, the ferrite system under investigation over the studied range of temperature behaves as semi conducting materials.

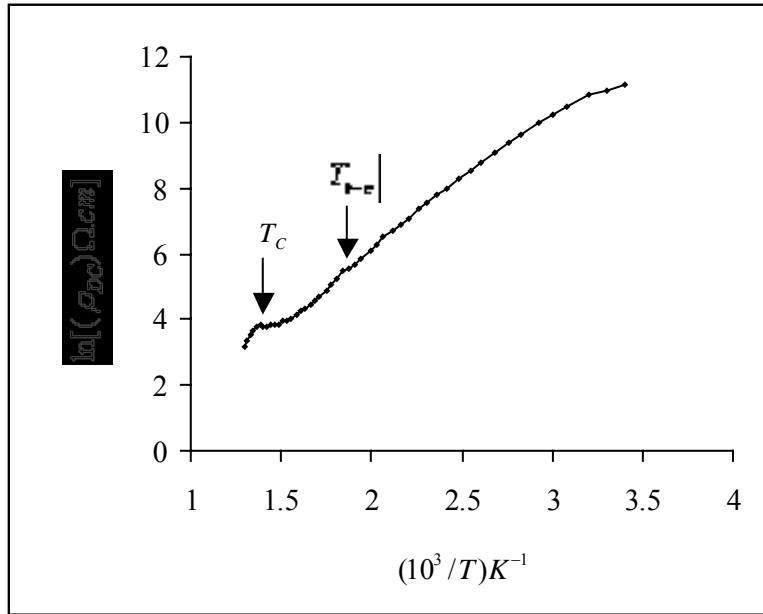


Fig. (5a): Variation of $\ln \rho_{DC}$ with $(10^3/T)$ for the sample with $s = 0.0$.

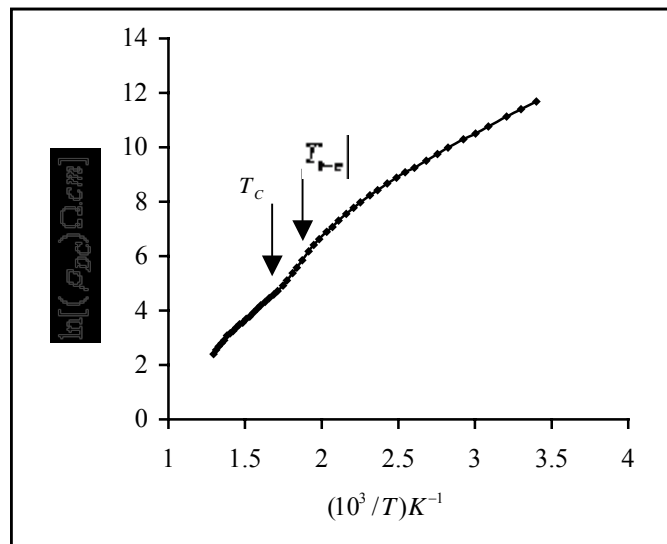


Fig. (5b): Variation of $\ln \rho_{DC}$ with $(10^3/T)$ for the sample with $s = 0.2$.

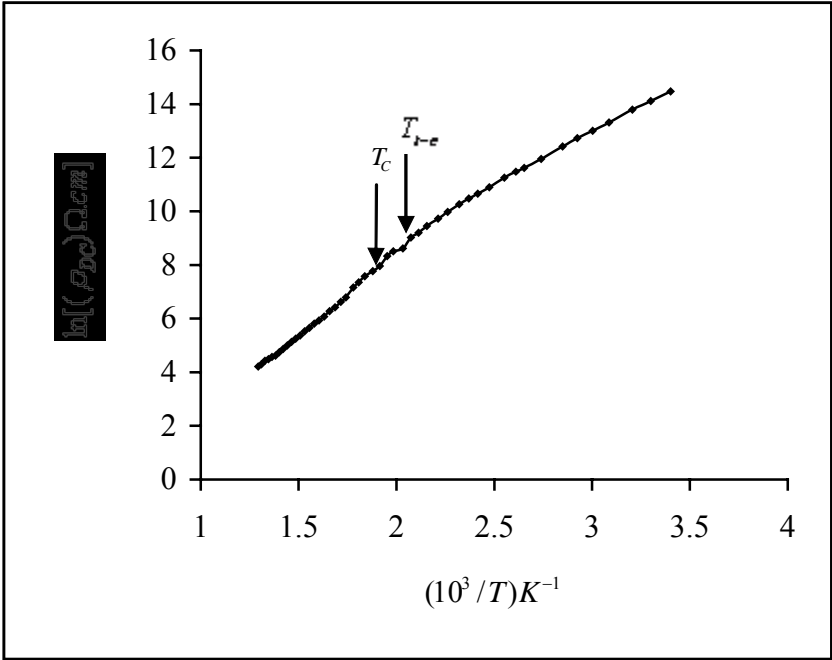


Fig. (5c): Variation of $\ln \rho_{DC}$ with $(10^3/T)$ for the sample with $s = 0.4$.

