Pre and post effect of swift heavy ion irradiation on infrared spectral evolution of $Y_{3+x}Fe_{5-x}O_{12}$ (*x* = 0.0 – 1.0) system

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ABSTRACT

Present work aims to investigate the effect of Y^{3+} - substitution and 50 MeV, Li^{3+} ion irradiation (fluence: 5 x 10^{13} ions/cm^2) on infrared spectral evolution of $Y_{3+x}Fe_{5-x}O_{12}$ (*x* = 0.0, 0.2 0.4, 0.6, 0.8 and 1.0) garnet system. Infrared absorption spectra for *x* = 0.0 – 0.6 compositions show three absorption bands while *x* = 0.8 – 1.0 compositions are characterized by two absorption bands, identical with IR spectra of rare earth ortho ferrites. The position and intensity of bands are found to be influenced by Y^{3+} - substitution. The intensity of absorption bands for *x* = 0.0 – 0.4 compositions is found to increase, while for *x* = 0.6 – 1.0 compositions no effect of swift heavy ion irradiation has been observed. The results have been explain in the light of SHII induced defect states, partial removal of un-wanted $YFeO_3$ phase and change in structural parameters. It seems that $YFeO_3$ phase is irradiation hard phase.

Keywords: Yttrium iron garnet; Swift heavy ion irradiation; IR spectroscopy

1. INTRODUCTION

The swift heavy ion irradiation (SHII) is considered to produce thermal and pressure-spikes in the irradiated material, consequently, modifications in physical properties of those materials are expected [1]. Yttrium iron garnet (YIG), $Y_3Fe_5O_{12}$, has been found to be a good material for the purpose of irradiation because of its stability, well known magnetic properties and the possibility of finding it in various crystalline forms [2].

On the application of external agencies (SHII, high energy ball milling, etc.) on Y^{3+}-excess YIG, $Y_4Fe_4O_{12}$, formation of the yttrium orthoferrite, $YFeO_3$, phase rather than non-stoichiometric phase is more likely as there is small lattice energy difference between the two phases, YIG and $YFeO_3$ [3].

SHII induced modifications in the microstructure of such materials are studied by means of X-ray diffractometry, scanning and transmission electron microscopy [4-5]. On the other hand, spectroscopy techniques like ^{57}Fe Mossbauer spectroscopy and electron paramagnetic spectroscopy can provide information about the change in local structure

restricted to only Fe ion or paramagnetic species in the irradiated system [1]. However, Raman spectroscopy and Infrared spectroscopy like techniques which are based on stretching and bending vibration modes between cation-anion may throw more light on the irradiated system.

Recent reports show that these techniques have been widely used for studying the irradiation induced effects on various class and different properties of materials [6-8]. Available reports indicate that various vibrational modes exhibit different sensitivity towards irradiation [9-13] but no discussion has been made on possible cause for such modifications [14]. Therefore, we have employed Fourier Transform Infrared spectroscopy (FTIR) as a tool for studying the SHI irradiation induced defects and its effects on Y^{3+}-substituted YIG system, $Y_{3+x}Fe_{5-x}O_{12}$ ($x = 0.0 - 1.0$).

2. EXPERIMENTAL DETAILS

The garnet system, $Y_{3+x}Fe_{5-x}O_{12}$, with variable compositions, $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0, was prepared by the high temperature solid state reaction route. Yttrium oxide (Y_2O_3) and ferric oxide (Fe_2O_3), both 99.9 % pure were procured from E. Merck, Mumbai, India. The oxides were mixed thoroughly in stoichiometric proportions to yield the desired composition and then wet-ground by blending with acetone in an agate mortar and pestle for 4 hours. The mixture was dried and pressed into pellets. These pellets were pre-sintered at 1200 °C for 24 hours. The samples were again powdered, pressed into pellets, sintered at 1500 °C for 24 hours and then slowly furnace cooled to room temperature at the rate of 2 °C / min. The pre sintering and sintering processes were carried out under air atmosphere.

