International Journal of Scientific Research in Physics and Applied Sciences
Vol.6, Issue.2, pp.5-9 April (2018)

Research Paper

E-ISSN: 2348-3423

50 MeV, Li^{3+} ion induced modifications in Mössbauer signature and hyperfine interaction parameters of $Y_{3+x}Fe_{5-x}O_{12}$ system

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Available online at: www.isroset.org

Received: 21/Feb/2018, Revised: 05/Mar/2018, Accepted: 23/Mar/2018, Online: 30/Apr/ 2018

Abstract– The consequences of swift heavy ion (SHI) irradiation (Li^{3+}, 50 MeV, fluence = 5×10^{13} ions/cm^2) on the Mössbauer signature and nuclear hyperfine interaction parameters of polycrystalline $Y_{3+x}Fe_{5-x}O_{12}$; x = 0.0, 0.2, 0.4 and 0.6 garnet system have been studied by means of ^{57}Fe Mossbauer spectroscopy at 300 K. It is found that the formation of yttrium orthoferrite ($YFeO_3$) phase for higher Y^{3+}- concentration compositions can effectively be reversed by swift heavy ion irradiation. Mössbauer spectral analysis reveals the formation of central enhancement in the irradiated samples that indicates the formation of localized paramagnetic centers. Hyperfine parameters analysis throws light on the presence of two magnetic phases corresponding to the ferrimagnetic garnet phase and week ferromagnetic $YFeO_3$ phase. The hyperfine interaction parameters of both the phases are highly influenced by SHII indicating a redistribution of cations and SHI induced formation of paramagnetic centers in the material.

Keywords– yttrium iron garnet; swift heavy ion irradiation; Mossbauer spectroscopy

I. INTRODUCTION

The iron Mossbauer spectroscopy is an important microscopic probe for ferrites to study the hyperfine interaction parameters, coexisting magnetic phases and to deduce unambiguously the distribution of Fe^{3+} -ions among the three antiferromagnetically coupled sublattices, tetrahedral (d-),octahedral (a-) and dodecahedral (c-) of the garnet structure. It is well known that when magnetic insulators are subjected to swift heavy ion irradiation (SHII), it leads to the creation of a wide variety of defect states in the materials [1] resulting in the modifications on their properties. Owing to the high sensitivity of superexchange interactions to any change in bond direction or length, the Mössbauer spectroscopy has been extensively used for the study of the SHI-induced modifications in the microstructure of spinel ferrites and garnets. The yttrium iron garnet: $Y_3Fe_5O_{12}$ (YIG) has been found to be a relevant material for the purpose of irradiation because of its stability, well known magnetic properties and the possibility to find it in polycrystalline, single crystal or thin epitaxial film form [2]. However, the majority of the work available in the literature deals with irradiation effect on various properties of single crystal and thin films of YIG [2 - 5].

We have earlier reported that substitution of Fe^{3+}-ions changes the magnetic properties of YIG system [6]. On the other hand, the influence of Y^{3+}-ion substituted for Fe^{3+} ion and swift heavy ion irradiation (50 MeV, Li^{3+} ion, fluence: 5×10^{13} ions/cm^2) on structural, infrared spectral, bulk magnetic, electric and dielectric properties of the $Y_{3-x}Fe_{+x}O_{12}$ garnet system have been studied earlier [7-12]. Relatively little is known regarding the effect of large (0.89 Å), non – magnetic (0 μ_B) Y^{3+} ions substitution for smaller (0.64 Å), highly magnetic (5 μ_B) Fe^{3+} ions and SHI irradiation on hyperfine parameters and microscopic magnetic phase evolution of yttrium iron garnet ($Y_3Fe_5O_{12}$) system by means of Mossbauer spectral analysis.

In introduction section, we discuss fundamentals of Mossbauer spectroscopy, swift heavy ion irradiation along with highlights of previous work done, while in experimental details section, description of synthesis procedure and characterization techniques employed has been given. The results and discussion section talk about results obtained, possible cause to explain the observations and important hyperfine interaction parameters determination. The interesting outcomes are summarized in the conclusion part.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of pure and Y^{3+}-substituted yttrium iron garnet system with general chemical formula, $Y_{3+x}Fe_{5-x}O_{12}$, x = 0.0, 0.2, 0.4 and 0.6, were synthesized by usual

