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# Electrical conductivity and thermoelectric power measurements of some lithium-titanium ferrites

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The electrical conductivity and thermoelectric power of some lithium-titanium ferrites with small amounts of manganese and zinc have been studied as a function of temperature in the range of 300–550 K and are reported here. The conductivity variation shows two different regions with a large variation in the activation energies. The possible mechanisms with respect to ionic conduction and electron hopping are discussed with the support of thermoelectric power measurements. Lattice parameters are also calculated from x-ray diffractograms for confirming the single-phase nature of the ferrites.

## I. INTRODUCTION

Ferrites have vast applications from microwave to radio frequencies. The low electrical conductivity resulting in low losses makes them attractive materials for microwave application. The order of magnitude of the conductivity greatly influences the dielectric and magnetic behavior of ferrites. Of particular interest, lithium-titanium ferrites have salient features like high Curie temperature, small resonance linewidth, etc. As a lithium compound, it finds use as a solid-state electrolyte also. The lithium ferrite spinel contains reducible iron ions and lithium ions and therefore it is expected that this material exhibits both electronic and ionic conductivities.<sup>1</sup>

In the present investigation, the electrical conductivity and thermoelectric power measurements of some lithium-titanium ferrites in the temperature range of 300–550 K are reported.

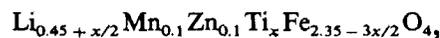
## II. EXPERIMENT

The electrical conductivity measurements are carried out by a two-probe method<sup>2</sup> on compressed, sintered pellets of about 1-cm diameter and 0.2-cm thickness. The electrode effects are confirmed to be minimum by repeating the measurements for two different thicknesses of the sample. The

cell with the pellet is maintained at a pressure of  $10^{-2}$  Torr and the temperature is monitored with a Phillips "Plastomatic" controller. A Keithley model 61DC solid-state electrometer is used for the conductivity measurements which are carried up to 550 K, during both heating and cooling cycles.

For thermoelectric power measurements,<sup>3</sup> pellets of 1-cm diameter and 0.5-cm thickness have been used. A temperature difference of about 10 K was maintained between the top and bottom surfaces of the samples.

The ferrite samples prepared by the conventional double-stage sintering process have been supplied by the Solid State Physics Laboratory, New Delhi. The composition of the samples is analyzed by chemical analysis while the Seebeck coefficient and x-ray patterns are also obtained to confirm the type of conductivity and single-phase nature of these samples, respectively. The samples have a general composition of



where  $x = 0.36, 0.46, 0.56, 0.66,$  and  $0.76$  and are designated as A, B, C, D, and E corresponding to the increasing concentration of lithium and titanium.

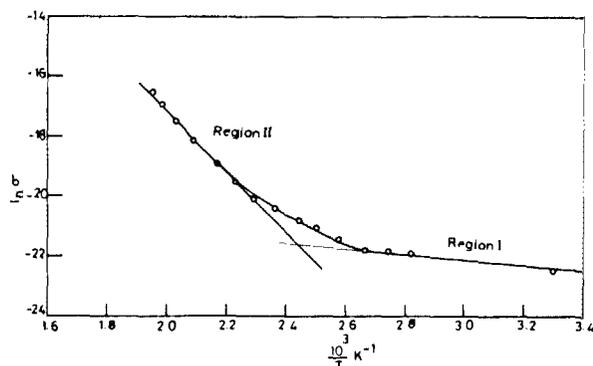


FIG. 1. Conductivity vs reciprocal temperature plot for sample B. The temperature corresponding to the point of intersection of the linear portions of the plot is taken as the transition temperature  $T_a$ .

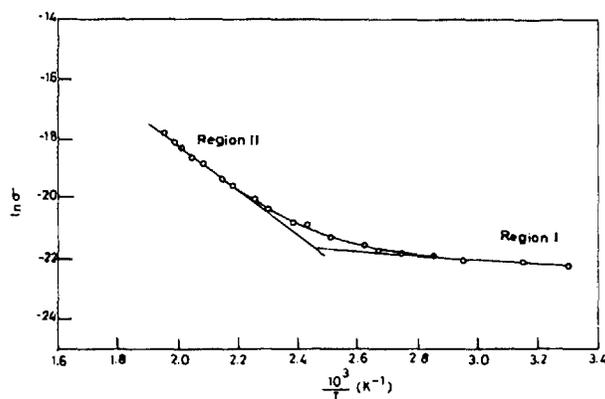


FIG. 2. Conductivity vs reciprocal temperature plot for sample C.

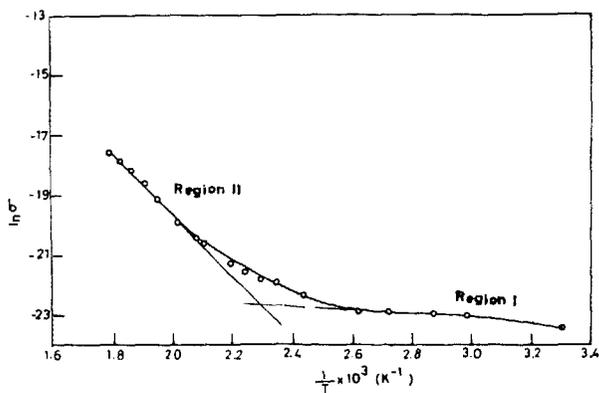


FIG. 3. Conductivity vs reciprocal temperature plot for sample D.

