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Ceramics International 33 (2007) 1543–1546

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Mössbauer spectroscopic studies of Fe^{3+}-substituted YIG

P.U. Sharma, K.B. Modi *, V.K. Lakhani, K.B. Zankat, H.H. Joshi

Department of Physics, Saurashtra University, Rajkot 360005, India

Received 15 March 2006; received in revised form 30 April 2006; accepted 28 June 2006
Available online 18 September 2006

Abstract

Compositional dependence of hyperfine parameters, determined through Mössbauer spectral analysis has been studied for $Y_{3-x}Fe_{5+x}O_{12}$ ($x = 0.0$, 0.1, 0.3 and 0.5) garnet system at 300 K. The Mössbauer spectra have been fitted with three sextets in the ferrimagnetic state corresponding to Fe^{3+} ions at tetrahedral (d), octahedral (a) and dodecahedral (c) sites of the crystal structure. It is observed that isormershift, quadrupole shift and hyperfine field of d-site show no significant variation with Fe^{3+} concentration. The change in hyperfine fields of a- and c-sites with composition (x) has been explained on the basis of strength of exchange integrals, change in isomershift can be understood due to s-electron charge distribution and asymmetric displacement of oxygen ions surrounding the a- and c-sites seems to be responsible for observable quadrupole shift. The magneton number values obtained from magnetization and Mossbauer data are in agreement to those calculated using Neel's three sublattice model of ferrimagnetism.

Keywords: Garnet; Mossbauer spectroscopy; Hyperfine interactions

1. Introduction

Yttrium iron garnet ($Y_3Fe_5O_{12}$:YIG) belongs to a large class of compounds crystallize in bcc structure. The knowledge of distribution of cations among the available octahedral (a), tetrahedral (d) and dodecahedral (c) sites in the garnet structure is useful in understanding their structural, magnetic and electrical properties.

The polycrystalline pure and substituted YIG is a subject of interest from various applications and physics point of view. Many research reports are available on various properties of non-magnetic cation substituted on a- and d-sites of YIG [1–3]. Majority of work deal with substitution of tetravalent and pentavalent cations on a- and d-sites along with divalent cations on c-site in order to maintain charge neutrality [1,4]. Few reports are available on magnetic ion substitution on a- and d-sites [5,6]. However, rare earth magnetic cation doped on c-site of YIG is very common [1,3]. So far no work has been reported on exclusive c-site substitution, with cations other than rare earths, except In^{3+} and Fe^{3+}-substituted YIG [7]. This work is restricted to X-ray and Mössbauer spectroscopic properties of typical compositions with $x = 0.18$ and 0.33 [7], without any emphasize on hyperfine parameters and its consequences. Since no work has been reported on detailed Mössbauer spectral analysis of any garnet system in general and $Y_{3-x}Fe_{5+x}O_{12}$ in particular, the present work is important from fundamental research point of view. It becomes interesting and complex too, when all the three sites of crystal lattice possess magnetic ions like Fe^{3+} as in the present case, to study the compositional dependence of hyperfine interactions, hyperfine parameters and cation distribution.

This work is continuation of our work on structural [8], magnetic [9], infrared spectroscopic [10] and elastic properties [11] of the $Y_{3-x}Fe_{5+x}O_{12}$ system.

2. Experimental

Four samples of Fe^{3+}-substituted Yttrium iron garnet ($Y_{3-x}Fe_{5+x}O_{12}$; $x = 0.0$, 0.1, 0.3 and 0.5) were prepared by usual double sintering ceramic technique. The starting materials were Y_2O_3 and Fe_2O_3 all 99.9% pure supplied by E. Merck. The oxides were mixed thoroughly in stoichiometric proportion to yield the desired compositions and wet ground. The mixture was dried and pressed into pellets. These pellets were pre-sintered at 1000 °C for 12 h. In the final sintering

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* Corresponding author. Tel.: +91 281 2578505x403; fax: +91 281 77885.
E-mail address: kunalbmodi2003@yahoo.com (K.B. Modi).