double sintering ceramic route as described elsewhere [11]. The X-ray powder diffraction measurements were done at room temperature (300 K) to study the influence of swift heavy ion (SHI) irradiation on phase formation and structural parameters. The experimental details and results are discussed in [11]. It has been found that (i) the compositions with x = 0.0 and 0.2 possess single phase *bcc* garnet structure (space group: O_h^{10} – Ia3d) while x = 0.4 and 0.6 compositions are of mixed phase (yttrium iron garnet phase and yttrium orthoferrite ($YFeO_3$) phase). (ii) Unwanted $YFeO_3$ phase can effectively suppress by SHI irradiation. The room temperature ^{57}Fe Mossbauer spectra were recorded before and after the SHI irradiation to investigate the consequences of SHI irradiation on nuclear hyperfine interaction parameters and Mossbauer spectral signature. Ambient Mossbauer measurements on the samples with the thickness (~ 0.15 mg $^{57}Fe/cm^2$) were done using 25 mCi ^{57}Co isotope in a (Pd) – matrix at constant acceleration mode in transmission geometry and 14.4 keV gamma rays were detected by Xenon – Methane filled proportional detector. The data were analyzed using NORMOS computer software [13] with an appreciable goodness-of- fit parameter.

III. RESULTS AND DISCUSSION

The Mossbauer spectra for pristine and SHI irradiated samples with x = 0.0, 0.2, 0.4 and 0.6 of $Y_{3-x}Fe_{5+x}O_{12}$ system are shown in Fig.1. The Mossbauer spectra were analyzed and hyperfine interaction parameters were refined using NORMOS computer software using non-linear least square minimization [13]. The solid lines through the data points are the results of computer fits of spectra obtained assuming equal line width for the a- and d- sites. The Mossbauer spectra of x = 0.0 and 0.2 compositions for pristine and irradiated samples, exhibit two normal Zeeman split sextets one due to the Fe^{3+} -ions on a-site and other due to the Fe^{3+} ions on d-site, which indicates the ferrimagnetic behavior of the samples. For pristine samples of x = 0.4 and 0.6 compositions, in addition to these magnetic components, a third magnetic sextet has been observed. It is found that the third component corresponds to $YFeO_3$ phase as confirmed by X-ray diffraction pattern analysis [11]. The Mossbauer spectra of x = 0.4 and 0.6 compositions for irradiated samples, exhibit a paramagnetic singlet or central enhancement superimposed on the magnetic sextets. The electronic energy loss (S_e) of 50 MeV Li^{3+} ions in this compound, calculated using the SRIM-98 code, is around 12 eV/Å which is less than electron energy loss threshold (S_{eth}) required to surmount the energy required for producing columnar amorphization that is of the order of 10^3 eV/ Å. This suggests that the SHI irradiation has generated points /cluster of defects. The generation of point/clusters of defects in these compounds inhibits the long range ferrimagnetic order through redistribution of cations in the localized defected region leading to the formation of paramagnetic centers. These paramagnetic centers resulted from breaking of magnetic ordering. The central paramagnetic enhancement in Mossbauer spectra can be explained on the basis of paramagnetic centers. In the present case, paramagnetic centers could have been created by re-distribution of cations induced by SHI-irradiation as observed earlier in Ti-substituted Al/Cr containing Li-ferrite systems [14]. The population of central singlet has been interpreted as due to some Fe^{3+} -ions being isolated from other Fe^{3+} -ions by non-magnetic Y^{3+} -ions, giving rise to a variation of cluster sizes which have little magnetic interaction with the surrounding. Furthermore, magnetic ordering within the cluster is accompanied by much faster relaxation, especially for smaller clusters and giving rise to the central paramagnetic components [15]. Thus, the central singlet in the Mossbauer spectra of the irradiated samples originates from the SHI-induced paramagnetic centers, and not due to an amorphous phase.

In contrast, the Mossbauer spectra of the x = 0.0 and 0.2 compositions after irradiation do not show the slightest sign of central paramagnetic singlet. This suggests that the presence of magnetic Fe^{3+} (5 μ_B) ions in the lattice seems to play an important role of keeping the long range order intact in spite of SHI induced defected regions/rearrangement of the cations, while the coexistence of higher concentration of non-magnetic Y^{3+}(x > 0.2) ions give rise to SHI induced localized paramagnetic centers.

The hyperfine interaction parameters deduced through Mossbauer spectral analysis are given in Table 1. It is seen that the nuclear hyperfine field (H_f) for the d-site is lower than that of the a-site for all the compositions before and after irradiation. This happens because of the Fe^{3+}-ions on the a-site, experience a stronger average magnetic coupling than the d-site ions due to more covalent nature of the Fe^{3+}-O^{2-} bond. The variation in the hyperfine field is due to the change in a-d, d-d and a-a interactions as the cation neighbors about given Fe^{3+} ion are changed. The magnetic hyperfine fields for pristine composition (x = 0.0) are found to be 490.2 kOe for the a-site and 397.3 kOe for the d-site in agreement with those reported earlier [16-17]. Because the non- magnetic Y^{3+} ions replace the magnetic Fe^{3+} ions at the tetrahedral (d-) sites and due to the prominent a-d superexchange interaction, the supertransferred hyperfine field at the a-site is influenced to a greater extent. Therefore, the a-site hyperfine field increases with Y^{3+}-substitution before and after irradiation for x = 0.0 - 0.4 compositions. This can be related to the increase of covalency. The average oxygen distance to 16(a) Fe^{3+} ion is about 2.01 Å while the tetrahedrally co-ordinate oxygen ions are at 1.87 Å from Fe^{3+} ion. Thus, the covalency character in the d-sites is

