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Transport properties of trivalent substituted Li-ferrites

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The electrical resistivity and thermoelectric power of $Li_{0.5}Fe_{2.5-x}R_xO_4$ (R = Al, La, Sm and Gd; $x = 0.0$ and 0.1) are studied. The distribution of the substituted ions over the different lattice sites is determined from IR spectra. The electrical resistivity is found to have a direct relation with the ionic radius of the substituted R ions. Meanwhile, the absolute value of thermoelectric power decreased with increasing ionic radius.

1. Introduction

Transport properties of ferrites are of great importance to select materials for specific applications. Some factors which affect the transport properties of ferrites, are the radius and the magnetic moment of the substituted ions. To study the effect of the ionic radius we aimed to substitute Fe^{3+} ions in $Li_{0.5}Fe_{2.5}O_4$ with Al^{3+} and La^{3+}, both of them are non magnetic while their ionic radii are quite different ($r_{Al} = 0.54$ Å and $r_{La} = 1.14$ Å). To see the effect of the magnetic moment, we substituted Fe^{3+} ions with Gd^{3+} and Sm^{3+}, both of them have nearly the same ionic radius ($r_{Gd} = 1.02$ Å and $r_{Sm} = 1.04$ Å) while their magnetic moments are quite different ($\mu_{Gd} = 7.5\ \mu_B$ and $\mu_{Sm} = 1.5\ \mu_B$).

2. Experimental techniques

Samples of the chemical formula $Li_{0.5}Fe_{2.5-x}R_xO_4$ (R = Al, La, Sm and Gd; $x = 0.0$ and 0.1) were prepared using the standard ceramic technique. High purity, 99.9%, Fe_2O_3, R_2O_3 and Li_2CO_3 were mixed together according to their molecular weights. The mixture of each sample was ground to a very fine powder and then presintered at 900°C for 6 hrs. The presintered powder was ground again and then pressed under a pressure 4×10^8 Pa into a disc shape. The samples were finally sintered at 1200°C for 6 hrs and then slowly cooled to room temperature. X-rays diffraction patterns were performed using a diffractometer type PW3710 with Cu K_α radiation. The infrared (IR) spectra were carried out using Pekrin–Elmer 783 spectrometer. Indium amalgam was used as a contact for electrical resistivity measurements and the sample was pressed directly against two platinum electrodes for thermoelectric power measurements. A temperature difference of 5°C was kept constant during thermoelectric power measurements. The calculated percentage error was about 2%.

3. Results and discussion

The x-ray diffraction patterns showed that all samples have simple cubic spinel structure. The lattice parameter remains nearly, within the experimental error, the same as that the unsubstituted sample ($x = 0.0$) which is refered to as R = None.

The IR spectra of the investigated samples recorded in the range 200–1000 cm^{-1} are shown in Fig. 1 IR spectrum of pure Li-ferrite (R = None) indicates the presence of three main bands. The first primary band ν_1^* at 590 cm^{-1} is due to the vibrations of Fe-O (Fe^{3+}) bond in the tetrahedral sites. It shows a splitting of three secondary bands $\nu_1(1)$, $\nu_1(2)$ and $\nu_1(3)$ at 712, 669 and 553 cm^{-1} respectively. The second primary band ν_2^* at 403 cm^{-1} is due to the vibrations of Fe-O (Fe^{3+}) bond in the octahedral sites. It is splitted to another peak at 374 cm^{-1}. The splitting of the primary bands is attributed to the presence of the Fe^{2+} ions in the octahedral sites, which causes Jahn–Teller distortion. This distortion produces deformation in the crystal field and hence produces the splitting of the absorption bands [1]. The third band which appears at 333 cm^{-1} indicates the presence of the Fe^{2+} ion in the mentioned composition. The bands at 470 and 440 cm^{-1} can be attributed to Li-O vibrations [2]. Fig. 2 illustrates the dependence of the wave numbers ν_1^* and ν_2^* on the ionic radii of R ions. One can observe that the Al ion leads to an increase of both the wave numbers of ν_1^* and ν_2^*. This indicates that the Al ions are distributed between the A and B sites of the lattice. Thus decreasing the bond length of the Fe-O (Fe^{3+}) and hence increasing the wave numbers. In the case of R = Gd and Sm, there are no changes in the wave number of ν_1^* while there is a shift to a lower wave number for ν_2^* peak. This means that the Gd Sm ions are only distributed in the B-sites leading to an increase in the bond length of Fe-O (Fe^{3+}) in the octahedral sites, which causes a decrease in the wave number of ν_2^* peak. This result is in agreement with the work reported by Kolekar [3] on Gd-substituted Cu-Cd mixed ferrites. Finally, in the case of R = La, there are no changes of the wave numbers ν_1^* and ν_2^*. This means that the La ion does not enter into the A or B-sites and resides at the grain boundaries. The presence of the La ions at the grain boundaries has been reported in case of Cu-ferrite [4].