### III. RESULTS

The electrical conductivity of all these ferrites is measured up to a temperature of 550 K from room temperature. The variation of conductivity with temperature of some typical ferrites is shown in Figs. 1–3. The behavior is similar to that known in the case of similar ferrites with a change in the slope of graphs at a certain temperature.<sup>4</sup> Such a change is markedly observed in the case of all samples listed in Table I. The change in slope was originally anticipated to be due to Curie temperature but the measured Curie temperatures for other stoichiometric compositions of lithium–titanium ferrites<sup>5</sup> are all higher than these temperatures. Hence it may be due to the change in the conduction mechanisms.

The stoichiometric formula of these ferrites from chemical analysis along with lattice parameters are shown in Table I. The activation energies calculated from the two different regions in the figure are shown in Table II, along with the transition temperatures. The *p*- or *n*-type nature of the charge carriers below and above the transition temperature is determined from the sign of Seebeck coefficient and are listed in Table II. The Seebeck coefficient versus reciprocal of temperature plots in the cases of all the samples are shown in Fig. 4. All the ferrites studied have zinc and manganese as invariables while titanium and lithium are variables in the stoichiometry.

TABLE I. Chemical formulas and lattice constant of the samples.

Sample code	Chemical formula	Lattice constant in Å
A	$\text{Li}_{0.63}\text{Zn}_{0.1}\text{Mn}_{0.1}\text{Ti}_{0.36}\text{Fe}_{1.81}\text{O}_4$	8.381
B	$\text{Li}_{0.68}\text{Zn}_{0.1}\text{Mn}_{0.1}\text{Ti}_{0.46}\text{Fe}_{1.66}\text{O}_4$	8.361
C	$\text{Li}_{0.73}\text{Zn}_{0.1}\text{Mn}_{0.1}\text{Ti}_{0.56}\text{Fe}_{1.51}\text{O}_4$	8.360
D	$\text{Li}_{0.78}\text{Zn}_{0.1}\text{Mn}_{0.1}\text{Ti}_{0.66}\text{Fe}_{1.36}\text{O}_4$	8.369
E	$\text{Li}_{0.83}\text{Zn}_{0.1}\text{Mn}_{0.1}\text{Ti}_{0.76}\text{Fe}_{1.21}\text{O}_4$	8.305

### IV. DISCUSSIONS

In general it has been well established that lithium ferrite is an inverse spinel,  $\text{Fe}^{3+}[\text{Li}_{0.5}\text{Fe}_{1.5}^{3+}]\text{O}_4$ .<sup>6</sup> Lithium ferrite contains reducible iron ions and lithium ions and therefore it is expected that this material exhibits both electronic and ionic conductivities.<sup>7</sup> Tretyakov and Rapp,<sup>8</sup> in a study of oxygen partial pressure in equilibrium with lithium ferrite, showed that their thermodynamic data on ferrites was consistent with the reaction for the reduction of stoichiometric compound. It was assumed that lithium-ion interstitials are formed in preference to iron interstitials.

Of the cations present in the sample, zinc and manganese do not have significant influence on the conduction mechanisms because they are present in a small amount in the composition. Furthermore, zinc has preference for tetrahedral sites, and manganese is trivalent in the stoichiometry. The influence of the nonmagnetic ion of high valency  $\text{Ti}^{4+}$  on the magnetic properties of this compound is not discussed in this paper.

The conductivity of all these ferrites at room temperature is in the range of  $0.06\text{--}2.8 \times 10^{-10} \text{ } \Omega \text{ cm}^{-1}$ . The variation of conductivity with temperature can be divided into two regions in all samples. In region I the activation energy of all the samples is in the range of 0.07–0.1 eV, while in region II it varies from 0.5 to 0.9 eV. The variation of activation energy with lithium concentration shows a gradual decrease with increase of concentration up to the ferrite C and then increases as given in Fig. 5. The Seebeck coefficient ( $\theta$ ) was also measured in all these ferrites from room temperature up to 550 K. The variation shows that all the samples are of *n* type up to a certain temperature beyond which samples

TABLE II. Values of transition temperatures obtained from conductivity and thermoelectric power data and activation energy.

