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Infrared spectroscopic study of Fe^{3+} substituted yttrium iron garnet

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Various properties of ferromagnetic semiconductors can be understood through the study of the relations between their structure and response to electromagnetic radiation. Since the electric and magnetic properties of these materials are dependent on the precise configuration of the atoms or ions in their structures, methods of nondestructive analysis are especially suited to such investigations. In particular, the vibrational, electronic and magnetic dipole spectra can give information about the position and valence of the ions in the crystal lattices [1].

To our knowledge no work has been reported on infrared spectroscopy study of the garnets. An attempt has been made to analyze infrared spectrum of $Y_{3-x}Fe_{5+x}O_{12}$ system on the basis of theory developed by Waldron *et al.* [1] for the spinel ferrites.

Four samples of Fe^{3+} substituted yttrium iron garnet with general formula $Y_{3-x}Fe_{5+x}O_{12}$ ($x = 0.00$, 0.05, 0.15 and 0.30) were prepared by usual double sintering ceramic technique. The starting materials were Y_2O_3 and Fe_2O_3 all 99.3% pure supplied by E. Merck. The oxides were mixed thoroughly in stoichiometric proportion to yield the desired composition and wet ground using acetone. The mixture was dried and pressed into pellets with pressure of 2×10^3 kg/cm^2. These pellets were pre-sintered at 1000 °C for 12 h. In the final sintering process pellets were kept at 1200 °C for 24 h and then slowly cooled to room temperature at the rate of 2 °C/min.

The powder X-ray diffraction (XRD) patterns for all the composition were recorded at 300 K with a Philips (PW1710) diffractometer using Cu K_α radiation. The XRD patterns showed sharp lines corresponding to the single phase garnet structure with no extra lines corresponding to any other phase. The stoichiometry of the powdered samples were checked by EDAX [2]. The infrared spectra at room temperature (300 K) were recorded in the wave number range of 400–1000 cm^{-1}. For the present samples BRUKER IFS 66v FT-IR spectrometer was used to carry out infrared spectroscopic studies in the KBr medium. The analysis was carried out at R.S.I.C., IIT, Chennai.

The room temperature (300 K) infrared spectra for $Y_{3-x}Fe_{5+x}O_{12}$ system with $x = 0.00$, 0.05, 0.15 and 0.30 are shown in Figs 1 and 2. It can be seen from the figures that IR spectra of Fe^{3+}-substituted yttrium iron garnets are found to exhibit three bands in the range 400–700 cm^{-1}. The high frequency band ν_1 is around 657 cm^{-1}, mid frequency band ν_2 is around 605 cm^{-1} and the lower frequency band ν_3 is around 565 cm^{-1}. The absorption band ν_1 is caused by the stretching vibrations of the tetrahedral metal-oxygen bond, the absorption band ν_2 is caused by the metal-oxygen vibration in octahedral sites and the absorption band ν_3 is due to the dodecahedral metal-oxygen bond. The band position and intensities are given in Table I. The difference in band position is expected because of the difference in the Fe^{3+}-O^{2-} for the tetrahedral (d), octahedral (a), dodecahedral (c) complexes. It was found that cation–anion distance of d-site (1.88 Å) is smaller than that of the a-site (2.00 Å), which is again smaller than that of the c-site (2.43 Å) [3]. This can be interpreted on the basis of the strength of covalent bonding of cations at the respective sites. No shift in band position is observed for ν_1 and ν_2 band while slight variation has been observed for ν_3 band as a function of content (x). The constancy in the position of ν_1 and ν_1 bands is due to the fact that the substituted Fe^{3+} ions seems to occupy the larger dodecahedron (c)-sites without affecting a- and d- sites in the system [2]. The band ν_3 shifts towards lower frequency side. It is known that the decrease in bond length enhances the fundamental frequency and therefore the center frequency should shift towards higher frequency side. Levine [4] has correlated the decrease in bond length to an increase in covalent character. In the present system, the increase in Fe^{3+} content decreases Y^{3+} content, which results in a decrease of covalent character in the garnets. These results are in consistent with our earlier results on Zn-substituted copper ferri chromate spinel ferrite system [5].