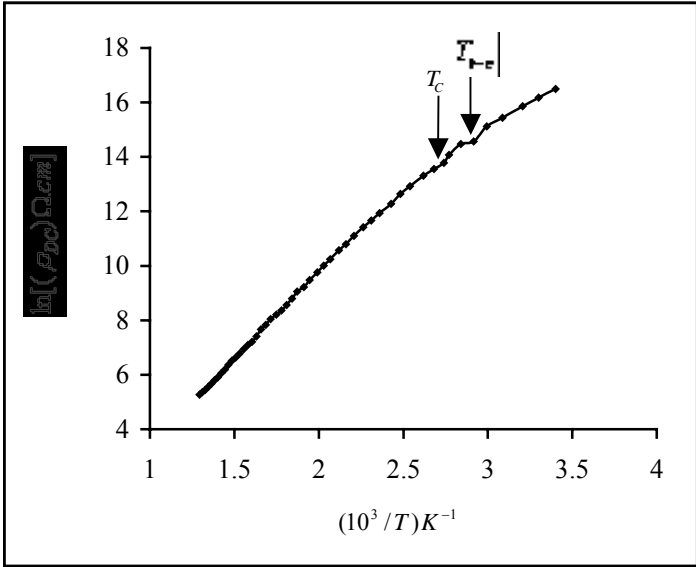


Fig. (5d): Variation of $\ln \rho_{DC}$ with $(10^3/T)$ for the sample with $s = 0.6$.

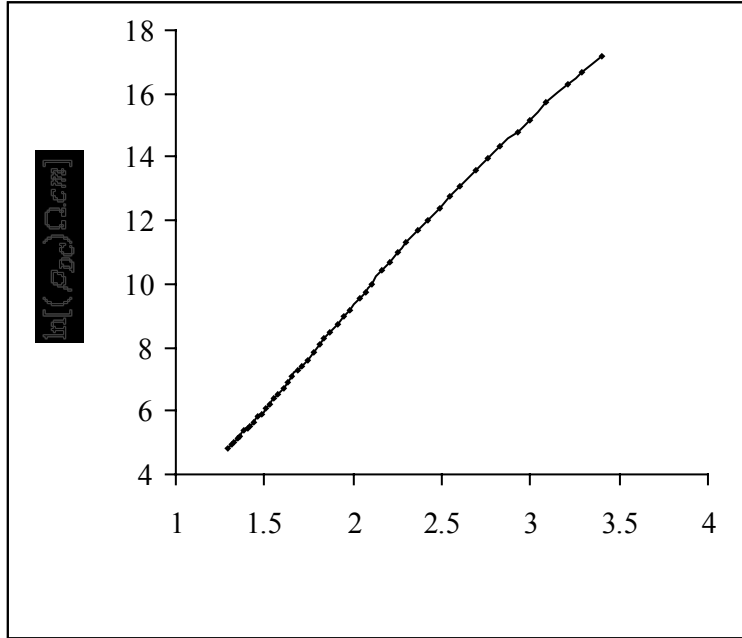


Fig. (5e): Variation of $\ln \rho_{DC}$ with $(10^3/T)$ for the sample of $s = 0.8$.

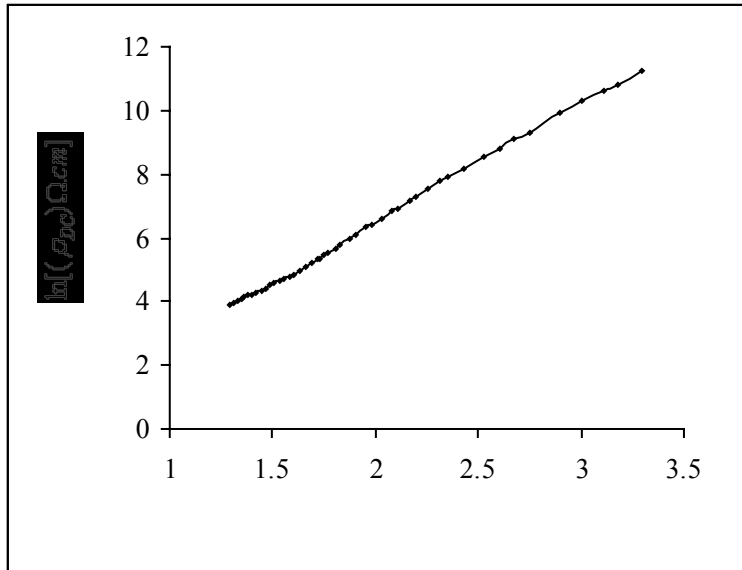


Fig. (5f): Variation of $\ln \rho_{DC}$ with $(10^3/T)$ for the sample with $s = 1.0$.