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doi:10.1016/j.ceramint.2006.06.012

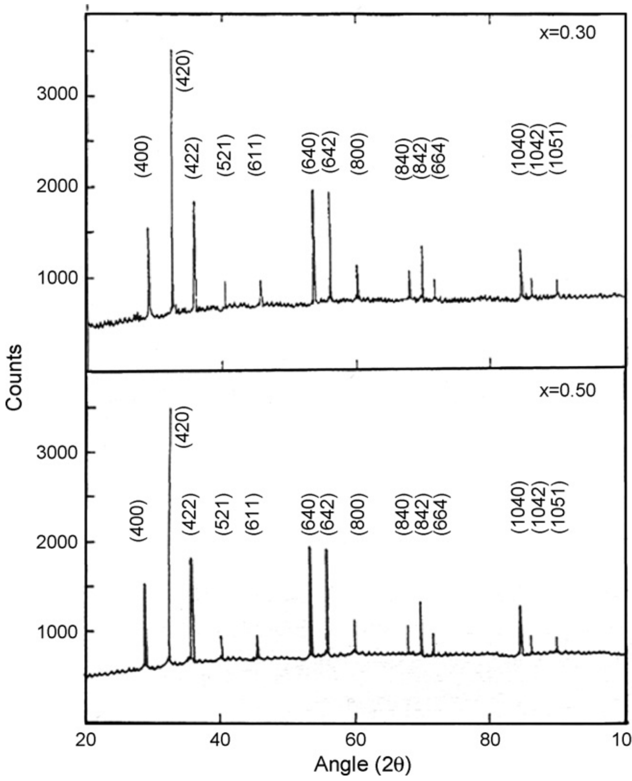

Fig. 1. X-ray diffraction patterns for $x = 0.3$ and 0.5 samples.

process pellets were kept at 1200 °C for 24 h and then slowly cooled to the room temperature at the rate of 2 °C/min.

The powder X-ray diffraction patterns for all the compositions were recorded at 300 K with a Philips (PW 1700) diffractometer using Cu Kα radiation. No structural phase other than the expected bcc garnet phase has been detected in XRD patterns (Fig. 1). The chemical stoichiometry of the powdered samples was checked by energy dispersive analysis of X-ray (EDAX) [8] No trace of any impurity was found in the EDAX patterns for these samples. Thus, the EDAX and XRD characterizations have ascertained the compositional purity and structural monophase nature of the specimens. Mössbauer spectra of the samples were recorded at 300 K using a conventional constant acceleration Mössbauer spectrometer with ^{57}Co radiation source embedded in a rhodium matrix. Calibration spectra with 99.8% pure iron powder (procured from Aldrich) were taken before and after each measurement.

3. Results and discussion

The ^{57}Fe Mössbauer spectroscopy is an important probe for garnet and spinel ferrites to study the structural changes, hyperfine interaction, magnetic behaviour and to deduce unambiguously the distribution of Fe^{3+} ions among sublattices of garnet structure. We have earlier reported that substitution of Fe^{3+} ions changes the magnetic properties of the YIG system [9]. One therefore expects that the internal hyperfine magnetic field experienced by the Fe nucleus would also be affected by Fe^{3+}-substitution and such changes should be reflected in the ^{57}Fe Mössbauer spectra.

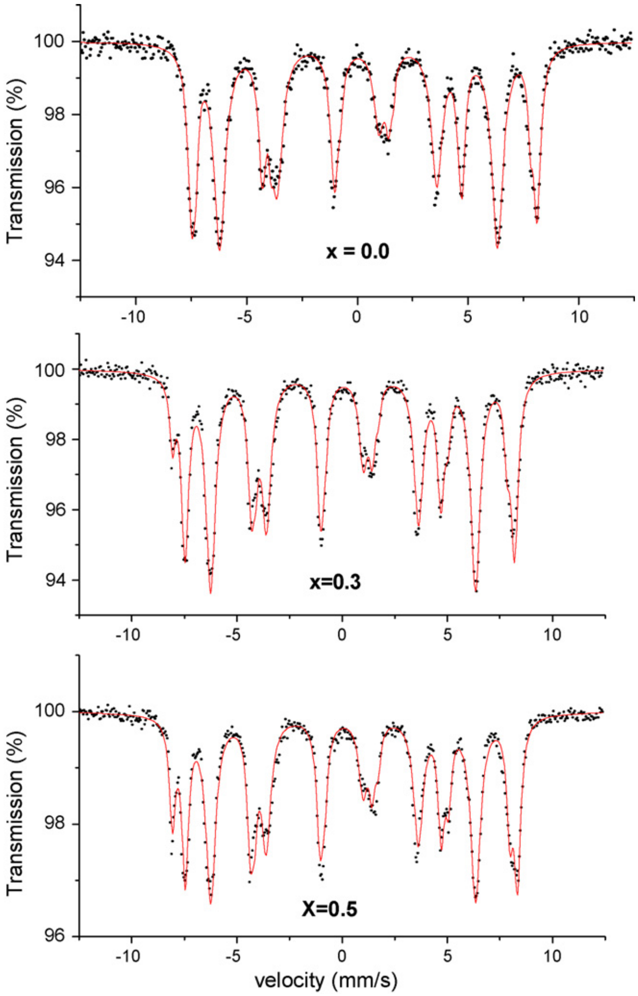

Fig. 2. Mössbauer spectra of Y–Fe–O system at 300 K.

