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DC Electrical Properties of Molybdenum Substituted Lithium Ferrites

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ABSTRACT: DC electrical properties of molybdenum substituted lithium ferrites with general formula $Li_{(1+3y)/2}Mo_yFe_{2.5-5y/2}]O_4$ where 'y' varies from 0.05 to 0.5 insteps of 0.05. DC resistivity with compositional substituents were studied which are increases up to 0.15 and then <u>decreseas</u> to y=0.25 then again increases slowly to maximum y = 0.5. The DC resistivity increases with temperatures to particular value then decreases with with further increasing temperature thereby two types of plots forming for each sample one is corresponding to paramagnetic regions and second is ferromagnetic region. Activition energies were calculated which are decreases up to y = 0.35 and increases to 'y' = 0.40 and finally decreases again. Polaran radii were calculated which are increases up to y=0.25 then decreases at y=0.30 and finally increases.

KEYWORDS: Lithium ferrites, DC resistivity, activation Energies, Polaran radius.

I. INTRODUCTION

Ferrites are an important class of ceramic magnetic oxide materials that come under category of compounds having iron oxide as major component. Ferrites are also an important class of technological materials that have been recognized to have significant potential in application ranging from millimeter wave integrated circuitry to transformer cores and magnetic recording hence. It has wide variety of applications. The technological importance of ferrites increases continuously as many applications require the use of magnetic materials such as permanent magnets.

Field of ferrites has attracted the attention of scientists and technologists for a long time since a wide variety of applications such as electrical and magnetic devices used over wide range of frequencies require their high resistivity and low loss behavior [1] as one of the significant properties. Resistivity of the ferrites is very high compared to resistivity of individual meat oxides. The high resistivity of ferrites facilated to reduce the eddy current losses so as to be useful in industrial applications. The combination of magnetic and electrical characteristics in addition to desirable properties over appreciable range of temperatures lead to many industrial applications of ferrites. Ferrites find the applications because of their desirable electrical and magnetic properties which depend on the cation distribution in A and B sites, site occupancy, super oxide linkages, strengths of linkages, magnetic interactions, conduction mechanism, grain size, dynamics of grain boundary motion.Lithium ferrites belong to the category of soft ferrites because of their loop characteristics like high remanent ratio. Lithium ferrites are more advantages than other spinel ferrite [2] due to their significant properties such as high Curie Temparature (T_c),High dieleectric constant at high frequency,High saturation Magnitization, low coercievitivity etc.

II. RELATED WORK

Lithium ferrites are very significant material and having potential applications. Lot of work is going on since last decades in such a way, Manjula et al [3] studied the electrical conductivity and the thermoelectric power of some lithium –titanium ferrites with small amounts of manganese and zinc as a function of temperature in the of 300-550K. The conductivity variation shows two different regions with a large variation in the activation energies. In region1, the conduction is attributed to electron hopping from Fe^{2+} to Fe^{3+} as evident by the low activation energy (about 0.1 ev)



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and the presence on n-type charge carries observed from seeback coefficient measurements. The high value of activation energy in region II is attributed to the lithium-ion conduction process.

The magnetic properties of $Li_{0.3+0.5x}Zn_{0.4Znx}$ Fe_{2.3-1.5x}O₄ ferrites are reported by Sattar et al [4]. They found that saturation magnetization increases up to x = 0.02 (0.02% mole) and then it decreases. The initial permeability increased while the Curie temperature remains constant with increasing x. The composition dependence of the dc electrical resistivity is found to support the hopping conduction mechanism. Resistivity and dielectric constant of mixed $Li_{0.5}Mg_xTi_xFe_{2.5-2x}O_4$ were reported by Bellad et al [5] and found the compositional variation which indicates the inverse trends.

III. EXPERIMENTALDETAILS

The ferrite samples were prepared by conventional standard Ceramic method with appropriate proportions AR grade Li_2CO_3 , MoO_3 , Fe_2O_3 powders were calculated as per stichiometry. Then all the chemicals were taken in an agate mortar and were thoroughly ground for 6 hours and methanaol is added and again ground until drying. The dried mixture was placed in aluminium crucibles and calcinated at 625°C for 4 hrs. The related powder was ground again for 4 hrs and granulated using a 10% of PVA binder. The granulated powder was compressed uniaxially under pressure of 5 Tones / cm² in stainless steel dies to make pellets and toroidal samples. The pellets and toroidal samples were placed on a platinum foil and sintered at 1200 °C for 4 hrs and subsequently cooled to room temperature at the rate of 3 °C/ min in air atmosphere. Finally the samples were rubbed on plain glass plate using carborandom powder to remove any oxide layer formed during sintering and for smooth surtace.

