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DC Electrical Properties of Antimony Substituted Lithium Ferrites

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Abstract: ***This paper discusses the DC electrical properties of antimony substituted lithium ferrites with compositional formula [$Li_{0.5+x}$ $Sb_xFe_{2.5-2x}$ O_4]; where x=0.0 to 1.0 insteps of 0.1 prepared by conventional standard ceramic method sintered at1200 ^oC. It has been studied by means of compositional and temperature dependent resistivity in the range of 303-773K. It is found that the Neel's temperatures, increase up to x=0.3 then decrease up to x= 0.5 then again increase and maintain a constant. The resistivity of the samples is found found in the range between 10^4 -10^9Ω-cm at room temperature. The activation energies were calculated in ferromagnetic and paramagnetic regions and are found to lie in between 0.02 and 0.4 eV. They are found to be decreasing up to x=0.2 then increase to x=0.4 further decrease to x=0.9 finally increase at x=1.0 with continuous increases of antimony. It shows that these belong to semiconductor materials. The polaran radius and jump length were also calculated. The polaran radius is increases up to x=0.3 then gradually increases with continuous increase of antimony concentration. The conduction mechanisms were studied using polaran radius and it is confirmed that conduction mechanism takes place between Fe^{2+} and Fe^{3+}.***

Keywords: Soft ferrites, Lithium ferrites, electrical resistance, activation energy, polaran radius.

I. INTRODUCTION

Lithium ferrites belongs to a category of soft ferrites that are used as different kinds of magnetic and microwave devices for high frequency and other applications due to their high Curie temperature, high squareness ratio, superior temperature stability of saturation magnetization, low intrinsic linewidth and low magnetic losses (1-5). The properties of ferrites are strongly dependent on the crystal structure and cation distribution, which are governed by type of doping, sintering temperature, atmosphere, and method of preparation (6). $Li_{0.5}Fe_{2.5}O_4$ has face centered cubic inverse spinel structure in which all Li^+ ions and 3/5 of all Fe^{3+} ions occupy the octahedral B sites whereas the remaining Fe^{3+} ions occupy the tetrahedral A sites. Electrical related properties of resistivity and dielectric constant are two important parameters in ferrites. The present study is helpful to find the application of these materials as transformer cores and is also in fabrication of capacitors, microwave devices and devices required for pulse mode applications. Lithium ferrites are widely used in microwave devices due to their very high resistivity and low dielectric losses. High resistivities are obtained in stoichiometric ferrites containing no ferrous ions. Low resistivities in ferrites are caused by the simultaneous presence of ferrous and ferric ions on equivalent lattice sites (octahedral sites). Resistivity in ferrites can be increased by the addition of substituent ions in presence of small amount of Fe^{2+}. This process leads to reduction in eddy current losses and improvement of magnetic properties. The conduction in ferrite materials is basically described by the phenomenon of the hopping of electrons between the ferrous and ferric ions occupying octahedral sites in the spinel lattices, in addition to impurity conduction and polaron hopping mechanism. The aim of the present study is to see the influence of high valence cations viz. Sb^{5+} (0.62 Å) which is comparable to the ionic radius of ferric ion (0.64 Å) on different conduction mechanisms. These ions have oxidizing properties and can influence the properties of lithium ferrites due to their substitution. The resistivity is one of the important properties of ferrites because at high frequencies it shows effect on eddy current losses which may result in significant loss of energy, since eddy current loss is inversely proportional resistivity. Ferrites have very high resistivity which is one of the considerations for microwave applications. At high frequencies where eddy current loss cause significant losses in energy. The electrical properties of ferrites are sensitive to preparation method, sintering temperature, sintering time, rate of heating and rate of cooling [7-8].

II. EXPERIMENTAL DETAILS

The ferrite samples with compositional formula [$Li_{0.5+x}$ Sb_x $Fe_{2.5-2x}$] O_4 (where x = 0.0 to 1.0 insteps of 0.1) were prepared by conventional standard ceramic method. The appropriate proportions of Li_2CO_3,Fe_2O_3 and Sb_2O_5 were taken and thoroughly mixed