Mössbauer spectra recorded at 300 K for samples with $x = 0.0$, 0.3 and 0.5 are shown in Fig. 2.The Mössbauer spectra were analyzed and the hyperfine interaction parameters were refined by computer software using least squares method and assuming each spectrum to be a sum of Lorentzian functions. The Mössbauer spectra of all the compositions exhibit three superimposed asymmetric Zeemann split sextets due to Fe^{3+} ions at tetrahedral (d), octahedral (a) and dodecahedral (c) sites. The three sextets for $x = 0.0$ composition is rather unexpected, because it is well established that Fe^{3+} ions occupy d- and a-sites in the ratio of 3:2, as a result two sextets may be expected. The hyperfine parameters deduced through Mossbauer spectra are given in Table 1.

We note that the isomer shift for d-site shows no significant variation with Fe^{3+}-substitution while that for a- and c-site shows considerable changes. This indicates that s-electron charge distribution of the Fe^{3+} ions on a- and c-site are influenced by Fe^{3+}-substitution. The value of isomer shift for a-site is well within the range of Fe^{3+} isomer shift values (0.2–0.3 mm/s), on the other hand for d-site and c-site values lying below and above the range. The isomer shifts for Fe^{3+} at different sites are different. The isomer shift for d-site is the smallest ~0.11 mm/s and is independent of Fe^{3+}-substitution.

Table 1
Mössbauer parameters: isomer shift (I. S.), quadrupole shift (Q. S.), hyperfine field (H_f) and line width (W) for Y–Fe–O system at 300 K

Content (x)	Site	I.S. (mm/s)[a] ±0.02	Q.S. (mm/s) ±0.02	H_f (kOe) ±1 kOe	W (mm/s)	Area (%)
0.0	d	0.11	0.07	397	0.56	60
	a	0.35	0.13	478	0.37	33
	c	0.45	−0.18	493	0.21	7
0.1	d	0.11	0.02	397.5	0.51	59
	a	0.30	−0.20	485	0.32	32
	c	0.35	0.02	496	0.29	9
0.3	d	0.12	0.03	398	0.49	56.5
	a	0.27	−0.6	494	0.28	33.9
	c	0.37	0.17	502	0.38	10
0.5	d	0.11	0.04	398	0.50	54.5
	a	0.29	−0.50	500	0.31	30
	c	0.40	0.27	507	0.34	16

[a] With respect to Fe-metal.

The isomer shift at c-site is greater than that at a-site and is influenced by the amount of Fe^{3+}-substitution. As all the iron ions are in the trivalent state, the change in isomer shift signifies that the 3s electron density at the nucleus of Fe^{3+} ion is governed by the kind of bonding it makes with the neighbouring oxygen ions. The difference in the neighbouring environment (tetrahedral, octahedral or dodecahedral) can cause different stretching of d-electrons and partial hybridization resulting in different distribution of 3s electron.

The compositional variation of quadrupole shift in the magnetic sextets is given in Table 1. It shows that the quadrupole shift of d-sites remains the same for all the samples and is around 0.1 mm/s which falls in the range corresponding to that produced in Fe^{3+} ion in such an environment. The quadrupole shifts of a- and c-sites show significant variation with increase in Fe^{3+}-substitution. The substitution of Fe^{3+} in the system creates an asymmetric displacement of oxygen ions surrounding a- and c-sites. Fe^{3+} is normally a spherically symmetric ion and therefore Q_{local} is expected to be zero, hence the quadrupolar interaction seen in our case for a- and c-sites must arise from the Q_{lattice}. This creates an asymmetry or distortion at the lattice site leading to significant quadrupole shift. The external substitution of Fe^{3+} changes the amount of oxygen displacement resulting in corresponding change in quadrupole shift.

It is seen that (Table 1) the nuclear hyperfine field for d-site is lower than that of the a- and c-sites, further $H_c > H_a$, for all the samples. This happens because the c-site Fe^{3+} ions experience a stronger average magnetic bonding with d- and a-sites Fe^{3+} ions compared to the d- and a-site Fe^{3+} ions for which some of the bonds are with diamagnetic Y^{3+} at c-sites. The magnetic hyperfine fields for pristine composition ($x = 0.0$) are found to be 478 kOe for a-sites and 397 kOe for d-sites (Table 1), are in agreement with reported earlier [7].

