

Electrical Resistivity of the $\text{Cu}_{0.7+x}\text{Cd}_{0.3}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$ Spinel System

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ABSTRACT

The physical and chemical properties of solids have some sort of relation with the mechanism of charge transport, which can be understood from the measurement of electrical conductivity which is the inverse of electrical resistivity has been studied by snoek [1]. The electrical conductivity of ferrite depends much upon the amount of iron present in the lattice in the ferrous state. The conductivity increases with increase of ferrous ions. The activation energy (ΔE) is the energy needed to release the electron from the ion for a jump of neighboring ion.

Keywords: Electrical resistivity, Activation Energy, Spinel ferrite, Ferromagnetism, Paramagnetism and Curie temperature.

INTRODUCTION

In ferrites, the substitution of a cation that tends to remain in lower valence state leads to p-type conduction and substitution of cation that tends to remain in higher valence state leads to n-type conduction [2,3,4]

Apart from inherent properties of the material conductivity will also depend upon i) porosity ii) grain size [5] iii) chemical in-homogeneity caused during preparation heat treatment etc. Klinger [6] reported the conduction mechanism in ferrites and stated that the hopping of polaron is the main conduction mechanism in ferrites. Many authors have reported the d.c. electrical properties of ferrites [7-9].

Ferrites have a wide Spread role in many technological Applications due to their magnetic properties, high electrical resistivity, low eddy currents and dialectic loss. Ferrites are

extensively used in microwave device, computers, memory Chips, magnetic recording media etc. It is well Known that when ferrites are sufficiently diluted with non-magnetic atoms, they can show a wide Spectrum of magnetic structure, ferromagnetic Order, cluster spin Glass etc. [10]

Copper ferrite and copper containing ferrites have been Focus of continuous interest in the recent years. The spinel Ferrites containing varying amount of zinc form a class of important material. It has been reported that the addition of tetravalent ions like Ti^{4+} , Ge^{4+} , Sn^{4+} in Copper ferrite influences structural and magnetic properties of the system[11]

Several Studies have been reported on the addition Zr^{2+} ions in copper, magnesium and other ferrites [12-17]. However, no reports have been found in the literature regarding structural, cation distribution, electrical and magnetic properties of $Cu_{0.7+x}Cd_{0.3}Zr_xFe_{2-2x}O_4$ ($x = 0.0$ to 0.5) mixed ferrites.

EXPERIMENTAL PROCEDURE

Sample Preparation

Ferrite sample having compositional formula $Cu_{0.7+x}Cd_{0.3}Zr_xFe_{2-2x}O_4$ ($x = 0.0$ to 0.5) were prepared by conventional ceramic technique. The analytical grade reagent of Fe_2O_3 , CuO , CdO_2 and ZrO_2 (all 99.9% pure, supplied by E. Merck) were mixed in proper Proportions and were finely ground. The finely ground powder was sintered at $700^{\circ}C$ for 12 hours and then slowly cooled to room temperature at a rate of $2^{\circ}C/minute$. The sintered powder was reground and sieved through a mesh (100 BSS) and pellets of 1cm diameter were prepared under a pressure of 5 tones/inch². Polyvinyl alcohol (PVA) was mixed as a binder during the preparation of pellets. The pellets were finally sintered at $980^{\circ}C$ for 24 hours and slowly cooled to room temperature at the rate of $2^{\circ}C/minute$ using muffle furnace with controller.

RESULTS AND DISCUSSION

Electrical Resistivity

The variation of the d.c. resistivity as a function of temperature for all the compositions of the series are shown in *Figure 1(a,b,c)* as a plot of $\log \rho$ versus $10^3/T$ curves of all the sample

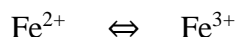
are almost linear at low temperature then a gradual change of slope occurs, and finally the curves exhibit once again a linear behavior at high temperature in all the cases.

It can be also seen from the graph (*Figure 1*) that each sample shows break near Curie temperature which is attributed to the transition from ferromagnetic region to Paramagnetic region. The activation energy in ferri and paramagnetic regions was calculated by using the following equation,

$$\rho = \rho_0 \exp \left(\frac{\Delta E}{KT} \right)$$

and the values are tabulated in *Table 1* It is observed from the *Table 1* that the Values of activations energy in ferromagnetic region are lower than that of paramagnetic region. The lower activation energy in the ferromagnetic region is attributed to the magnetic ordering due to decrease in concentration of current carriers [18], while the change in activation energy is attributed to the change in conduction mechanism [19].