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in an agate mortar in the presence of methanol. The dried mixture was pre-sintered at 625 ^{o}C for 4 hrs. The related powder was ground again and granulated using a small amount of PVA binder. Finally granulated powder was compressed uniaxially under a pressure of 5 tones/cm^2 in a stainless steel die to make pellets and the samples were sintered at 1200 ^{o}C for 4hrs for good densification. The samples were cooled in the furnace in air atmosphere at the rate of 3^{0}C/min. Due to sintering at 1200 ^{0}C lithium volatility occurs and as a result Fe^{2+} ions exists [9]. DC(Direct Current) resistivity of the samples were measured by the conventional two- probe method in which the samples is placed in between spring-loaded copper electrodes. The current through samples were measured using Kiethly model 614 electrometer. A DC voltage of 5V is applied across the surface of the samples. Although each sample has nearly 3mm and 12 mm diameter, the diameter and radius of each sample were calculated using screw guage and vernier calipers. The resistivity of the each sample were calculated using the well known relation at.

$$\rho = \frac{RA}{d} \quad (1)$$

Where A represents the area of cross-section and 'd' is the thickness of the sample and R is resistance of the sample. The resistivity variation with temperature was measured up to 500 ^{o}C. To avoid temperature gradient between the two circular surfaces, sufficient time was allowed for the sample to be stable at a particular temperature.

III. RESULTS AND DISCUSSIONS

A. Variation of D. C. Resistivity with Composition

Variation of DC resistivity at room temperature with composition as a function of antimony (x) [$Li_{0.5+x}$ Sb $_x Fe_{2.5-2x}$] O_4] is shown in the Fig.1.For antimony substituted lithium ferrites, the resistivity (ρ) is found to increase up to x = 0.9 then suddenly decreases at x=1.0. The resistivity ρ_{DC} of all ferrites are lie in between 10^4 -10^9 Ω-cm (Fig. 1). These are almost agrees with the reported values [10]. The knowledge of variations in resistivity with temperature, field 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 [11]. Substitution of Fe^{3+} ions by Sb^{5+} and Li^{1+} ions is one possible mechanism used to understand the variation of resistivity with substituent concentration. Lithium ions have a strong preference for octahedral sites [12,13]. In addition to this, lithium ferrite spinels may exhibit ionic conductivity also as it contains reducible iron and lithium ions [14,15]. The variation of resistivity can be explained on the basis of Verwey mechanism [16], which indicates hopping of electronics between the ions of the same element existing in more than one valancy state and distributed randomly over crstallographically equivalent lattice sites. The mechanism responsible for conductivity in ferrites is mainly due to exchange of electrons between Fe^{3+} and Fe^{2+} [17-18]. Fe^{2+} ions may be formed due to partial evaporation of lithium due to sintering at 1200 ^{o}C [9]. The amount and percentage of Fe^{2+} and Fe^{3+} presence in the samples were determined by photochemical Redox titration method .These Fe^{2+} ions preferentially occupy the B sites and B-B hoping between Fe^{2+} and Fe^{3+} is the dominant mode of conduction. Fe^{2+} presence is one the important factors that amount causes the dielectric relaxation content. If the ferrous (Fe^{2+}) ions are not present in the ferrite, the dielectric relaxation is not seen generally [19]. The resistivity increases with composition and finally decreases which can be explained from Heywang's model [20] . 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 due to increase of grain boundary resistance of the samples with increase of applied field. And the 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 [21], ionic drift [22] and charge trapping [23].

B. Temperature Dependence of Resistivity

Temperature variations for antimony substituted lithium studied in range between 303K and 773K . The plots of log (ρ) versus 10^3/T for various samples are shown in Fig.1 and the variation is non-linear. The temperature dependence of resistivity is given by the Arrhenius equation:

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$$\rho_{Dc} = \rho_o \exp(\Delta E/kT) \quad (2)$$

Where ρ_{Dc} is the DC resistivity due to d.c. at the temperature T, ρ_o represents the temperature independent constant, K is the Boltzmann's constant and E_g or ΔE is the activation energy. Upon an electron jump, a displacement of the ions in the neighborhood of the electron occurs. It has been pointed out by Jonker [24] that in the intrinsic semiconductors the influence of temperature on the concentration of the conduction carriers is relatively small. This means that the temperature influence on the conductively is only a result of the change of the mobility of the electrons or holes with temperature. Using the above expression and the experimental curves, the activation energy for all the samples are computed and listed in the Table 1. When increasing the temperature, the resistivity is also increasing up to x=0.9 then decreases the resistivity for x=1.0. The corresponding Neel's temperatures were observed to increase up to x=0.3 then decrease up to x= 0.5 then increases constantly. This is due to the variation of grain size the and reduction of Fe^{3+} to Fe^{2+}. The resistivity at x= 1.0 is due to the presence of small grain size and high percentage of Fe^{2+}.

