JOURNAL OF MATERIALS SCIENCE 28 (1993) 6070–6073

Cation distribution investigation of the system $Li_{0.5}Fe_xGa_{2.50-x}O_4$ by X-rays, electrical conductivity and Mossbauer studies

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Structural, electrical and Mossbauer studies were carried out for the system $Li_{0.5}Fe_xGa_{2.5-x}O_4$. All the compounds with $0 \leqslant x \leqslant 2.5$ crystallised with cubic spinel structure. Lattice constant values calculated from XRD analysis were found to increase with increasing x. X-ray intensity calculations indicated that Li^{1+} occupies only the octahedral site and Ga^{3+} and Fe^{3+} ions occupy both octahedral and tetrahedral sites. Activation energy and thermoelectric coefficient values decreased with increasing values of x. All the compounds studied were p-type semiconductors and possess low mobility values of 10^{-7}–10^{-9} $cm^2 V^{-1} s^{-1}$. Mossbauer data show the presence of iron in the Fe^{3+} state and the isomer shift values for all the compositions of the system are within the range of high spin ferric compounds. The probable ionic configuration for the system is suggested as:

$$Ga^{3+}_{1-\alpha}Fe^{3+}_{\alpha}[Li^{1+}_{0.5}Fe^{3+}_{x-\alpha}Ga^{3+}_{2.5-x+\alpha}]O^{2-}_4$$

1. Introduction

Ferrites have interesting structural, electrical and magnetic properties which are suited for a variety of applications. These properties depend crucially upon the nature, the valence states and distribution of metal ions over two sites in the spinel (AB_2O_4) lattice. Blasse [1] investigated the analogous system $Li_{0.5}Fe_{2.5-x}M_xO_4$ (where M = V, Cr or Rh). He observed that in $Li_{0.5}Fe_{2.5}O_4$, Li^+ ions occupy the octahedral site. On substituting M in place of iron he further observed migration of Li^+ ions from the octahedral to the tetrahedral site. The above results indicate that the substituted metal ions have a stronger preference for the octahedral site.

Kapitonove [2] investigated the cation distribution in lithium galloferrites with varying compositions and firing temperatures. From Mossbauer studies he observed that the quadrupole splitting increases with increase in firing temperature. We have reported the various properties of different spinel systems and a reasonably clear picture of their structure and transport properties has emerged [3–7]. We have selected the system $Li_{0.5}Fe_xGa_{2.5-x}O_4$ for this investigation from the viewpoint of determining the cation distribution using X-ray diffraction, electrical conductivity, thermoelectric power and Mossbauer spectroscopic studies.

2. Experimental procedure

The compositions of the system $Li_{0.5}Fe_xGa_{2.5-x}O_4$ (where $0 \leqslant x \leqslant 2.5$) were prepared by the ceramic technique where stoichiometric proportions of Li_2CO_3, Fe_2O_3 and Ga_2O_3 powders were ground in acetone. The homogeneous mass was pellatized using a 2% solution of polyvinyl acetate as a binder medium. The pellets were heated at 1173 K for 100 h. X-ray diffractometer patterns were recorded using CuK_α radiation with a Ni filter. The distribution of monovalent and trivalent cations amongst the octahedral and tetrahedral sites in the lithium galloferrites samples was determined from the ratios of the intensities of the X-ray diffraction lines, I_{220}/I_{440}, I_{220}/I_{400} and I_{400}/I_{422}. Conductivity measurements from room temperature to 773 K were carried out by the two probe technique. Thermoelectric coefficients were calculated by taking measurements from 300 K to 573 K.

Mossbauer spectra for the system $Li_{0.5}Fe_xGa_{2.5-x}O_4$ (where x = 0.5, 1.0, 2.0 or 2.5) were recorded at room temperature using a constant velocity drive operating in conjunction with a 250 channel analyser. The absorber was prepared by spreading 20 mg of sample over a 1 cm diameter disc. The calibration was done after every sample using standard iron foil.

3. Results and discussion

3.1. X-ray analysis

All the compositions of the system $Li_{0.5}Fe_xGa_{2.5-x}O_4$ could be indexed in terms of single phase cubic spinel structure. No reflection other than those belonging to

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spinel structure were observed in the patterns. The values of the lattice parameter a are compiled in Table I. From this table, it is observed that the values of a progressively increase on going from $Li_{0.5}Ga_{2.5}O_4$ to $Li_{0.5}Fe_{2.5}O_4$. In order to determine the cation distribution, XRD intensities were calculated using the formula suggested by Buerger [8]:

$$I_{hkl} = |F_{hkl}|^2 \cdot P \cdot L_p$$

where notations have their usual meanings. The ionic configuration based on site preference energy values suggested by Miller [9] for individual cations can be written as:

$$Ga^{3+}_{1-\alpha}Fe^{3+}_{\alpha}[Li^{1+}_{0.5}Fe^{3+}_{x-\alpha}Ga^{3+}_{2.5-x+\alpha}]O^{2-}_4$$