The irradiation experiment was performed in high vacuum chamber with a typical vacuum maintained at 1×10^{-6} mbar. For the present investigation, the bulk samples were irradiated with swift heavy ion, (50 MeV, Li^{3+} ion beam, fluence dose: 5×10^{13} ions/cm^2) by using 15 UD pelletron accelerator at IUAC, New Delhi, India. The garnet material was uniformly spread (thickness of about 20 mg/cm^2) in a aluminum ring of 10 mm diameter on a thin aluminium foil.

The uniform thickness was achieved by mixing powder using liquid GE varnish. Using a magnetic scanner the ion beam was uniformly scanned over the area of 100 mm^2. By measuring the charge falling over the sample surface under the secondary electron suppressed geometry the fluence value was determined.

The samples to be irradiated were mounted on the four sides of the target ladder (on copper block), which were separated from each other by a distance of about 10 mm. The ladder current was measured with the help of current integrator and scalar counter. The electronic energy loss, Se, of 50 MeV Li^{3+} ions in these compounds calculated using the SRIM − 2003 code is found to be 12 eV/Å, which is much less than the threshold energy value, (S_{eth} ~1.2 keV/Å), needed for producing columnar amorphization.

Therefore, it is expected that SHI-irradiation has generated point/cluster of defects.

The samples were characterized for phase formation and structural parameters determination by X-ray powder diffractometry with a Philips, Holland, Expert MPD automated diffractometer, using CuKα radiation (λ = 1.54 Å) graphite monochromator and Xe-filled proportional counter. Data were collected in a 2θ range, 25-80°, at a scan speed of 2°/min at 300 K. Room temperature (300 K) infrared spectra were recorded in the wave

number range 400-800 cm^{-1} using Parkin-Elmer IR spectrometer. For recording IR spectra, powders were mixed with potassium bromite (KBr) in the ratio 1:100 by weight to ensure uniform dispersion in the KBr pellet. The mixed powder was then pressed in a cylindrical dye to obtain clear disc.

3. RESULTS AND DISCUSSION

The detail discussion on influence of Y^{3+} (0.89 Å) ion substitution for Fe^{3+} (0.64 Å) ion and pre and post effect of SHI irradiation by Li^{3+} ion beam (energy: 50 MeV and fluence: 5 x 10^{13} ions/cm^2) on various physical properties of $Y_{3+x}Fe_{5-x}O_{12}$ system can be found in [15-19]. The resultant out comes that help to explain compositional dependence of infrared spectra evolution before and after SHI irradiation are: (a) The un-substituted yttrium iron garnet, $Y_3Fe_5O_{12}$ ($x = 0.0$), and 4 atomic percentage Y^{3+} - excess YIG, $Y_{3.2}Fe_{4.8}O_{12}$, ($x = 0.2$), show single phase *bcc* garnet structure with space group, O^h_{10} Ia3d, the compositions with $x = 0.4$ and 0.6, possess mixed phase characteristics of YIG phase and yttrium orthoferrite, $YFeO_3$ phase (space group: P_{nma}) while $x > 0.6$ compositions are dominated by $YFeO_3$ phase. (b) The un-wanted $YFeO_3$ phase can effectively be suppressed by swift heavy ion irradiation for $x = 0.4$ and 0.6 compositions, while for higher concentration of Y^{3+} -substituted YIG, $x > 0.6$ no such effect has been observed, it seems that $YFeO_3$ phase is irradiation hard phase. (c) The lattice constant value of YIG phase initially increases for 12.380 Å for the $x = 0.0$ to 12.384 Å for the $x = 0.2$ compositions. (c) The lattice constant value suddenly drops from 12.384 Å for the $x = 0.2$ to 12.374 Å for the $x = 0.4$ composition, which suggests incomplete Y^{3+} - substitution in the garnet structure, and thus levels off for higher concentration x, ($x > 0.6$). (d) After irradiation by swift heavy ion, lattice constant value for YIG phase shows random change that suggests non-uniform effect of the irradiation, while lattice parameters of $YFeO_3$ remain uninfluenced by SHI irradiation. Figure 1 shows X-ray powder diffractograms for the two representative compositions, $x = 0.0$ and 0.6 of the system $Y_{3+x} Fe_{5-x}O_{12}$ recorded at 300 K.