C. Activation Energy

The plots of log_{10}^{ρ} v 1/T for the entire specimen are given in Fig. 3. A change in slope was observed for all the samples which is in agreement with the earlier observations on similar materials [25]. Two ranges of activation were obtained corresponding to the two slopes. Fig. 2 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 [26] of the respective sample.The existence of two parallel conduction mechanisms with different activation energies may therefore be responsible for this change in slope [27]. The observed curves of Fig. 3 is divided into two regions with different activation energies: region 1 or low temperature region with E_P between 0.132 eV and 0.653 eV and region 2 or high temperature region with E_f between 0.049 eV and 0.202 samples with different x values. As mentioned above lithium ferrites mayexhibit ionic conductivity too in addition to electronic conductivity . The ionic conduction has high activation energy [28], 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 increases. The values of activation energy lie in the range 0.038 - 0.451 eV indicates that conduction is intrinsic. As shown in Fig.3 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 as follows: At high temperature, the thermal. energy is sufficient to create vacancies and the activation energies represent a sum of the energies required for vacancy generation and electrons hopping. 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 [29] or to the change in the conductivity mechanism [30]. This anomaly strongly supports the influence of magnetic ordering upon the conduction process. The activation energies for conduction are computed from log_{10}^{ρ} versus 10^3/T plots and are presented in Tables 1. It is decreases up x = 0.2 and then increases to x = 0.4 further decreases up to x = 0.9 and finally increases again with continuous addition of antimony. 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 [31-32]. The activation energies 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 higher than the transition energy of Fe^{2+} and Fe^{3+} which indicate that the polaron conduction mechanism is favored. 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 appropriate in the case of ferrites rater than the collective electron (band) model. In ferrites ,the charge carriers are not completely free but are strongly localized in the d-shell. The localization may be due to the electron-phonon interaction (or formation of polarons). 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 [33] :

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$$r_p = \frac{1}{2}\left[\frac{\pi}{6N}\right]^{\frac{1}{2}} \quad (3)$$

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 x = 0.0 to 1.0 are summarized in Table 1. The polaran radius is increase up to x=0.2 then decrease at x=0.3 again increases gradually.It is seen that these values are smaller than inter ionic distances [34], 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 [35-36]. Based on the small polaron model the conduction phenomenon in region1 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 [37] 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 x are observed for the present system . According to Ahmed et al [38], the effect of x on ΔE is greater if the substituted cations occupy B-sites. Devale et al [39] suggested that almost no change in ΔE is observed when the substitution is made on A- sites without disturbing the B-sites.

Table.1 Jump length (L), Activation energy(E), Polaran radius of [$Li_{0.5+x}$ $Sb_xFe_{2.5-2x}$]O4

S.No	Content (x)	Jump length (L) (Å)	Acivation Energy Ep (eV)	Ef (eV)	ΔE = EP−Ef (eV)	Polaran radius (r_p) (Å)
1	0.0	2.945	0.674	0.2724	0.4016	0.735
2	0.1	2.959	0.5865	0.3019	0.2846	0.738
3	0.2	2.965	0.499	0.3315	0.1675	0.740
4	0.3	2.957	0.4855	0.2757	0.2098	0.738
5	0.4	2.970	0.4721	0.2200	0.2521	0.741
6	0.5	2.984	0.3548	0.2319	0.1229	0.744
7	0.6	2.996	0.3427	0.2555	0.0872	0.747
8	0.7	3.003	0.3307	0.2792	0.0515	0.749
9	0.8	3.022	0.3232	0.2863	0.0369	0.754
10	0.9	3.036	0.3157	0.2934	0.0223	0.757
11	1.1	3.517	0.4504	0.3774	0.0730	0.877

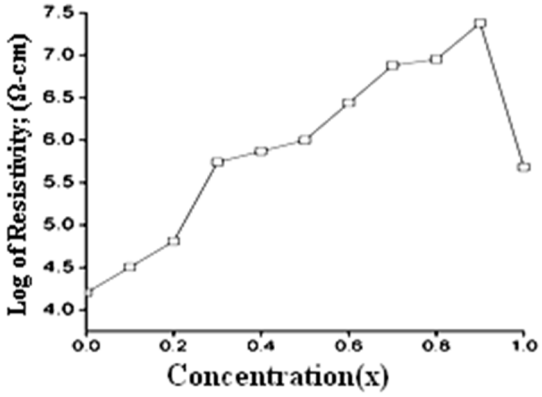


Fig. 1 Compositional variation of DC resistivity with antimony concentration (x).