In Table II the results of intensity calculations for various possible models of $Li_{0.5}Ga_{1.0}Fe_{1.5}O_4$ and $Li_{0.5}Fe_{2.5}O_4$ are listed. From this table it is observed that monovalent lithium ions occupy only the octahedral site and gallium and iron ions occupy both sites. The general ionic configuration of the system can be written as:

$$Me^{3+}[Li^{1+}_{0.5}Me^{3+}_{1.5}]O^{2-}_4$$

where

$$Me = Ga^{3+} \text{ or } Fe^{3+}$$

3.2. Electrical properties

All the compositions of the system $Li_{0.5}Fe_xGa_{2.5-x}O_4$ were found to be semiconducting in nature. Plots of $\log \rho$ versus $10^3/T$ are shown in Fig. 1. The plots show no break or inflexion over the temperature range studied, indicating stable oxidation of cations such as Li^{1+}, Fe^{3+} and Ga^{3+}. Room temperature resistivity for $Li_{0.5}Ga_{2.5}O_4$ was found to be $7.2 \times 10^6\ \Omega$cm, whereas that for $Li_{0.5}Fe_{2.5}O_4$ was found to be $7.2 \times 10^5\ \Omega$cm. But activation energy for $Li_{0.5}Ga_{2.5}O_4$ was found to be more than double as compared to $Li_{0.5}Fe_{2.5}O_4$, indicating difficulty in charge transfer.

Thermoelectric power measurements showed that all the compounds are p-type semiconductors. The values of the thermoelectric coefficient (α) were found to decrease from $+309\ \mu V K^{-1}$ to $+124\ \mu V K^{-1}$ on going from $x = 0$ to $x = 2.5$ (Table I, Fig. 2). The p-type conductivity of all the samples rules out the possibility of the presence of Fe^{2+} ions along with Fe^{3+} ions at the octahedral site, otherwise n-type conductivity would have been observed, at least in the iron-rich compositions, due to hopping of electrons between Fe^{2+} and Fe^{3+} ions. These results indirectly support the ionic configuration obtained from the intensity calculations.

TABLE I Lattice constant (a), activation energy (ΔE) and thermoelectric coefficient (α) values for the system $Li_{0.5}Fe_xGa_{2.5-x}O_4$

Composition	Lattice constant a (Å)	Activation energy ΔE (eV)	Thermoelectric coefficient α ($\mu V K^{-1}$)
$Li_{0.5}Ga_{2.5}O_4$	8.215	0.64	309
$Li_{0.5}Fe_{0.5}Ga_{2.0}O_4$	8.235	0.56	274
$Li_{0.5}Fe_{1.0}Ga_{1.5}O_4$	8.265	0.51	255
$Li_{0.5}Fe_{1.5}Ga_{1.0}O_4$	8.291	0.45	196
$Li_{0.5}Fe_{2.0}Ga_{0.5}O_4$	8.310	0.37	165
$Li_{0.5}Fe_{2.5}O_4$	8.334	0.30	124

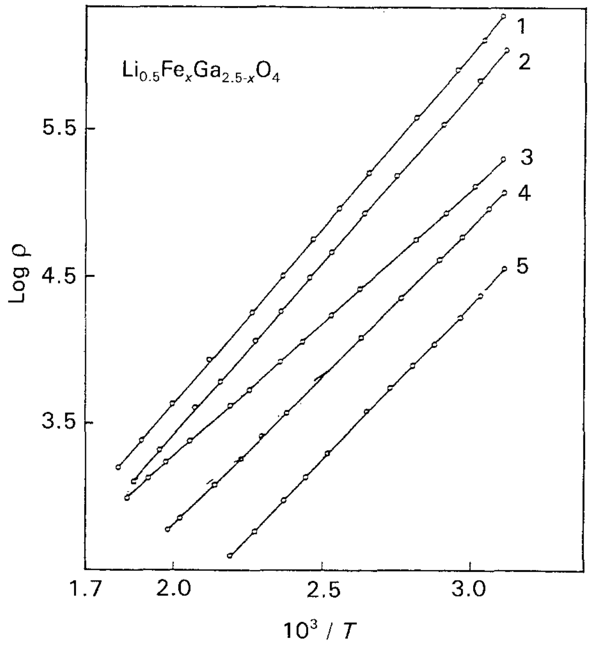

Figure 1 Electrical resistivity as a function of temperature for various samples X, 1:0; 2:0.25; 3:0.50; 4:0.75 and 5:1.00.