The increase in cation–anion and cation–cation bond length with x may be due to the replacement of larger Y^{3+} ions with Fe^{3+} having smaller ionic radius, which

TABLE I Position of IR absorption bands (ν_1, ν_2, ν_3 and ν_4), intensity (I_1, I_2, I_3 and I_4), and ferrous ion concentration for $Y_{3-x}Fe_{5+x}O_{12}$ system

Content x	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_4 (cm^{-1})	I_1 (%)	I_2 (%)	I_3 (%)	I_4 (%)	Fe^{2+} (%)
0.00	656.5	604.1	572.5	474.3	4.63	12.04	6.48	8.33	0.85
0.05	656.5	605.5	568.1	476.1	2.31	13.89	6.55	7.41	0.78
0.15	656.6	605.8	566.3	478.1	4.63	17.59	8.33	2.31	0.62
0.30	656.8	606.0	565.9	480.3	8.33	27.78	13.42	12.03	1.12

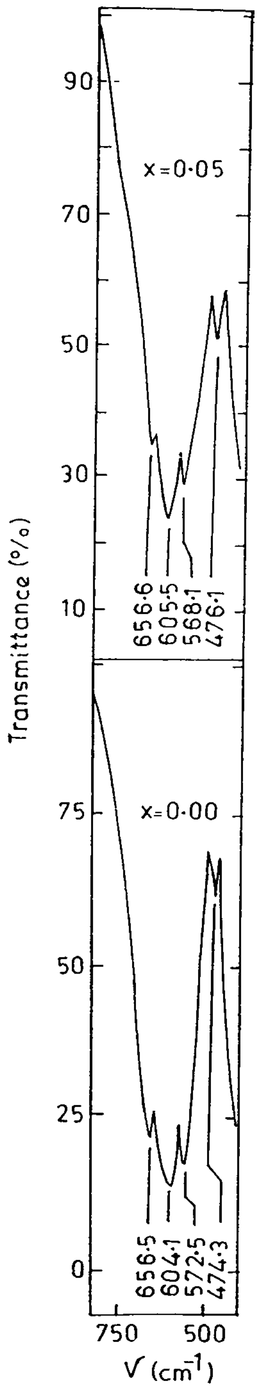

Figure 1 Infrared spectra of $Y_{3-x}Fe_{5+x}O_{12}$ system with $x = 0.00$ and 0.05 samples.

increases the cation–cation and cation–anion distances. The increase in cation–cation and cation–anion distance on increasing Fe^{3+} concentration should result in the weakening of strength of magnetic interaction, as expected our magnetization measurements [2] shows reduction in ferrimagnetism on increasing content x. The variation of Neel temperature deduced through thermal variation of a.c. susceptibility measurement (Table II) with x, shows enhancement of strength of magnetic interactions as Neel temperature increases with x [2] (Table II). This is due to fact that in present case non-magnetic Y^{3+} ($0\ \mu B$) is replaced by magnetic Fe^{3+} ($5\ \mu B$) that enhance the strength of magnetic interaction which in turn increase the Neel temperature.

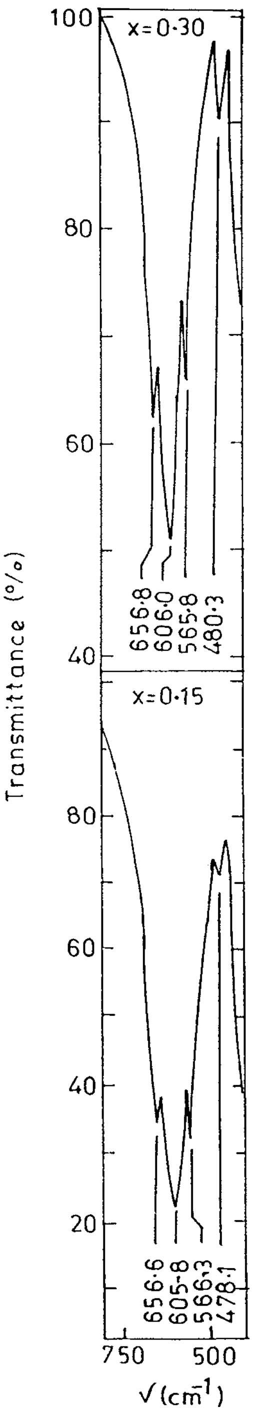

Figure 2 Infrared spectra of $Y_{3-x}Fe_{5+x}O_{12}$ system with $x = 0.15$ and 0.30 samples.