IV. RESULTS AND DISCUSSION

A. Variation of D. C. resistivity with composition



Fig.1 Compositional variation of d.c resistivity with molybdenum concentration(y)

For molybdenum substituted samples, it is slightly increases up to 0.15 and then decreases fastly to y=0.25 then again increases slowly to maximum y = 0.5. The knowledge of variations in resistivity with temperature, field



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and concentration of substituent ions would throw light in understanding conduction mechanism in the material clearly. Conduction in ferrites can be explained by hopping mechanism involving electron exchange between ions of the same element present in more than one valance state and distributed randomly over crystallographically equivalent lattice sites. In the present case electronic conduction takes place by hopping electrons between Fe^{2+} and Fe^{3+} ions present at octahedral (B) sites [6].

Lithium ions have a strong preference for octahedral sites [6]. In addition to this, lithium ferrite spinels may exhibit ionic conductivity also as its contains reducible iron and lithium ions. The variation of resistivity can be explained on the basis of Verwey mechanism [7], which indicates hopping of electronics between the ions of the same element existing in more than one valance state and distributed randomly over crstallographically equivalent lattice sites. The mechanism responsible for conductivity in ferrites is mainly due to exchange of electrons between Fe³⁺ and Fe²⁺ [8]. Fe²⁺ ions may be formed due to partial evaporation of lithium due to sintering at 1200 °C [9]. The amount and percentage of Fe²⁺ and Fe³⁺ presence in the samples were determined by photochemical Redox titration method. These Fe²⁺ ions preferentially occupy the B sites and B-B hoping between Fe²⁺ and Fe³⁺ is the dominant mode of conduction. Fe²⁺ presence is one the important factors that amount causes the dielectric relaxation content. If the ferrous (Fe²⁺) ions are not present in the ferrite, the dielectric relaxation is not seen generally.

The resistivity increases with composition and finally decreases which can be explained from Heywang's model [10]. The resistivity of ferrites is contributed by grain boundary as well as grains. As the field is applied, the Fermi level shifts and the potential barriers are modified due to increase in electron concentration and decrease in hole concentration. It results in increase of resistivity of all the samples were observed to increase with the duration of the applied field reaching a saturation value. It can be attributed to relaxation effects under the field due to dipolarization , ionic drift and charge trapping [11].

B. Temperature dependence of resistivity

Temperature variations for both series were studied in range between 303K and 773K for both series. The plots of log (ρ) versus 10³/T for various samples are shown in Fig. 2 and the variation is non-linear. The temperature dependence of resistivity is given by the Arrhenius equation:

 $\rho_{Dc} = \rho_o \exp(\Delta E/kT) \tag{3.1}$

Where ρ_{Dc} is the resistivity due to d.c. at the temperature T, ρ_0 represents the temperature independent constant, K is the Boltzmann's constant (K=1.3806503 × 10⁻²³ m² kg s⁻² K⁻¹) and E_g or Δ E is the activation energy needed to release an electron from the ion for a jump to the neighboring ion, so giving rise to electrical conductivity. From Fig.2 all the samples shows increasing resistivity with increasing Temperature to poarticular temperature (Neel Temperature) then decreases with further increasing temperature. Further it is observed that each curve devided into two regions, one is low temperature region (E_P) varying from 0.3 to 0.6 eV and secon region, high temperature region (E_f) varies from 0.05 to 0.2 eV.

Using the Arrhenius equation the activation energy for all the samples are computed and listed in the Table 1. The molybdenum substituted ferrites maintain the same trend similar to compositional variation.



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Fig.2 Variation of DC resistivity with substituent content molybdenum (y) versus Temperatures

C. Activation energy

From Fig.2 a change in slope was observed for all the samples which is in agreement with the earlier observations on similar materials [12]. Two ranges of activation were obtained corresponding to the two slopes. Figs. 3 shows the plot of activation energy (Ev) versus composition. The temperature at which change in slope is observed does not correspond to the measured Curie temperature [13] of the respective sample.

The existence of two parallel conduction mechanism with different activation energies may therefore be responsible for this change in slope . As mentioned above lithium ferrites may exhibit ionic conductivity too in addition to electronic conductivity . The ionic conduction has high activation energy [14], the conduction in region 2 (ferri magnetic region) may therefore be due to this mechanism. However, in region 1(paramagnetic region) with low activation energy the dominant mode of conduction may be electronic conduction. It is observed that the activation energy for both the regions increase. The values of activation energy for 'y' lie in the range 0.03 - 0.45 ev indicates that conduction is intrinsic.

As shown in Fig.2, the plot consists two straight line portions; hence there are two activation energies for the two different regions. The reasons for two slopes can be explained



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Table1	
$Jump \ length(L), activation \ Energy(E), Polaran \ radius \ of [Li_{(1+3y)'2}Mo_yFe_{2.5\cdot5y'2}]O_4$	Ferrites

S.No	Content (y)	Jump length (Å)	Activation Energy		⊿E=	Polaran
			Ep	Ef	EP-Ef (eV)	radius (r _P)
1	0.05	2.951	0.653	0.202	0.451	0.736
2	0.10	2.95	0.605	0.16	0.445	0.736
3	0.15	2,949	0.558	0.118	0.44	0.736
4	0.20	2.955	0.439	0.124	0.315	0.737
5	0.25	2.96	0.32	0.131	0.189	0.738
6	0.30	2.941	0.226	0.112	0.114	0.734
7	0.35	2.959	0.132	0.094	0.038	0.738
8	0.40	2.963	0.407	0.049	0.358	0.739
9	0.45	2.967	0.374	0.05	0.324	0.739
10	0.50	2.970	0.342	0.051	0.291	0.741