The Zeemann lines from d-sites are more broadened than those from a- and c-sites. This can be related to the fact that the d-sites exhibit a strong magnetic interaction with a- and c-sites giving rise to a large distribution of magnetic hyperfine field (MHF) coming from a perturbation in the three sublattices.

From the results of Mossbauer spectra, we can consider the cation distribution as follows. It is known that YIG is a ferrimagnetic oxide with three cation sites and the formula is given by:

$$\{Y_3{}^{+3}\}^c(Fe_2{}^{+3})^a[Fe_3{}^{+3}]^dO_{12}{}^{-2}$$

Considering the peak area ratio determined through Mossbauer spectral analysis, the cation distribution for the compositions are deduced as:

$$x = 0.0 \quad \{Y_{2.65}Fe_{0.35}\}^c(Fe_{1.65}Y_{0.35})^a[Fe_3]^dO_{12}{}^{-2}$$

$$x = 0.1 \quad \{Y_{2.53}Fe_{0.47}\}^c(Fe_{1.63}Y_{0.37})^a[Fe_3]^dO_{12}{}^{-2}$$

$$x = 0.3 \quad \{Y_{2.48}Fe_{0.52}\}^c(Fe_{1.78}Y_{0.22})^a[Fe_3]^dO_{12}{}^{-2}$$

$$x = 0.5 \quad \{Y_{2.15}Fe_{0.85}\}^c(Fe_{1.65}Y_{0.35})^a[Fe_3]^dO_{12}{}^{-2}$$

According to the Neel's three sublattice, collinear spin model [1], the magnetic moment per formula unit at 0 K in units of μ_B is n_B^N which can be expressed as:

$$n_B^N(x) = [M_d(x) - M_a(x)] - M_c(x)$$

Table 2
Magnetic number (n_B), Curie temperature (T_c) and exchange integral (J) for Y–Fe–O system

Content (x)	n_B (μ_B) 80 K [9]	n_B^N (μ_B)	n_B^M (μ_B)	T_c (K) [9]	J_{ad} (cm^{-1})	J_{ac} (cm^{-1})	J_{dc} (cm^{-1})
0.0	4.79	5.0	5.0	545	14.91	5.09	3.78
0.1	4.35	4.5	4.44	550	15.13	5.99	4.42
0.3	3.42	3.5	3.29	560	14.75	6.14	4.73
0.5	2.70	2.5	2.11	562	15.37	8.18	6.07

where M_d, M_a and M_c are the d-, a- and c-sublattice magnetic moment in units of μ_B calculated using cation distribution formula and magnetic moment of 5 μ_B for Fe^{3+} ions. The variation of magneton number (n_B) at 80 K obtained from magnetization data [9] and n_B^N values for all the compositions (Table 2) are in good agreement, confirming the collinear spin ordering in the system. The small observed difference between n_B^N and n_B values may be due to thermal effects.

A check for the presence of a canted spin (non-collinear) structure follows from the apparent proportionality between (H_f) and the average sublattice magnetization. By neglecting intra-site interactions (J_{dd}, J_{cc} and J_{aa}) between the ions on the same site, it can be shown that:

$$\mu(x) = \frac{H_d(x)}{H_d(0)} M_d(x) - \frac{H_a(x)}{H_a(0)} M_a(x) - \frac{H_c(x)}{H_c(0)} M_c(x)$$

where H_d, H_a and H_c are hyperfine field values (Table 2).

The values of magnetic moment per formula unit $n_B^M \approx \mu(x)$ as a function of Fe^{3+}-content (x) were determined from above equation the same are presented in Table 2. There is reasonable agreement among the value of $n_B^M(x)$ obtained from Mössbauer data, $n_B(x)$ from magnetization and $n_B^N(x)$ calculated from Neel's model, confirming a collinear magnetic structure.

In such garnet systems, formation of yttrium orthoferrite ($YFeO_3$) and α-Fe_2O_3 is quite probable [12,13]. If it is so, it would have reflected in X-ray diffraction, magnetization and Mössbauer spectroscopic measurements. In X-ray diffraction pattern it appears as extra Bragg's reflections, which do not correspond to the bcc phase of YIG. The presence of antiferromagnetic $YFeO_3$ and unreacted Fe_2O_3 lowers the saturation magnetization value [12]. There are reports showing the presence of an additional sextet in Mössbauer spectrum has been observed with hyperfine field value $\geq$510 kOe corresponding to $YFeO_3$ or α-Fe_2O_3 phase formation [12,13]. In the present case, no such indications have been observed, ruling out any formation of unwanted phases in the system.