Table 1. Mössbauer hyperfine interaction parameters for pristine and irradiated samples of $Y_{3+x}Fe_{5-x}O_{12}$ system at 300K.

sample	***site***	***lines***	***H_f (kOe) ± 1 kOe***		***Width (mm/s) ±0.03 mm/s***		***Area % ±1%***		***I.S (mm/s)* ±0.02 mm/s***		***Q.S (mm/s) ±0.02 mm/s***	
			Pristine	***Irr.***	***Pristine***	***Irr.***	***Pristine***	***Irr.***	***Pristine***	***Irr.***	***Pristine***	***Irr.***
x = 0.0	a	6	490.17	488.27	0.429	0.382	40.29	38.11	0.380	0.380	0.051	0.054
	d	6	397.34	395.42	0.443	0.452	59.71	61.89	0.152	0.147	0.022	0.018
x = 0.2	a	6	492.46	493.99	0.362	0.394	48.75	46.41	0.372	0.374	0.048	0.022
	d	6	396.54	397.02	0.539	0.456	51.25	53.59	0.153	0.150	0.024	0.006
x = 0.4	$YFeO_3$	6	485.30	476.71	0.419	0.466	30.67	16.13	0.387	0.368	-0.013	-0.126
	d	6	396.93	398.49	0.489	0.596	43.53	41.40	0.155	0.150	0.020	0.037
	a	6	501.49	497.75	0.305	0.315	25.80	40.32	0.356	0.358	0.023	0.008
	singlet	1	-	-	-	0.573	-	2.15	-	0.045	-	-
x = 0.6	a	6	482.92	486.58	0.277	0.352	20.40	25.27	0.387	0.379	-0.033	0.010
	d	6	394.62	397.56	0.463	0.490	33.41	33.05	0.154	0.153	0.006	0.0002
	$YFeO_3$	6	500.30	500.49	0.354	0.328	46.19	36.71	0.353	0.360	0.012	0.005
	singlet	1	-	-	-	1.438	-	4.97	-	0.252	-	-