Infrared spectroscopy is one of the most powerful analytical techniques, which offers the possibility of chemical identification, vibration modes present for organic and inorganic substances. The technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region. After the absorption of infrared radiations, the molecules of a chemical substance vibrate at many rates of vibrations, giving rise to closed packed absorption bands, called IR absorption spectrum, which may be extended over a wide wavelength range. Various bands present in IR spectrum are corresponding to the characteristics functional group and bonds present in chemical substance.

Infrared (IR) absorption spectra for $Y_{3+x}Fe_{5-x}O_{12}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) system were recorded at 300 K in the wave number range 400-800 cm^{-1} are shown in Fig. 2. No absorption bands were observed above 675 cm^{-1}.

Infrared absorption bands can be associated with atomic motions through the response of applied frequency to chemical substance. A complete band assignment for YIG has been made by Hofmeister and Campbell [20]. The IR spectra for $x = 0.0$ - 0.6 compositions before and after irradiation show three bands and that can be assigned to asymmetric stretching of the tetrahedron in YIG [20]. They are characteristic bands of garnets. IR spectra for $x = 0.8$ and

1.0 compositions are characterized by two absorption bands, identical with IR spectra of rare earth ortho ferrites [21].

The observed shifting of these three characteristic absorption bands towards lower frequency side for $x = 0.2$ composition, as compared to un-substituted YIG, and then towards higher frequency side for $x = 0.4$ composition is consistent with variation of lattice constant value of YIG phase with Y^{3+} concentration (x) in the system. It is known that increase in site radius, as evident by increase in lattice constant value for $x = 0.0$ to 0.2 composition, hinders the fundamental frequency and therefore the centre frequency should shift towards lower frequency side as observed.

The shifting of absorption bands towards higher frequency side for $x = 0.2$ to 0.4 composition may be explain on similar line of argument. With further increase in Y^{3+}-substitution, intensity of absorption bands starts to decrease as well as three distinct bands getting merged in to an absorption band with centre frequency about 567 cm^{-1}. The presence of IR bands about 500 cm^{-1} and 420 cm^{-1} can be attributed to the $YFeO_3$ phase associated to the YIG phase in $x = 0.4$ and 0.6 compositions. The substitution of Y^{3+} ions for Fe^{3+} ions in the system will give rise to a microstructural distortion produced due to coexistence of $YFeO_3$ phase. The Fe-O bond lengths and angle show a variation because of the distortion. The Fe-O bond strength and Fe-O-Fe super-exchange interactions become weak so the intensity of bands decreases with increasing Y^{3+}- content (x) (Fig. 2) in the system.

It is also interesting to note that after irradiation intensity of absorption bands for $x = 0.0$ -0.4 compositions is found to increase, while for $x = 0.6 - 1.0$ compositions no effect of SHI irradiation on intensity has been observed. It is known that SHI- irradiation leads to the creation of a wide variety of defect states in materials. These defects restricts vibration rates of molecules and as a result intensity increases after irradiation for $x = 0.0 - 0.4$ compositions. For $x = 0.4$ composition partial removal of un-wanted $YFeO_3$ after irradiation as evident from X-ray diffraction pattern analysis resulting in reduction of distortion and intensity increases. The compositions with $x = 0.6$, 0.8 and 1.0 are dominated by $YFeO_3$ phase and no effect has been observed on intensity and position of absorption bands.

This may leads to conclude that $YFeO_3$ phase is irradiation hard phase. of electric dipole moment with interatomic distances, and the charge on each ion. It has been shown from infrared reflectivity data of $ZnFe_2O_4$ and $NiFe_2O_4$ that effective ionic charge of Zn, Fe, Ni and O is different from the actual ionic valence, with different magnitude at the A- and B- sites. For example, effective ionic charge of Fe^{3+} is + 2.86 for the A-site and + 2.88 for the B-site in $NiFe_2O_4$ while effective ionic charge of Fe^{3+} increases from +3 to +31.1 for the B-site in $ZnFe_2O_4$. Of course, this ionic charge is always close to the ionic valence of respective ion because of the radial spread of the electron orbital.