Sample	Transition temperature ( $T_a$ ) in K		Activation energy from conductivity data in eV		Type of prominent charge carriers	
	From conductivity data	From thermoelectric data	Below $T_a$	Above $T_a$	Below $T_a$	Above $T_a$
A	378.8	429.2	0.12	0.93	<i>n</i>	<i>p</i>
B	440.5	450.5	0.09	0.88	<i>n</i>	<i>p</i>
C	408.2	520.8	0.04	0.51	<i>n</i>	<i>n</i>
D	409.8	500.0	0.08	0.84	<i>n</i>	<i>n</i>
E	426.0	432.9	0.10	1.05	<i>n</i>	<i>n</i>

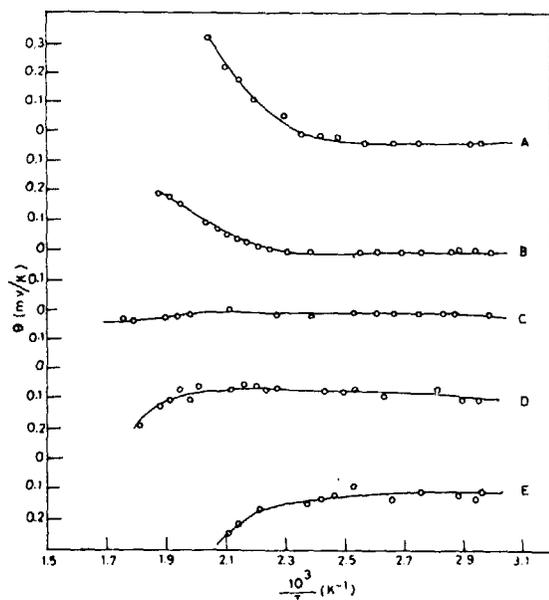


FIG. 4. Variations of Seebeck coefficient  $\theta$  with reciprocal temperature for the samples A, B, C, D, and E are shown. For the sake of clarity, the scales are shifted.

A and B are *p* type, while samples D and E are *n* type. Sample C shows a nearly flat response with temperature and is *n* type.

The transition temperature at which *n*-to-*p* variation occurs in A and B and abrupt variation in  $\theta$  occurs in samples D and E is given in Table II. The temperature at which transitions from region I to region II occur in conductivity plots is also given in Table II. However, the transition temperature of each sample from the above two data neither match with each other nor with Curie temperature. The comparison of activation energies with these type of charge carriers reveals that all the ferrites possess an *n*-type conduction mechanism in region I. This may be due to electron hopping between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in the octahedral sites.<sup>9</sup> The high activation energy in region II suggests that the conduction mechanism in region II can neither be attributed to electron hopping nor to the hole hopping. A different mechanism may be responsible for the conduction process. As it appears from Fig. 5, the activation energy in region II gradually decreases with increasing concentration of lithium, probably due to ionic conduction caused by lithium ions in the octahedral sites.

For a low concentration of lithium (sample A) lithium ionic conduction is responsible for the prominence of *p*-type charge carriers. As the titanium concentration is increased towards sample C, lithium is distributed on both octahedral and tetrahedral sites while a small amount of lithium occupies the tetrahedral site, as explained by Nogues<sup>10</sup> from the Mössbauer, neutron, and x-ray diffraction studies. This explains that many interstitial positions in the octahedral sites have been occupied by lithium, causing a net decrease in the activation process by lithium.

Increasing lithium concentration further, it is quite possible that a chemical diffusion of lithium may take place: lithium ions diffusing to the surface with a gradual increase

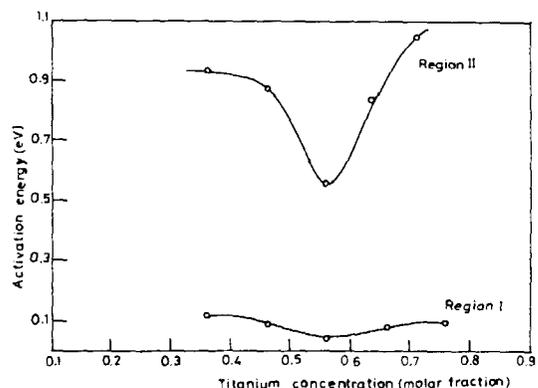


FIG. 5. Variation of activation energy with titanium concentration.

in the activation energy of the process.<sup>11</sup> As Rezlescu *et al.*<sup>12</sup> concluded, the number of cation vacancies appearing after lithium loss is equal to the number of  $\text{Fe}^{3+}$  ions which are converted to divalent  $\text{Fe}^{2+}$  ions, thus maintaining a high bulk electronic conductivity. This *n*-type mechanism may be present in samples C and D in region II.

## V. CONCLUSIONS

(1) All the samples studied have two regions of different activation energies as seen from the conductivity plots. In region I, the conduction is attributed to electron hopping from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  as evident by the low activation energy (about 0.1 eV) and the presence of *n*-type charge carriers observed from Seebeck coefficient measurements.

(2) The high value of activation energy in region II is attributed to the lithium-ion conduction process.

(3) With an increase in lithium concentration the activation energy passes through a minimum and then rises. At low concentration, *p*-type conduction is prominent and is due to conduction of lithium ions. At higher concentrations, the *n*-type mechanism was seen to be predominant and considered to be due to chemical diffusion of lithium ions to the surface, resulting in the formation of  $\text{Fe}^{2+}$  ions maintaining high electronic conductivity, as is confirmed by Dudley *et al.*<sup>11</sup>

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