*with respect to iron metal

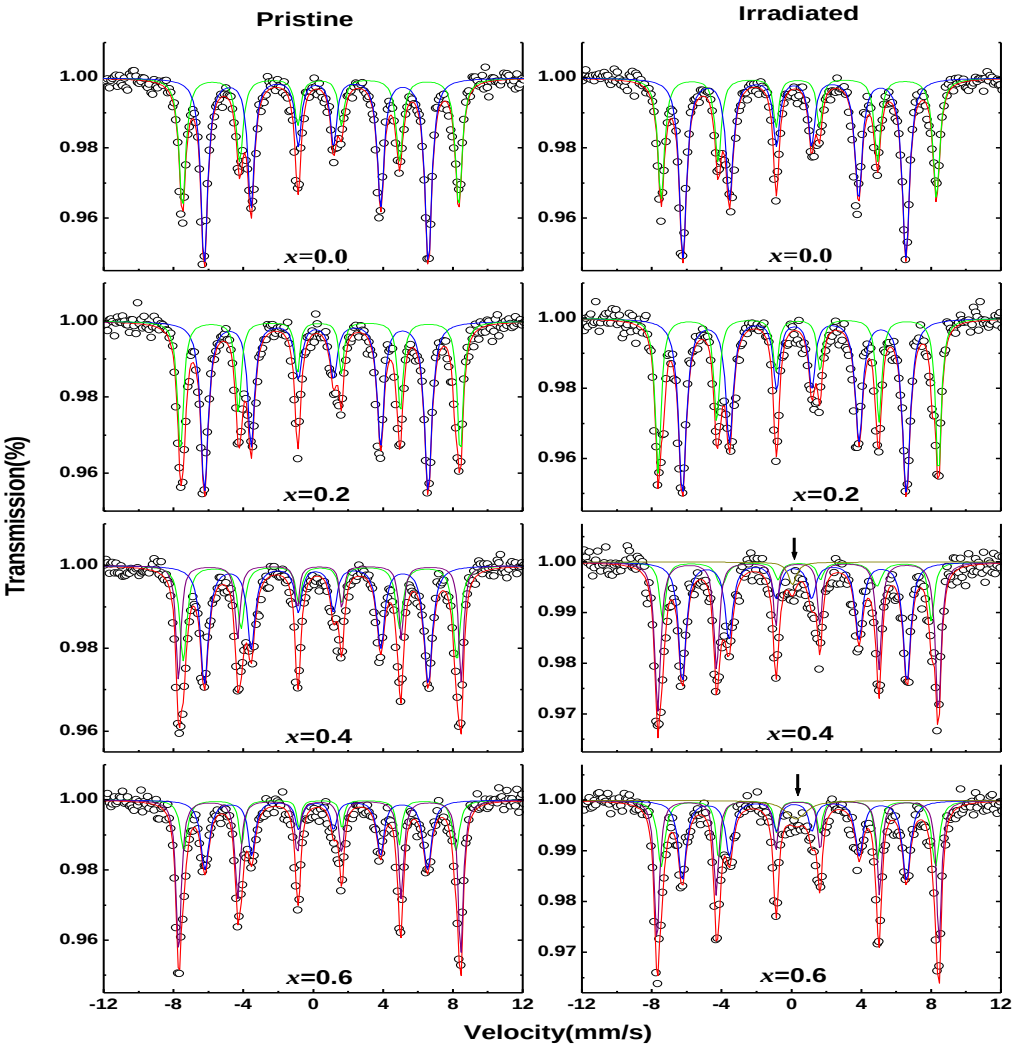

Figure 1. Mossbauer spectra recorded at 300K for x = 0.0, 0.2, 0.4 and 0.6 compositions of $Y_{3+x}Fe_{5-x}O_{12}$ system, before and after irradiation.

inherently stronger than in the a-sites and the substitution of Y^{3+} ions with larger ionic radius will give rise to a microscopic structural distortion of the a- and d-sites to different degrees, even though they belong to a like coordination. The observed small difference in H_f value for the a- and d-sites before and after irradiation suggests a redistribution of cations after irradiation.

It is evident from Table 1, that isomer shift IS(d) and IS of $YFeO_3$ phase IS(Y) values show very little change but IS(a) shows considerable change with Y^{3+}-substitution before irradiation. It is found that IS(d), IS(a) and IS(Y) values change with Y^{3+}-substitution after irradiation, indicating, in general, the s-electron charge distribution is influenced by Y^{3+}-substitution as well as by irradiation. As expected, the value of IS(a) is more positive than IS(d) because of larger Fe^{3+}-O^{2-} bond separation in the former. No quadrupole shifts (QS) for the d-site and $YFeO_3$ phase has been observed (within the experimental error) for magnetically split spectra before irradiation. After irradiation QS for the a- and d-sites as well as QS for $YFeO_3$ phase changes considerably, suggests that the co-existence of chemical disorder and overall cubic symmetry causes net quadrupole shifts in Zeeman sextets as well as contribute to change the width with Y^{3+}-substitution for pristine and irradiated samples. The hyperfine field, isomer shift and quadrupole shift values of the third sextet are in good agreement with those reported by Eibschutz et al. [18] for $YFeO_3$.

It is seen that the area corresponding to $YFeO_3$ phase decreases after the SHII for x = 0.4 and x = 0.6 compositions, accompanied by the evolution of singlet due to induced paramagnetic centers. This explains the transformation of $YFeO_3$ phase into the garnet phase, after irradiation. It is well known that a swift heavy ion on passing through the materials loses its energy by electronic energy loss S_e (inelastic process). This energy is being deposited in the form of electronic excitation or ionization, responsible for generating defect states, in fact, in the present study; S_e not only dissolves the unreacted $YFeO_3$ phase but also participates in modifying the properties of the main system, without any contamination.

It is clear from Table 1 that, Mössbauer parameters of the garnet phase and $YFeO_3$ phase are affected by SHII. The Mössbauer spectroscopic study results reveal that SHII leads to the formation of required garnet phase leaving behind the defected $YFeO_3$ phase. Furthermore, it is interesting to note that when all other parameters of $YFeO_3$ phase remain unaffected by SHII, nuclear hyperfine interaction parameters are highly influenced by SHII.

IV. Conclusions

The central enhancement observed in the Mössbauer spectra of the irradiated samples is not due to amorphization but its origin lies in the formation of localizing paramagnetic centers. The hyperfine interaction parameters of both phases are highly influenced by SHII. The various parameters (except for hyperfine interaction parameters) of $YFeO_3$ phase remain unaffected by SHI-irradiation, suggests $YFeO_3$ is irradiation hard phase as compared to $Y_3Fe_5O_{12}$ phase. This inherent property of $YFeO_3$ may find application in a material suitable for pelletron and other radiation prone environment.

ACKNOWLEDGEMENT

One of the authors (PUS) is thankful to Professors H. C. Verma IIT-Kanpur and Ravi Kumar, IUAC-New Delhi (presently at NIT – Hamirpur, India) for providing the experimental facility of Mossbauer spectroscopy and irradiation study respectively. KBM and PYR are thankful to University Grants Commission, New Delhi, India for providing financial assistance in form of Major Research Project scheme and fellowship respectively.

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