On the other hand, the decrease of $\ln \rho_{DC}$ with $(10^3/T)$ shows more than one slope. The change in slope may be attributed to the existence of different competing conduction mechanisms. The first change of slope occurs at an intermediate temperature referring to the structural change from tetragonal structure to cubic structure [22].

The variation of temperature T_{t-c} at the phase transition changes from tetragonal structure to cubic structure will be listed in table (2). The comparison with the results taken from the initial permeability measurements is quite clear.

s	Initial Permeability Results		DC Resistivity Results	
	$(T_C)K$	$(T_{t-c})K$	$(T_{t-c})K$	$(T_{t-c})K$
0	727	540	723	542
0.2	635	587	633	584
0.4	519	505	522	504
0.6	360	346	361	343
0.8	-	-	-	-
1.0	-	-	-	-

Table (2): Values of T_C and T_{t-c} determined by the initial permeability and the DC resistivity measurements for the mixed Cu-Zn spinel ferrite.

The second change in slope is due to the magnetic transition from ferrimagnetic state to paramagnetic state [23]. The temperature at which the magnetic ordering transitions occurred is in good agreement with the Curie temperature point T_C , as in table (2).

In the table (2) there is a small deviation of the T_C value from the initial permeability and the resistivity measurements. This indicates that, the magnetic transition can be manifested in the transport property. However, this change of slope could not be observed in the composition with $s > 0.6$, since it is considered as a diamagnetic material at room temperature. The same behavior was shown in the Cd spinel ferrite which also, known as the diamagnetic substance at room temperature [24]. Such a trend can be ascribed to the structural effect.

According to the initial permeability measurements, the mixed Cu-Zn spinel ferrite was formed in the mixed structure between tetragonal structure and cubic structure for the samples with $s \leq 0.6$. This structure is reflected on the results of $\ln \rho_{DC}$ as shown in the figure (5a to 5f), which depends on the anisotropic energy constant of each phase.

The dependence of temperature of the electrical conductivity for the samples of the mixed Cu-Zn spinel ferrite has been investigated from room

temperature up to 773 K. The plot of the logarithm of the electrical conductivity $\ln \sigma T$ versus $(10^3/T)$ is shown in figures (6a and 6b).

It is noticed that, the value of $\ln \sigma T$ increases with the increase of temperature up to a certain value at which a change of the slope has occurred.

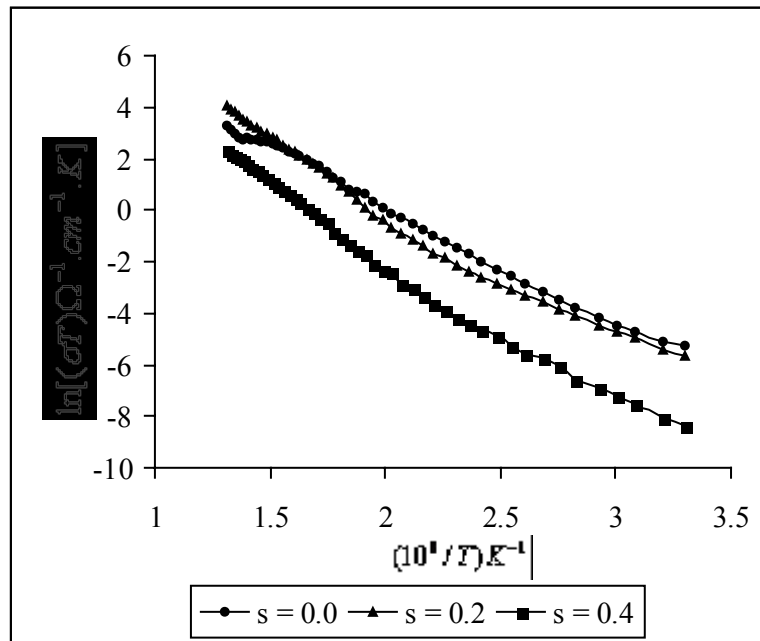


Fig. (6a): Variation of $\ln \sigma T$ with $(10^3/T)$ for the samples with $s = 0.0$, $s = 0.2$ and $s = 0.4$.

