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Effect of Iron Concentrations on Some Physical Properties of the System $Li_{0.5}Fe_xGa_{2.5-x}O_4$

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Abstract

A series of $Li_{0.5}Fe_xGa_{2.5-x}O_4$systems were prepared for x = 0, 0.25, 0.5, 0.75 and 1 by the general ceramic method. X-ray diffraction showed that all compositions have single phase Spinel cubic structure. The lattice parameter increased with enhancing iron concentration. The thermoelectric coefficient decreased with increasing x, and the majority carriers are holes. The increase of the jump length of hole increased the electrical conductivity. Jump-length increased with iron concentration and the rate of jumping gave rise to the electrical conductivity. The concentration of Fe^{3+} ions in Lithium gallate is important, for such structures may have application in communication technology.

Key Words: Ferrite, jump length, jump rate, lattice parameter, hopping conduction.

1. Introduction

As ferrites have electrical and magnetic properties that have application in various applied communications technology, we have carried out a study of the structural and electrical properties of the $Li_{0.5}Fe_xGa_{2.5-x}O_4$ system [1]. Calculations from x-ray diffraction measurements indicated that Li^{1+}occupy only octahedral sites and Ga^{3+} and Fe^{3+} ions occupy both octahedral and tetrahedral sites. The thermoelectric coefficient values decreased with increasing iron concentrations. All the compounds studied were p-type semiconductors. Various investigators have studied the jump length of electrons in the octahedral sites and electrical conductivity as a function of Zinc concentration in $Mn_{1-x}Zn_xFe_2O_4$ systems [2–11]. When $Al^{3+}$is substituted for Fe^{3+} the jump length was found to decrease with aluminum concentration, and is attributed to the smaller atomic size of Al^{3+}. The presence of a small amount of Fe^{2+} at one site in the lattice is sufficient enough to ionize in the adjacent site; the resulting electron is then used by an adjacent Fe^{3+}, allowing for another i.e. $Fe^{3+}+ e \leftrightarrow Fe^{2+}$ reaction, and a propagating chain of such reactions. The presence of a single phase in all the solid solutions, as confirmed from x-ray diffraction studies, confirms the idea that the conductivity mechanism in these ferrites is intrinsic in nature for the single phase Spinel structure [12]. In the present work we report the results of our investigations on the dependence of dc electrical conductivity on the jump length of holes and jump rate of these carriers in the composition $Li_{0.5}Fe_xGa_{2.5-x}O_4$.

2. Experimental

Compositions of the $Li_{0.5}Fe_xGa_{2.5-x}O_4$system for x = 0, 0.25, 0.5, 0.75, 1 were prepared by the general ceramic method [1–3]. High purity Li_2CO_3 and Fe_2O_3 powders were mixed in proper stoichiometric proportions and well-milled. The mixed oxides were sintered in a furnace at 1000 °C for 4 hr. The fine powders were pressed in the form of a tablet of 1 cm diameter and 1 mm thickness, then sintered at 1200 °C for 4 hr. X-ray diffraction analysis using Cu-K_α radiation showed all the compositions are single phase Spinel cubic. Conductivity measurements at room temperature were carried out using a Keithley 610C electrometer. Thermoelectric coefficients were determined at 40 °C for the various x.

2.1. X-ray analysis

X-ray analysis showed that samples had developed cubic single phase Spinel structure. Considering the crystal as a set of planes characterized by the interplaner distance d_{hkl}, the values of d_{hkl} are calculated directly from the x-ray diffraction pattern via Bragg's law:$2d\sin\theta = n\lambda$, where λ is the wave length of the x-ray radiation and θ is the Bragg angle. In case of the cubic system, the lattice parameter a is calculated via the relationship

$$a = d_{hkl}(h^2 + k^2 + l^2)^{1/2},$$

where h, k, l are the indices of the planes. The variation of the lattice parameter a with Fe concentration in $Li_{0.5}Fe_xGa_{2.5-x}O_4$ is shown in Figure 1. The figure shows that the lattice parameter a increases with iron substitution x. The variation could be explained considering the ionic radii of the substituted ions. The radius of the substituted ion Fe^{3+} is 0.64 Å, which is larger than that of Ga^{3+}, which has a 0.62 Å radius; so the lattice constant is expected to increase with Fe concentration. This behavior agrees well with the variation of lattice constant due to iron substitution in $Li_{0.5}Fe_xGa_{2.5-x}O_4$ [1].