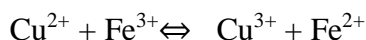
Electrical conductivity in ferrites can be explained on the basis of Verwey and de Boer mechanism [20]. According to them, in oxides containing ion of a given element present in more than one valence state, the exchange such as



Take place in the crystallographic ally equivalent sites of the crystal as a result of transition. According to Van Uitert [21, 22] the production of such ions in more than one valence state is likely during the preparation of ferrites depending upon sintering conditions. In Cd-Zr ferrites, partial reduction of trivalent ion into divalent ion takes place at elevated firing temperature due to vitalization of zirconium. Conduction in these ferrites can be explained on the basis of hopping mechanism. The conduction in n-type specimen is predominantly due to the hopping of electron from Fe^{3+} to Fe^{2+} ions. The electron hopping between B-A sites under normal condition has very small probability compared to that of B-B Hopping. between A-A sites does not exist for the simple reason that there are only Fe^{3+} ions at the A-Sites and any Fe^{2+}

ions formed during the processing preferentially occupy B-sites only. The hopping probability depends upon the separation between the ions involved and the activation energy [23].

The presence of copper on the octahedral site in the spinel, forms conduction mechanism



Which explain conduction mechanism in Cu-Zr ferrites.

In the present system, Cu^{2+} ions are replaced by Zr^{2+} ions and thus conduction phenomenon is ruled out.

From *Table 1*, It is intersecting to note that the transition temperature decreases as Zr^{2+} content is increased. This is to be expected since the A-B interaction will decrease with Zr^{2+} content and hence Curie temperature will be decreased.

It is observed from *Table 1* that the activation energy in ferromagnetic region for the present system increases with increase in the content of Zr^{2+x} . The activation energy for paramagnetic region decreases with increase in the concentration of Zr content x. It is also observation from the *Table 1* that the resistivity at 500 K increases with increase in Zr concentration

The increase in resistivity of the mixed system with increasing zirconium concentration for constant Cd^{2+} values is perhaps due to electron-hole compensation. As the number of Cd^{4+} ions are fixed in the system and Zr^{2+} has strong preference to A-site, the explanation for increase in resistivity with increase in Zr content Will have to be related to statistical distribution of both Fe^{3+} ions Cu^{2+} ions over A and B-site. Since copper ferrite is partially inverted ferrite.

Table.1: Activation energy, Transition temperature (T_i) and resistivity at temperature of $\text{Cu}_{0.7+x}\text{Cd}_{0.3}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$ system

Composition X	Resistivity at 500 K	Activation Energy (ev)	Activation Energy (ev)	Transition
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	(KΩ cm)	Ferri region (E _f)	Ferri region (E _f)	ΔE = E _p - E _r (ev)	Temperature in K
0.0	28.18	0.305	0.671	0.366	689
0.1	37.81	0.267	0.595	0.338	666
0.2	50.11	0.317	0.566	0.249	623
0.3	56.23	0.422	0.495	0.038	593
0.4	89.12	0.427	0.470	0.048	573
0.5	177.82	0.494	0.595	0.100	513

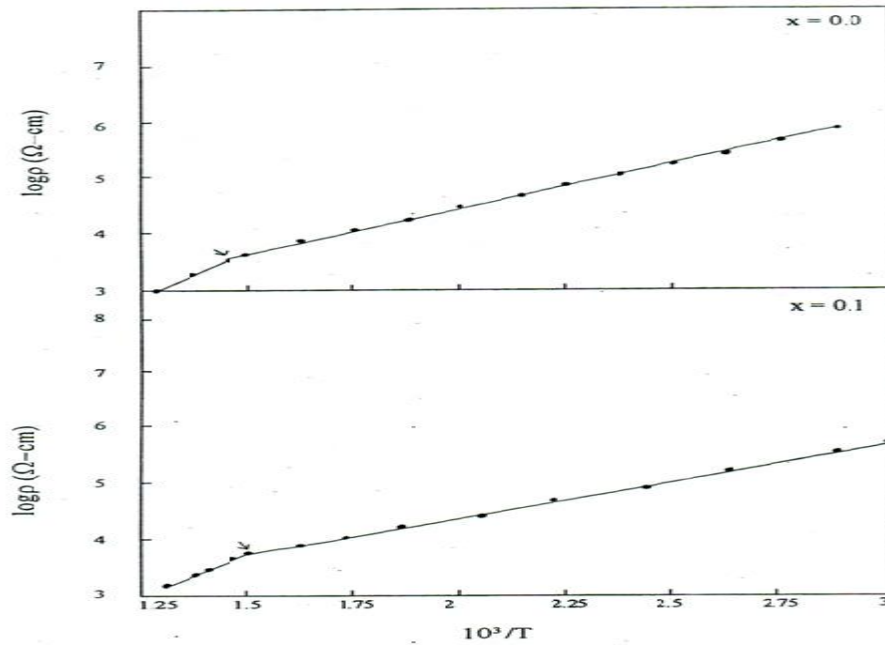


Figure. 1.a) Plot of Log ρ versus $10^3/T$ for $\text{Cu}_{0.7+x}\text{Cd}_{0.3}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$ system for $x = 0.0, 0.1$