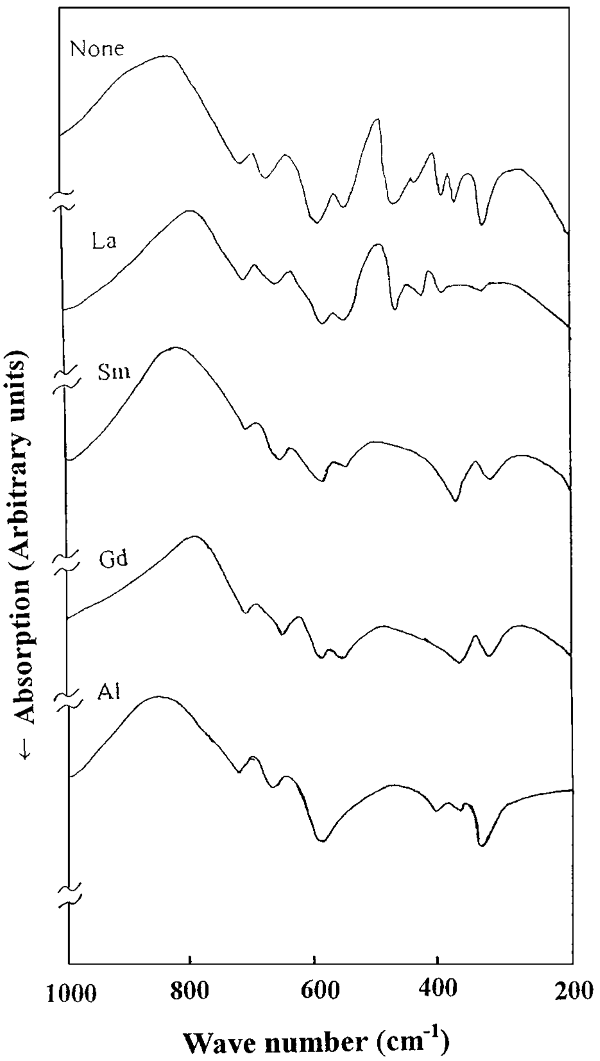

Figure 1 IR spectra of $Li_{0.5}Fe_{2.5-x}R_xO_4$ (R = Al, Gd, Sm and La) where $x = 0.0$ and 0.1.

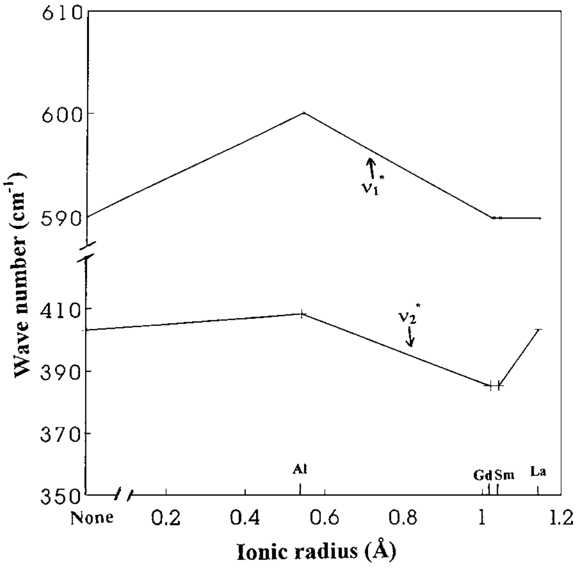

Figure 2 The effect of the radius of R ions on the position of ν_1^* and ν_2^* bands.