TABLE II Comparison of intensity ratios for $Li_{0.5}Ga_{1.0}Fe_{1.5}O_4$ and $Li_{0.5}Fe_{2.5}O_4$

A-site cation	B-site cation	I_{220}/I_{440}		I_{220}/I_{400}		I_{400}/I_{422}	
		obs.	calc.	obs.	calc.	obs.	calc.
$Li_{0.5}Ga_{1.0}Fe_{1.5}O_4$							
$Ga^{3+}_{1.0}$	$Li^{1+}_{0.5}Fe^{3+}_{1.5}$		1.002		4.970		0.494
$Fe^{3+}_{1.0}$	$Li^{1+}_{0.5}Ga^{3+}_{1.0}Fe^{3+}_{0.5}$		0.642		1.562		1.691
$Ga^{3+}_{0.4}Fe^{3+}_{0.60}$	$Li^{1+}_{0.5}Ga^{3+}_{0.6}Fe^{3+}_{0.9}$	0.770	0.777	2.439	2.439	1.049	1.049
$Li^{1+}_{0.5}Fe^{3+}_{0.5}$	$Ga^{3+}_{1.0}Fe^{3+}_{1.0}$		0.189		0.208		12.520
$Li^{1+}_{0.5}Ga^{3+}_{0.5}$	$Ga^{3+}_{0.5}Fe^{3+}_{1.5}$		0.287		0.392		6.290
$Li_{0.5}Fe_{2.5}O_4$							
$Fe^{3+}_{1.0}$	$Li^{1+}_{0.5}Fe^{3+}_{1.5}$	0.762	0.762	2.157	2.156	1.221	1.223
$Li^{1+}_{0.2}Fe^{3+}_{0.8}$	$Li^{1+}_{0.3}Fe^{3+}_{1.7}$		0.509		0.956		2.752
$Li^{1+}_{0.5}Fe^{3+}_{0.5}$	$Fe^{3+}_{2.0}$		0.226		0.254		10.110

3.3. Mossbauer studies

Mossbauer effect studies were carried out with a view to investigating the valency of iron and the effect of minute distortions produced around the Fe^{3+} nucleus due to dissimilar charges such as Li^{1+}, Ga^{3+} at the octahedral site. The advantage of the Mossbauer technique is that it picks up even minute lattice distortions which cannot be detected by X-ray techniques, since the latter can only be used to observe the effect of long range order distortions.

From Table III it is observed that the isomer shift values for all the compositions of the system are within the range of high spin ferric compounds and the values of the isomer shift vary between 0.33 and 0.38 mm s^{-1}. Hence we rule out the possibility of the presence of Fe^{2+} ions in the system and we can say that iron is present in the 3 + oxidation state only.

In Figs 3–5 we show the Mossbauer spectra for the compositions $x = 0.5$, 1.0, 2.0 and 2.5, respectively. Isomer shift quadrupole splitting and hyperfine field values are listed in Table III. The compositions $x = 0.5$ and 1.0 showed a paramagnetic doublet with quadrupole splitting of 0.27 and 0.41 mm s^{-1}, respectively. We have already seen that isomer shift values for all the compounds of $Li_{0.5}Fe_xGa_{2.5-x}O_4$ do not vary much (0.33–0.38 mm s^{-1}). The spectra for $x = 2.0$ and 2.5 are six line, and line widths are considerably higher as compared to standard iron line widths. These line widths actually result from the superposition of two six line patterns, one due to tetrahedral Fe^{3+} and other due to octahedral Fe^{3+}. In order to find out the fraction of tetrahedral and octahedral Fe^{3+} ions, a standard computer programme was used and spectra were resolved into two sextets and the ratio of octahedral to tetrahedral Fe^{3+} ions was obtained from the computer fit. It was found to be 1.2 for $x = 2.0$ and 1.5 for $x = 2.5$. From these results the ionic configuration for $Li_{0.5}Ga_{0.5}Fe_2O_4$ can be written as