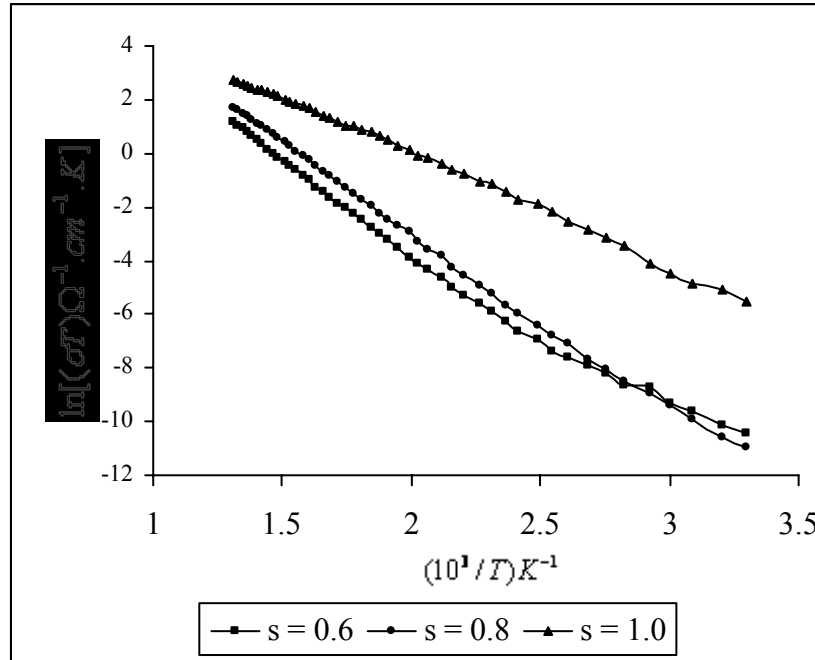


Fig. (6b): Variation of $\ln \sigma T$ with $(10^3/T)$ for the samples with $s = 0.6$, $s = 0.8$ and $s = 1.0$.

The dependence of the *DC* conductivity on temperature in figures (6a and 6b) fulfils the relation [23]

$$\sigma = \frac{S'''}{T} e^{(-E_a/kT)}$$

(8)

where S''' is a constant given by $(ne^2 d^2 \nu / k)$ [25], where d is the distance between the nearest neighbor cations, ν is the frequency of vibration of the crystal lattice and n is the number of the charge carriers.

The *DC* conductivity is useful to calculate the different activation energies for the given ferrite system from the slope of the figure (6a and 6b). The activation energy values of the different conduction mechanisms are calculated and listed in table (3). This table includes the values of the activation energy for the ferrimagnetic region E_f and for the paramagnetic region E_p for the studied compositions at room temperature.

s	Activation Energy	
	$(E_f)eV$	$(E_p)eV$
0.	0.27	0.79
0.2	0.19	0.58
0.4	0.13	0.54
0.6	0.06	0.48
0.8	-	-
1.0	-	-

Table (3): Values of the activation energy E_f and E_p

At the present work, it is noticed that, the activation energy in the ferrimagnetic region varies from $0.27eV$ to $0.06eV$ for the samples with $s \leq 0.6$, while the activation energy could not be determined for the samples with $s > 0.6$, where these samples known as diamagnetic. Similar results were, also, observed for various ferrite systems [26].

It is clear that, the activation energy in the paramagnetic region is higher than that in the ferrimagnetic region. This is attributed to the occurrence of the polaron hopping mechanism. The activation energy decreases with nearly greater than $0.4eV$, which clearly suggest the conduction, is due to polaron hopping. This result has a good agreement for the various ferrite systems [27,28] and it, also, was observed for the mixed *Cd* ferrite [29], which considering a diamagnetic substance.

4. Conclusion

1. The initial permeability has been determined as a function of temperature. It showed an increase with temperature. The maximum value was observed just below the **Curie** temperature It increases by further addition of the Zn^{2+} ions for all samples with $s \leq 0.6$ and showed two peaks (hump shape).
2. The thermal initial permeability measurements were taken as a test of the formation and the homogeneity of the samples, because the initial permeability is related to the magnetization and the ionic structure.
3. The *DC* resistivity was measured for the mentioned samples in a wide range of temperatures from $300K$ to $730K$. It continuously decreases as a function of temperature and shows many slopes. This is attributed to the existence of different competing conduction mechanisms.
4. The *DC* conductivity was useful to calculate the activation energies of the given ferrite system. The variation of electric conductivity with the reciprocal of temperature illustrated that, the electric conductivity increases with increasing temperature.
5. The values of the activation energies of the different conduction mechanisms were determined in the ferrimagnetic and paramagnetic

regions. In the paramagnetic region the activation energy was higher than that of the ferrimagnetic region. This is attributed to the existence of polaron-hopping.

6. The samples with $s = 0.8$ and $s = 1.0$, may have a high resistivity at zero absolute temperature for all the prepared samples.

5. References

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