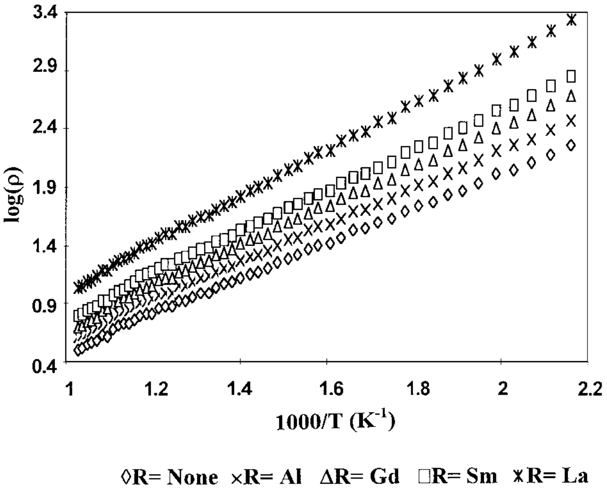

Figure 3 The variation of the resistivity, log(ρ), with temperature.

Fig. 3 shows the variation of the electrical resistivity, log(ρ), with 1000/T for the investigated systems. The results are represented for $T > 450$ K. It is obvious that the electrical resistivity decreases with increasing temperature. There is a change in activation energy on passing the Curie temperature (T_c). The Curie temperatures of the present samples are also listed in Table I. One can notice that the sample with R = Gd has the maximum value of T_c. Despite La^{3+} and Al^{3+} are non-magnetic ions, the value of T_c of the sample R = La is nearly equal to that of the sample with R = None and the value of T_c of R = Al is greater than that of R = Sm. These results could be explained in terms of the effect of the cation distribution of the R-ions between A and B sites. From IR study it is found that both of the Gd and Sm ions occupy B-sites while Al ions are distributed between A and B-sites. As the Gd ion has the maximum magnetic moment and it occupies B-site, it increases the total magnetic moment in B-sites and consequently it increases A-B interaction which leads to an increase of the Curie temperature. In the case of samples with R = Al the cation distribution could be considered as $(Fe_{1-a}Al_a)$ $[Li_{0.5}Fe_{1.5-(x-a)}Al_{x-a}]$ O_4 where "a" depends upon the amount of Al^{3+} ions in the sample. From the above cation distribution, it is observed that the presence of some amount of Al^{3+} ions in the A-sites displaces the same amount of Fe^{3+} from A- to B-sites. On the other hand, from IR study, the cation distribution of the sample with R = Sm, could be assumed as (Fe) $[Li_{0.5}Fe_{1.4}Sm_{0.1}]$ O_4. From the above two cation distributions, the amount of Fe^{3+} in B-sites for the sample with R = Sm should be less than that of R = Al. This causes the A-B magnetic interaction in the sample with R = Al to be larger than that of R = Sm. This causes the Curie temperature of the sample with R = Al to be higher than that of R = Sm. The sample with R = La has nearly equal value of T_c as that of R = None. This supports our assumption that the La^{3+} ions reside at the grain boundaries. It is also observed that the resistivity and the activation energy have increased for all substituted samples relative to that of the sample with R = None (see Table I). Also the resistivity and the activation energy $(E_\rho)_{\mathrm{ferri}}$ (in the ferrimagnetic region) of the substituted samples increase as the ionic radius of the dopant ion increases. This could be explained as follows: The substitution of R ions instead of Fe ions decreases the Fe^{2+} ion concentration which leads the resistivity and hence activation energy to increase. Also

TABLE I Curie temperatures (T_c), porosity ($p\%$), resistivity (ρ), activation energies (E_ρ) and thermoelectric power (α) for the different samples

R	T_c (K)	p (%)	ρ (Ω cm)	$(E_\rho)_{\rm ferri}$ (eV)	$(E_\rho)_{\rm para}$ (eV)	α (μV)/K
None	882	3.2	1.6×10^3	0.3	0.42	−1089
Al	877	2.6	1.3×10^4	0.32	0.41	−940
Gd	914	3.6	5×10^4	0.34	0.51	−851
Sm	873	3.7	7.9×10^4	0.35	0.43	−841
La	883	5.6	3.1×10^5	0.4	0.48	−812

the presence of R ions in the B sites impedes the motion of the charge carriers. This means that the electron transfer that takes place between Fe^{3+} and Fe^{2+} is not favored in the case of substituting Fe^{3+} with R^{3+}. This suggests that R ions does not take part in the conduction mechanism. This result is in agreement with the work reported on Cu-Zn[5] and Cu-Cd[6] ferrites. As the ionic radius of R ion increases the distance between Fe^{2+} and Fe^{3+} increases and so the electrical resistivity and the activation energy increase. From Table I it is also obvious that the larger the porosity the higher is the magnitude of the electrical resistivity. This is expected behavior because the number of scattering centers of charge carriers increases as the porosity increases.