$$Ga^{3+}_{0.1}Fe^{3+}_{0.9}[Li^{1+}_{0.5}Fe^{3+}_{1.1}Ga^{3+}_{0.4}]O^{2-}_4$$

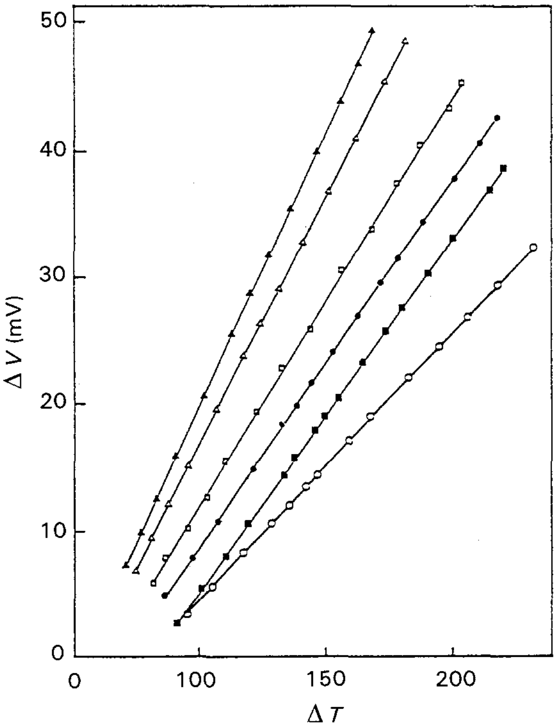

Figure 2 Thermo emf as a function of temperature X, (○):0; (■):0.5; (●):1.0; (□):1.5; (△):2.0 and (▲):2.5.

TABLE III Isomer shift (I_s), quadrupole splitting (Q_s) and hyperfine field (H_n) values for the system $Li_{0.5}Fe_xGa_{2.5-x}O_4$

x	I_s (mm s^{-1}) ± 0.02	Q_s (mm s^{-1}) ± 0.02	H_n (KO_e) ± 5
0.50	0.38	0.27	
1.00	0.37	0.41	
2.00	0.34	0.034	473
2.50	0.33	0.017	509

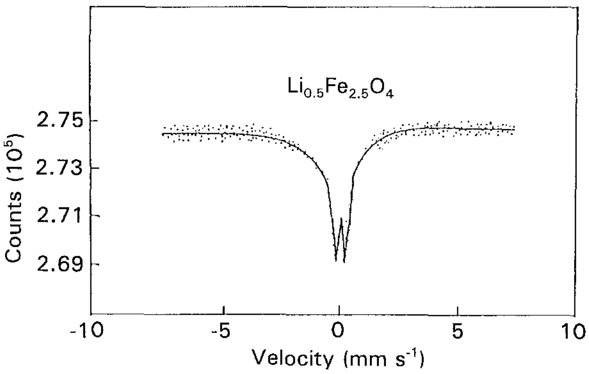

Figure 3 Mossbauer spectrum of $Li_{0.5}Fe_{0.5}Ga_{2.0}O_4$ at 300 K.

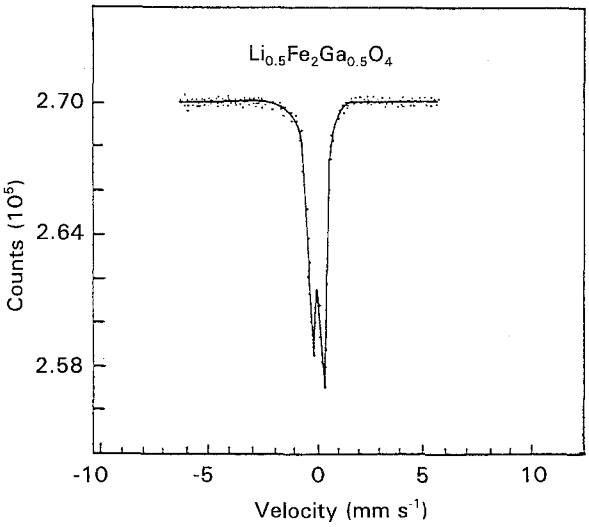

Figure 4 Mossbauer spectra of $Li_{0.5}Fe_{1.0}Ga_{1.5}O_4$ at 300 K.

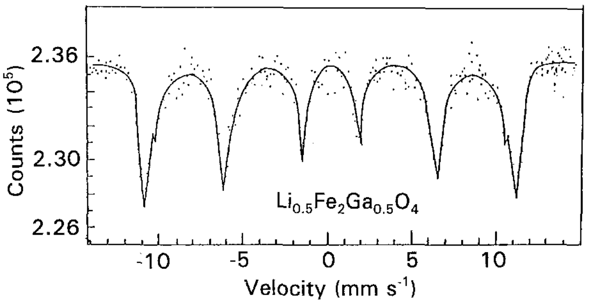

Figure 5 Mossbauer spectra of $Li_{0.5}Fe_2Ga_{0.5}O_4$ at 300 K.

and that for $Li_{0.5}Fe_{2.5}O_4$ can be written as

$$Fe^{3+}[Li^{1+}_{0.5}Fe^{3+}_{1.5}]O^{2-}_4$$

Thus the overall ionic configuration of the system can be written as

$$Ga^{3+}_{1-\alpha}Fe^{3+}_{\alpha}[Li^{1+}_{0.5}Fe^{3+}_{x-\alpha}Ga^{3+}_{2.5-x+\alpha}]O^{2-}_4$$

The above configuration is supported by site preference energy, X-ray intensity calculations and electrical conductivity data.

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Received 29 June 1992
and accepted 18 September 1992