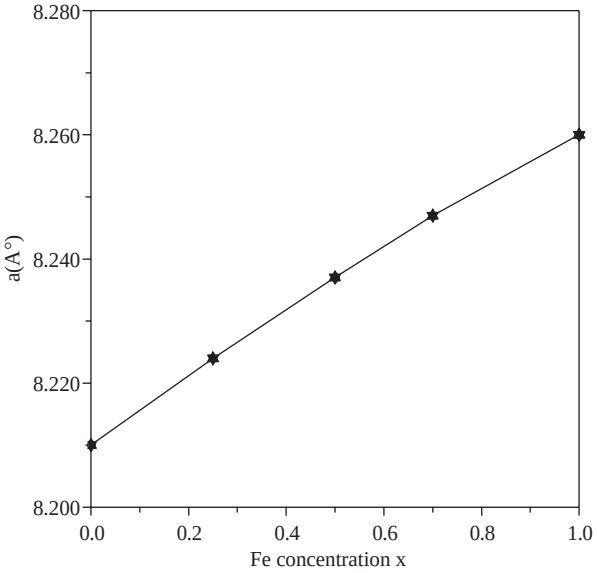

Figure 1. Effect of iron concentrations, x on the lattice parameter a (Å).

2.2. Effect of the jump length on the electrical resistivity

The jump length of electrons is estimated from the relation [4]

$$L = \frac{a\sqrt{2}}{4},$$

where a is the lattice parameter.

The variation of electrical resistivity as a function of jump length L is shown in Figure 2. Conversely, the figure shows conductivity increasing with jump length. Supposing electron hoping between A and B sites are far less frequent than hopping among only B sites, then hopping probability is largely a function of the separation between B sites; with the consequence that as the hopping length increases, the electrical resistivity decreases. The concentration of iron is larger at octahedral sites, increasing the population of Fe^{3+} and Fe^{2+} and, in turn, leads to an increased hopping length between $Fe^{3+} \leftrightarrow ?$ Fe^{2+}, thereby decreasing the electrical resistivity. The behavior of our results is similar to that in [5, 6].

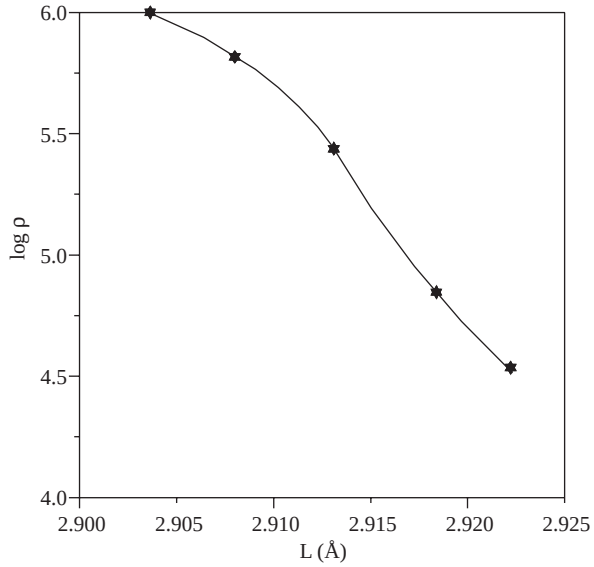

Figure 2. Effect of jump length L on the electrical resistivity.

2.3. Effect of iron concentration on the electrical resistivity

The effect of iron concentration x on the electrical resistivity of the systems $Li_{0.5}Fe_xGa_{2.5-x}O_4$ is shown in Figure 3. Here, one can see that the electrical conductivity increased with Fe concentration. The n-type conduction is due to electron hopping between Fe^{3+} and Fe^{2+}ions as

$$Fe^{3+} + e \longleftrightarrow Fe^{2+},$$

and the presence of Ga^{3+} on the octahedral sites [1] favors the p-type conduction mechanism due to hole transfer from Ga^{3+} to Ga^{2+} ions as

$$Fe^{2+} + Ga^{3+} \longleftrightarrow Fe^{3+} + Ga^{2+}$$

$$Ga^{2+} + h \longleftrightarrow Ga^{3+},$$

suggesting the presence of both n- and p-type conduction [7, 8]. Thus the conductivity can be expressed as $\sigma = \sigma_e + \sigma_h$, where σ_e and σ_h is due to electronic and hole conduction, respectively.

The p-type conduction is predominantly due to hole hopping between Ga^{3+} and Ga^{2+} in our systems, a characteristic which agrees with results obtained in the study of Ni-Al ferrites [9] and Ni-Zn ferrites [10].

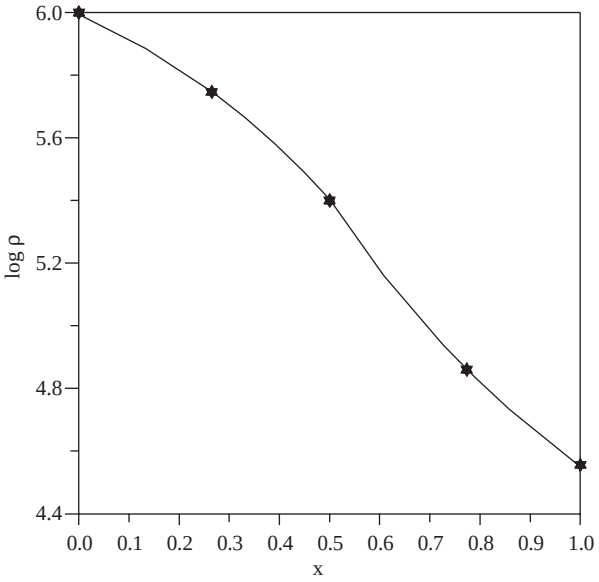

Figure 3. Dependence of log resistivity on iron concentrations x.