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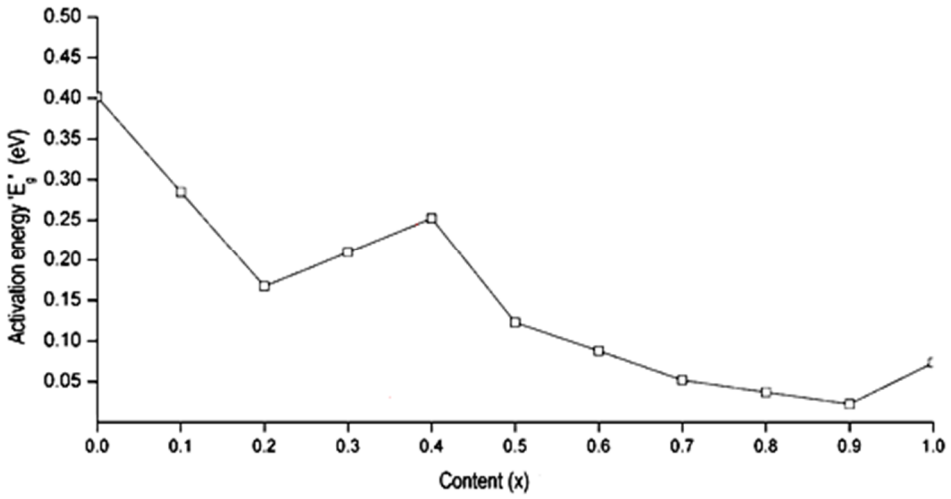


Fig.2 Variation of activation energies with substituent concentration antimony (x)

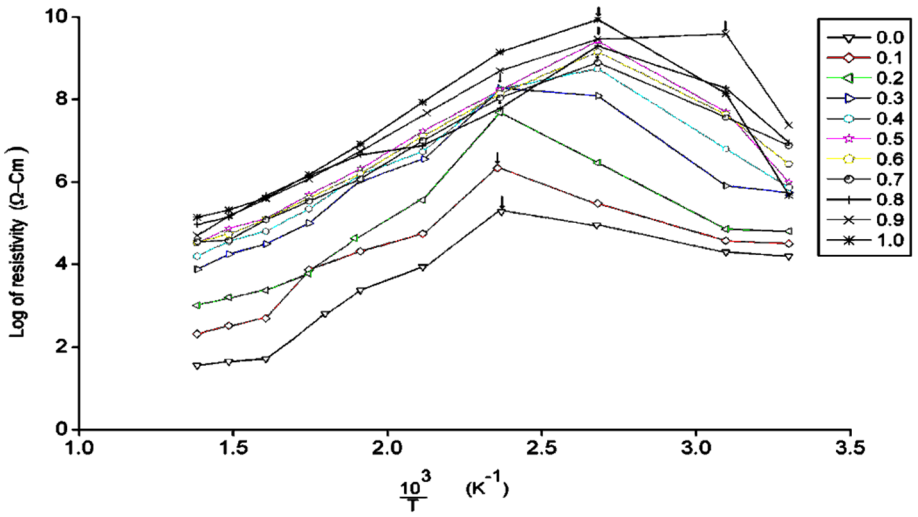


Fig.3 Variation of DC resistivity with temperature for different antimony (x) content. T_N values estimated are indicated by (⬇)