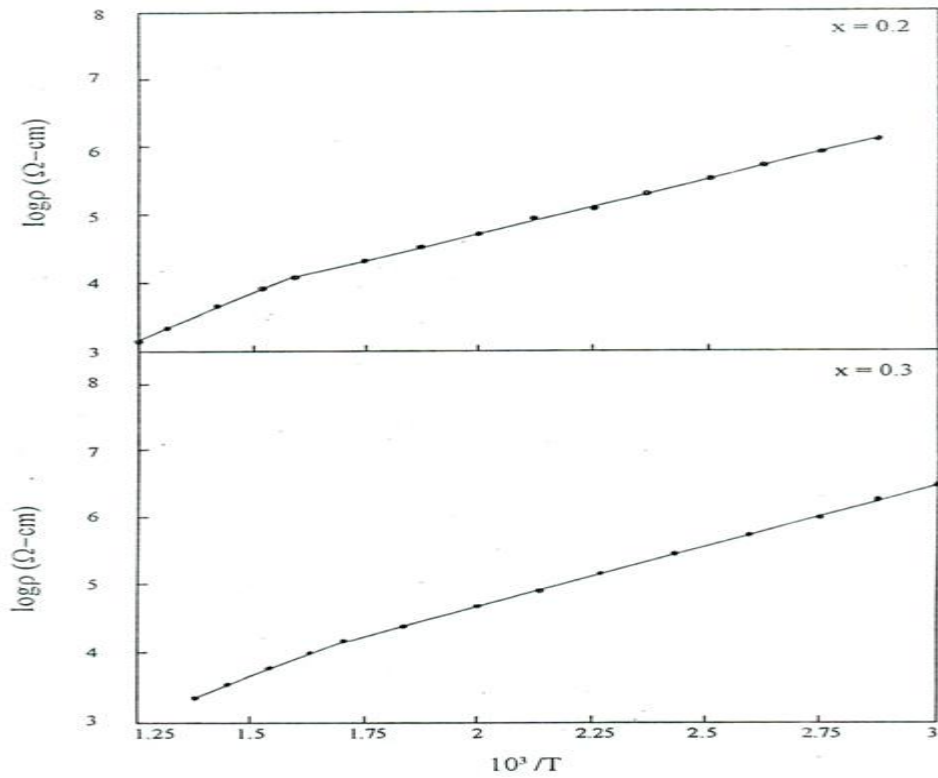


Figure. 1.b) Plot of Log ρ versus 10³/T for Cu_{0.7+x}Cd_{0.3}Zr_xFe_{2-2x}O₄ system for x = 0.2, 0.3

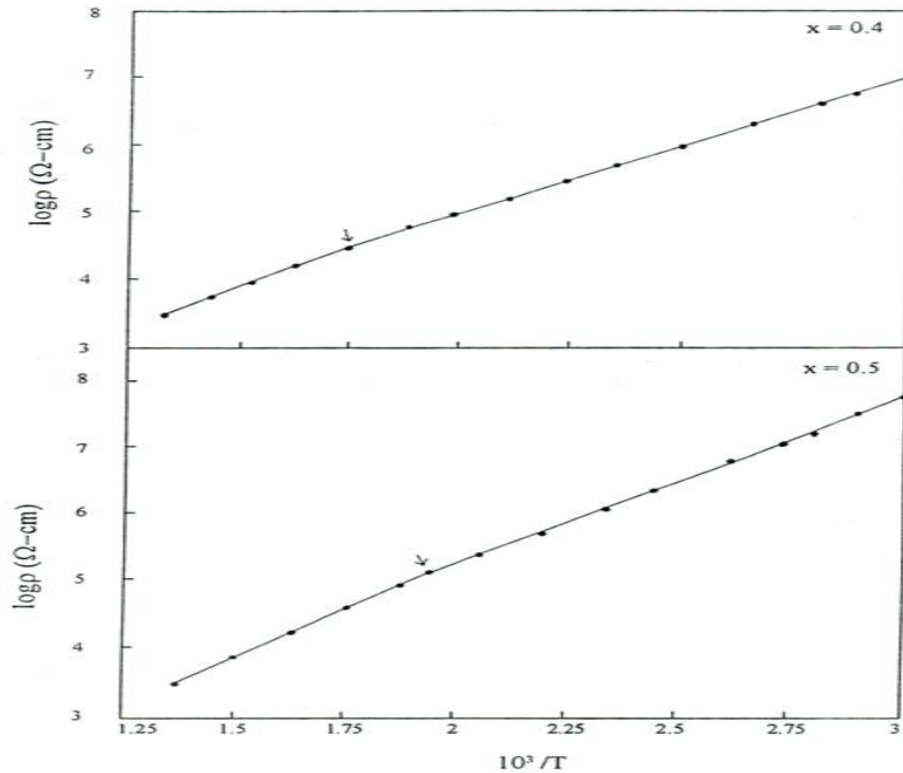


Figure. 1.c) Plot of $\text{Log } \rho$ versus $10^3/T$ for $\text{Cu}_{0.7+x}\text{Cd}_{0.3}\text{Zr}_x\text{Fe}_{2-2x}\text{O}_4$ system for $x = 0.4, 0.5$

CONCLUSIONS

The electrical Conductivity phenomenon is explained on the basis of hopping mechanism of electrons. The active energy in ferrimagnetic region increases with Zr content, whereas, it decreases in paramagnetic region.

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