It is well known that the a-d exchange interaction is the strongest interaction in garnets irrespective of the rare earth ion involved. The cation distribution determined through magnetization measurement at 80 K [2] can be expressed as:

$$\left\{Y^{+3}_{3-x}Fe^{+3}_{x}\right\}^{c}\left\lfloor Fe^{+3}_{2}\right\rfloor^{a}\left(Fe^{+3}_{3}\right)^{d}O^{-2}_{12}$$

TABLE II Magneton number (n_B), Neel temperature (T_N), exchange interactions (J) for $Y_{3-x}Fe_{5+x}O_{12}$ system

Content x	n_B (μ_B) 80 K	T_N (K) ± 2 K	J_{ac} (cm^{-1})	J_{cd} (cm^{-1})
0.00	4.79	545	–	–
0.05	4.57	550	1.79	2.68
0.15	4.14	563	3.17	4.75
0.30	3.42	560	4.46	6.69

It is seen that in present case magnetic ion concentration on a- and d-site remain unaltered for all the compositions so there is no change in a-d exchange interactions. In this situation Neel temperature values are governed by a-c and c-d interaction, though they are considered to be weak interactions [3].

In order to support our arguments, that the strength of magnetic interaction increases with increasing dopant concentration (x), we have estimated the value of the exchange integral J_{ac} from T_{N} values by using the following relation [6]:

$$T_{\mathrm{N}} = \frac{2S(S+1)}{3K}\sqrt{\frac{\lambda}{\mu}}\, Z_{\mathrm{ac}} \cdot J_{\mathrm{ac}}$$

where the value of S, spin for Fe^{3+} ions, is 5/2; Z_{ac} the number of nearest neighbors to the a-site is 6; $\lambda[=(2/5)((2-x/2)]$ is the fraction of magnetic ions at the a site, with x as the amount of non magnetic ions at the octahedral site, which in our case is 0.4 as x is 0; $\mu[=(3/5)(y)/3]$ is the fraction of magnetic ions at the c-site, with y as the fraction of magnetic ions at dodecahedral site, k is the Boltzmann constant and J_{ac} is the average exchange integral which is to be evaluated.

On the basis of this formula, J_{ac} value and in similar way the value of J_{cd} for all the compositions have been estimated and are given in Table II. It can be seen from Table II that J_{ac} and J_{cd} values increases with increasing x value, in support with our argument.

The intensity of bands ν_1, ν_2, and ν_3 are found to increase with increase in Fe^{3+}-concentration (x). The increase in intensity is accompanied by the sharpening of bands (Figs 1 and 2). This may be attributed to the change in the Fe^{3+}-O^{2-} complexes in the system.

It is known that the intensity ratio is a function of the change of dipole moment with inter-nuclear distances ($d_{\mu}d_{\mathrm{r}}$) [7]. This value represents the contribution of the ionic bond Fe^{3+}-O^{2-} in the lattice. So, one can conclude that the IR spectra can give an idea about the change in the molecular structure of the ferrites like garnet. On the substitution of Fe^{3+} for Y^{3+} in the system the inter-nuclear distances decrease which in turn enhance the intensity of the band as measured by their IR absorption bands.

In the spinel ferrites the band ν_3 is assigned to the divalent metal ion-oxygen complexes in the octahedral sites [8]. In present case both the cations are trivalent (Y^{3+} and Fe^{3+}). Our earlier results suggest small amounts of Fe^{2+} in the system [2]. Based on above results the new band (ν_4) seen around the frequency of 477 cm^{-1} may be due to Fe^{2+}-O^{2-} complexes in the system. The intensity of ν_4 band is found to change according to the Fe^{2+} ion concentration in the system [2] (Table I).

In conclusion, the ν_1, ν_2 and ν_3 absorption bands are caused by the stretching vibrations of the tetrahedral, octahedral and dodecahedral metal-oxygen bond respectively. The ν_4 band may be due to Fe^{2+}-O^{2-} complexes and its intensity changes according to the concentration of ferrous ions in the system. The constancy in the position of ν_1 and ν_2 bands is due to the fact that substituted Fe^{3+} ions seems to occupy larger dodecahedral sites without affecting a- and d-sites in the system and shifting of ν_3 band towards higher frequency side is due to increase in the strength of magnetic interactions with increasing dopant concentration.

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