It is possible to estimate the value of the exchange integral J_{ad}, J_{ac} and J_{dc} from Curie temperature (T_c) [9] by using the following equation [14]:

$$T_c = \frac{2S(S+1)}{3k} \sqrt{\frac{\lambda}{\mu}} Z_{ad} J_{ad}$$

where the value of S, spin for Fe^{3+} ions is 5/2; Z_{ad} the number of nearest neighbours to the a-site is 6; $\lambda = [\{2/(5+x)\}\,(2-y)/2]$ the fraction of magnetic ions at the a-site, with y the amount of non-magnetic ions at the octahedral site; $\mu = [\{3/(5+x)\}(3-z)/3]$ the fraction of magnetic ions at the d-site, z the amount of non-magnetic ions at the tetrahedral site; k the Boltzmann constant and J_{ad} is the average exchange integral which is to be evaluated. In similar manner values of J_{ac} and J_{dc} have been calculated and presented in Table 2. It can be seen that $J_{ad} > J_{ac} > J_{dc}$, i.e. the a–d exchange interaction is the strongest interaction in a garnet irrespective of the presence of rare earth ion [1]. It is interesting to note that J_{ad} remains almost constant while J_{ac} and J_{dc} increase with increasing Fe^{3+}-substitution in the system. Now it is possible to explain compositional variation of hyperfine field in the light of the strength of exchange interactions. The observed compositional variation of H_d, H_a and H_c is similar to that of the variation of J_{ad}, J_{ac} and J_{dc}, respectively, suggesting that the hyperfine field of d-sites (H_d), octahedral sites (H_a) and dodecahedral sites (H_c) is governed by J_{ad}, J_{ac} and J_{dc} exchange interactions, respectively.

4. Conclusions

In conclusion, on Fe^{3+}-substitution around 13% of Y^{3+}-ions occupy octahedral sites. The magnetic ion concentration, isomer shift, quadrupole shift and hyperfine field for d-site remain unaffected while those for a- and c-sites show significant change with Fe-substitution. It is found that relative magnitude of hyperfine field is $H_c > H_a > H_d$, while strength of average exchange integral becomes $J_{ad} > J_{ac} > J_{dc}$. Magnetization and Mossbauer data support Neel's type of collinear spin ordering in the system.

Acknowledgement

One of the authors (KBM) is thankful to A.I.C.T.E., New Delhi, for providing financial assistance in the form of career award for young teachers.

References

[1] K.J. Standly, Oxide Magnetic Materials, second ed., Clerendon Press, Oxford, 1974, and references therein.
[2] T.T. Shrinivasan, Om Prakash, M.J. Patni, Trans. Ind. Ceram. Soc. 40 (1) (1981) 1.
[3] K.C. Patil, K. Suresh, J. Alloys. Compd. 209 (1994) 203.
[4] C.M. Srivastava, S.N. Shringi, B. Uma Rao, D. Bahadur, Om Prakash, Bull. Mater. Sci. 6 (1) (1984) 17.
[5] V.D. Murumkar, K.B. Modi, K.M. Jadhav, G.K. Bichile, R.G. Kulkarni, Mater. Lett. 32 (1997) 281.
[6] J. Smith, H.P. Wijn, Ferrites, Cleaver–Hame Press, London, 1959.
[7] Sung Ho Lee, Kwang Pyo Chae, Seok Won Hong, Young Bae Lee, Solid State Commun. 83 (2) (1992) 97;
Sung Ho Lee, Kwang Pyo Chae, Seok Won Hong, Young Bae Lee, J. Korean Phys. Soc. 28 (1995) 625.
[8] R.P. Vara, H.J. Shah, M.P. Pandya, M.C. Chhantbar, K.B. Modi, Ind. J. Pure Appl. Phys. 42 (2004) 117.
[9] K.B. Modi, H.J. Shah, U.N. Trivedi, R.P. Vara, M.C. Chhantbar, H.H. Joshi, Ind. J. Eng. Mater. Sci. 10 (2003) 502.
[10] K.B. Modi, R.P. Vara, H.G. Vora, M.C. Chhantbar, H.H. Joshi, J. Mater. Sci. 39 (2004) 2187.
[11] K.B. Modi, M.C. Chhantbaar, P.U. Sharma, H.H. Joshi, J. Mater. Sci. 40 (5) (2005) 1247.
[12] M. Ristic, I. Nowik, S. Popovic, I. Felner, Mater. Lett. 57 (2003) 2584.
[13] R. Justin Joseyphus, et al. J. Magn. Magn. Mater. 272–276 (2004) 2257.
[14] N. Miura, I. Oguro, S. Chicazumi, J. Phys. Soc. Jpn. 45 (1978) 5.