2.4. Seebeck coefficient

The thermoelectric power α is measured for all compositions at 40 °C and the results are shown in Figure 4. Thermoelectric power measurements showed that all compounds are p-type semiconductors. The values of the thermoelectric coefficient α were found to decrease from 300 μV/K to 120 μV/K as the iron concentration increases. This decrease is attributed to the ionization of some ferric ions to ferrous state during sintering process. The increase of hopping electrons between Fe^{3+} and Fe^{2+} with increasing iron concentrations caused the decrease of the hole hopping between Ga^{3+} and Ga^{2+}. This explains the reduction of the positive thermoelectric power with increasing ferric concentrations. The decrease of the hole hopping with increasing iron concentrations had previously been studied in [1], confirming the behavior of our results.

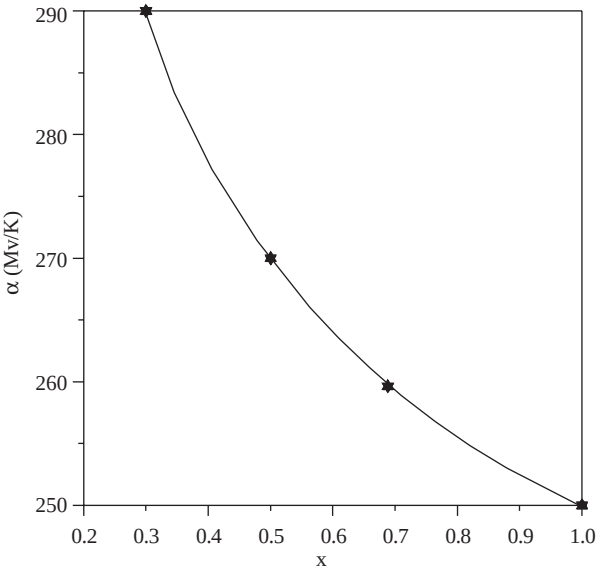

Figure 4. Effect of iron concentration x on the thermoelectric coefficient α.

2.5. Effect of iron concentrations on the jump rate of electrons

The jump rate of electron-hole pairs is estimated according to the relation [5, 6]

$$D = \frac{\sigma KT}{Ne^2} \tag{1}$$

$$D = a^2 P. \tag{2}$$

From Equations (1) and (2), the jump rate of the holes, p, is

$$P = \frac{\sigma KT}{Ne^2 a^2}, \tag{3}$$

where σ is the electrical conductivity, K is Boltzman's constant, N is the number of atoms $/m^3 = 4 \times 10^{28}$, e is the electric charge and a is the lattice parameter.

It is observed from Figure 5 that the jump rate of electron-hole pairs (number of electron-hole pairs which hop per second) increases with increasing x. The decrease of electrical resistivity with increasing x might be explained on the basis that Fe^{3+} ion substitute Ga^{3+} ion in the octahedral configuration. The increase of Fe^{3+} concentration at octahedral sites increased the hopping rate of electrons between $Fe^{3+} \leftrightarrow Fe^{2+}$ and the hole hopping between $Ga^{3+} \leftrightarrow Ga^{2+}$ leading to an increase in the conductivity. The behavior of our results is similar to that of the previous work on other ferrites in [11].

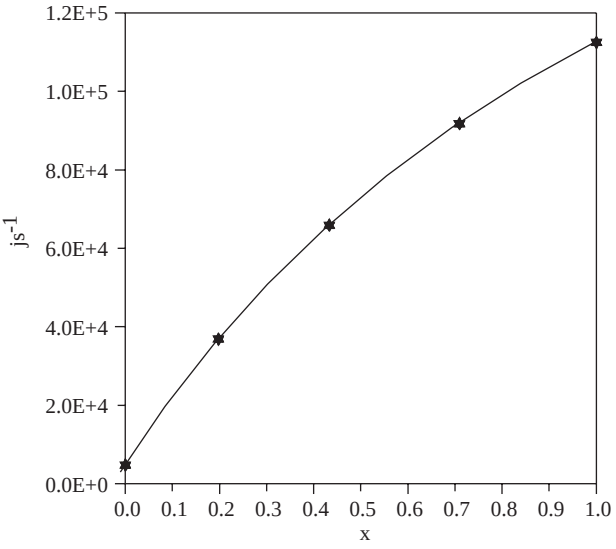

Figure 5. Effect of iron concentrations on the jump rate of electron-hole pairs (js^{-1}).

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