Fig.3 Varition of activation energies with substituent content of molybdenum(y)

as at high temperature, the thermal energy is sufficient to create vacancies and the activation energies represent a sum of the energies required fco vacancies generation and the motion of electrons into the vacancy. At lower temperature, the thermal energy is only large enough to allow the migration of electrons into vacancies already present in the crystal. A change in the slope may be due to Neel temperature [14] or to the change in the conductivity mechanism . This anomaly strong supports the influence of magnetic ordering upon the conduction process.

The activation energies for conduction are computed from log_{10}^{ρ} versus 10³/T plots and are presented in Table 1 which are decreases up to y = 0.35 and increases to 'y' = 0.40 and finally decreases again. According to the theory of magnetic semi conductors, one expects such a reduction in the activation energy of the system is due to it the transition from the paramagnetic to the ferromagnetic state. This is due to the fact that the ferromagnetic state is an ordered state while the paramagnetic state is disordered, thus charge carriers required more energy for the conduction. The high value of the activation energy in the paramagnetic state as compared to ferromagnetic state is due to the volume expansion [15]. The activation energies (Ei = 0.1eV) in the ferromagnetic region are much higher than the ionization energies of donar or acceptor and hence the possibility of band type conduction is ruled out. These values are also



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higher than the transition energy of Fe^{2+} and Fe^{3+} (Ei =0.2 eV), which indicate that the polaron conduction mechanism is favoured.

In ferrites, cations are surrounded by close packed oxygen anions and, as a first approximation, can well be treated as isolated from each other. There will be little direct overlap of the anion charge clouds or orbitals. Alternatively, the electrons associated with particular ions will largely remain isolated and, hence, a localized electron model is more. A small polaron defect is created when an electronic carrier becomes trapped at a given site as consequence of the displacement of adjacent atoms or ions. The entire defect (carrier plus distortion) then migrates by an activated hopping mechanism. An essential condition for the formation of a small polaron is that the value of polaron radius (r_p) should be less than the inter ionic distances. An attempt has been made to calculate the polaron radius (r_p) for all compositions studied by relation [16] :

$$r_p = \frac{1}{2} \left[\frac{\pi}{6N} \right]^{\frac{1}{2}}$$
 (3.2)

Where N= Number of sites per unit volume = $96/a^3$, in spinel ferrites 64 A (tetrahedral) and 32 B (octahedral) sites are available per unit volume. The calculated values of r_p for 'y' = 0.05 to 5.0 are summarized in Table. 1. It is seen that these values are smaller than inter ionic distances [17], and hence are appropriate for small conduction. The small polaron conduction in band like a manner up to a certain temperature. At higher-temperatures, the conduction is by activated hoping [17]. Based on the small polaron model the conduction phenomenon in region 1 is attributed to the presence of impurities, vacancies and defects, while that at higher temperatures is attributed to the small polaron hopping mechanism. According to Rezlescu et al [18] the change $\Delta E = E_p - E_f$ is associated with the ordering temperature roughly given by the relation $\Delta E = AkT_N$, where E_p and E_f are activation energies below and above T_N . It is important to note that small changes in ΔE with y are observed for the present system. According to Ahmed et al [19], the effect of 'y' on ΔE is greater if the substituted cations occupy B-sites. Devale et al [20] suggested that almost no change in ΔE is observed when the substitution is made on A- sites without disturbing the Bsites.

V. CONCLUSION

The compositional varation of DC restivity is explained on the basis of conduction mechanism involving electronic exchange between ions of the same element present in more than one valance state and distributed randomly over crystallographically equivalent lattice sites. Temperature varation of molybdenum substituted ferrites for all the samples shows increasing with increasing temperature to particular temperature (Kneel temperature) then decreases with increasing temperature . Each sample exhibits two types of behaviours, one is corresponding to paramagnetic and second is corresponding to ferrimagnetic region. The activation energies were calculated which were decreases to y= 0.35 then increases to y=0.40 then finally decrases. It is explained on the basis of the theory of magnetic semi conductors, i.e such a reduction in the activation energy of the system is due to it the transition from the paramagnetic to the ferromagnetic state is due to the fact that the ferromagnetic state is an ordered state while the paramagnetic state is disordered, thus charge carriers required more energy for the conduction. The high value of the activation energy in the paramagnetic state as compared to ferromagnetic state is due to the volume expansion The polaran radius are smaller than interIonic distances and hence one are appropriate for small conduction. The small polaron conduction in band like a manner up to a certain temperature. At higher temperatures, the conduction is by activated hoping based the small polaron model the conduction phenomenon in region 1 is attributed to the presence of impurities, on vacancies and defects, while that at higher temperatures is attributed to the small polaron hopping mechanism.

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