Table I shows also that the activation energy in the paramagnetic state, $(E_\rho)_{\rm Para}$, is larger than that in the ferrimagnetic state, $(E_\rho)_{\rm Ferri}$. This is due to the volume expansion of the samples during the magnetic transition [7, 8] which increases the activation energy as corroborated experimentally.

Fig. 4 represents the changes of thermoelectric power (α) with temperature for the investigated samples. The thermoelectric power (α) is negative over the whole range of temperature indicating that the electrons are the majority charge carriers. One can notice also that there is a decrease in the absolute value of α for substituted samples relative to that with R = None. This is due to the decrease of the amount of Fe^{2+} ions substituted by R ions [9]. It is observed that there is a variation of the behavior of (α) for all samples near to the Curie temperature. Table I gives the magnitude of α at T = 323 K. One can see that the thermoelectric power has an inverse relation with the porosity. According to Standley [10], the porosity of the sample has an inverse relation with the amount of Fe^{2+} ions. Therefore, the samples with high porosity have less amount of Fe^{2+} ions which leads the absolute value of the thermoelectric power to decrease.

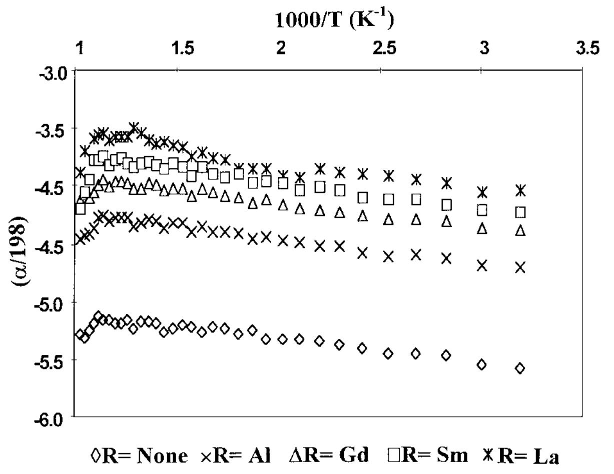

Figure 4 The variation of the thermoelectric power (α) with temperature.

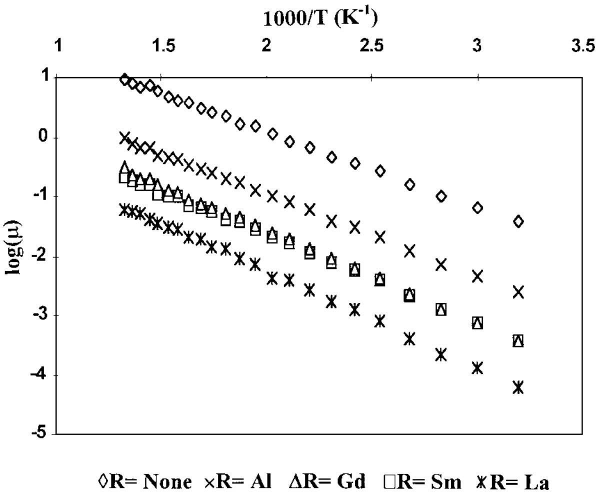

Figure 5 The temperature dependence of the mobility, log(μ).

To get more information on the conduction mechanism of these samples, we calculated the charge carrier mobility (μ) using values of the resistivity and thermoelectric power at different temperatures. The variation of the charge carrier mobility with temperature, Fig. 5, shows that the mobility increases strongly with increasing temperature. Such a behavior supports the hopping conduction mechanism.

4. Conclusions

1. Both the Gd and Sm ions occupy B-sites while Al ions are distributed between A and B sites. On the other hand, the La ions do not enter the spinel structure.

2. The electrical resistivity has a direct relation with the ionic radius of the substituted trivalent ion irrespective of the value of the magnetic moment.

3. The substituted R ions have no effect on the sign of (α) and the absolute value of α decreases with increasing ionic radius.

4. The obtained results support the hopping conduction mechanism in the studied systems.

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