IV. CONCLUSION

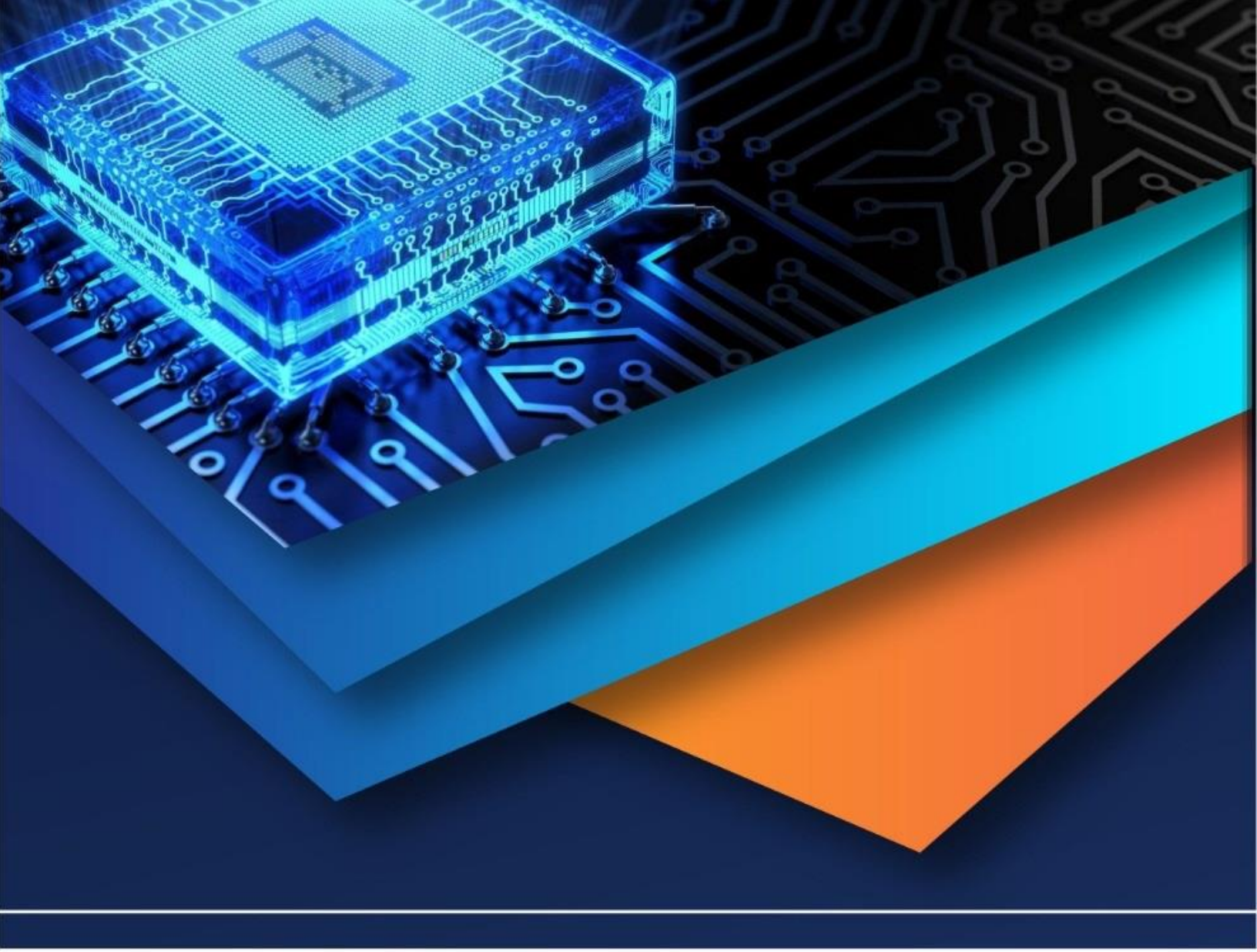
The DC resistivity increases up to x=0.9 and then decreases for Sb substituted lithium ferrites.The decrease in reestivity at x=1.0 may be due to the presence of small grain size and high percentage of Fe^{2+}. The same behaviour can also be seen with increasing temperature. But the Nell's temperatures were found to be varying i.e they increase up to x=0.3 then decrease up to x= 0.5 then increase and maintain a constant profile .The plots of (1/T) Vs. log of resistivity each has two regions i.e. paramagnetic and ferro magnetic regions are observed which reveal two types of conduction mechanism. The activation energies were observed to decrease up to x= 0.2 then increases up to x=0.4 from where they decrease again up to x=0.9 and finally increases in Sb substituted lithium ferrites. From their activation energies, Sb substituted lithium ferrites can be supposed to be intrinsic type semiconductor material. The small polaran radius increases which are smaller than interionic distances. The polaran radius is increase up to x=x=0.2 then decrease at x=0.3 again increases gradually.It The percentage of ferric and ferrous ions from all the specimens are estimated by photo chemical redox titration method for all the samples thereby it can be assumed that conduction mechanism takes place by electron hopping between Fe^{3+} and Fe^{2+}.

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