Similarly, as discussed earlier [20], atoms are displaced from their mean positions due to swift heavy ion irradiation. Based on the above facts, it is conjectured that for irradiated samples, relative displacement of atoms (d_i) and the effective charge on different ions (q_i) get change in such a way that the magnitude of electric dipole moment ($p_i = q_i d_i$) increases and as a result intensity of absorption band increases. For a thorough understanding infrared reflectivity measurements and Rietveld refinement of X-ray data may be useful.

4. CONCLUSIONS

The Y^{3+} ion substitution in YIG gradually transfer signature of IR spectrum corresponding to yttrium iron garnet phase ($x = 0.0 - 0.2$) – mixed phase ($x = 0.4 - 0.6$) – yttrium ortho ferrite phase ($x = 0.8 - 1.0$). The intensity and position of absorption bands are affected by SHI irradiation for YIG phase dominating compositions ($x = 0.0 - 0.6$), while they remain un-influenced for yttrium ortho ferrite rich compositions, $x = 0.8 - 1.0$. Infrared spectral evolution is in correlation with the results obtained from XRD patterns analysis. It seems that $YFeO_3$ phase is irradiation hard phase and may find application in radiation environment. The observed changes in nature of IR spectra after irradiation may be attributed to the cumulative effect of creation of point defects/vacancies, change in structural and microstructural properties.
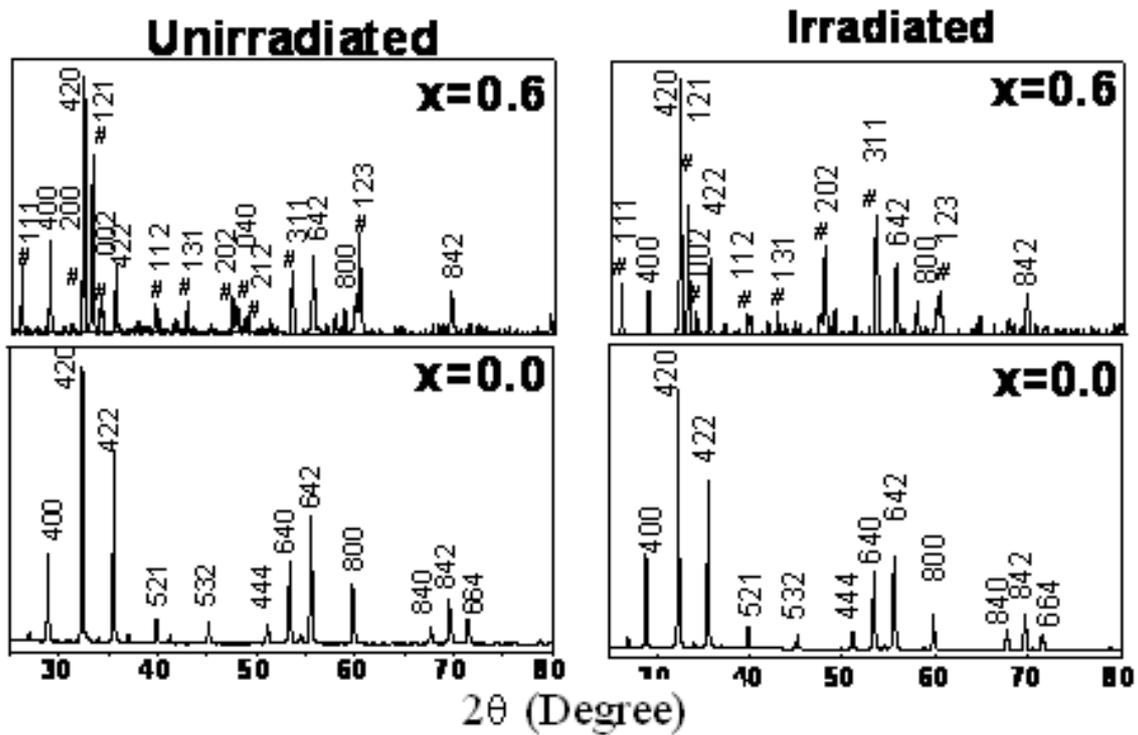

Fig. 1. Room temperature X-ray diffraction patterns for $Y_{3+x}Fe_{5-x}O_{12}$ system with $x = 0.0$ and 0.6, before and after irradiation by swift heavy ion.
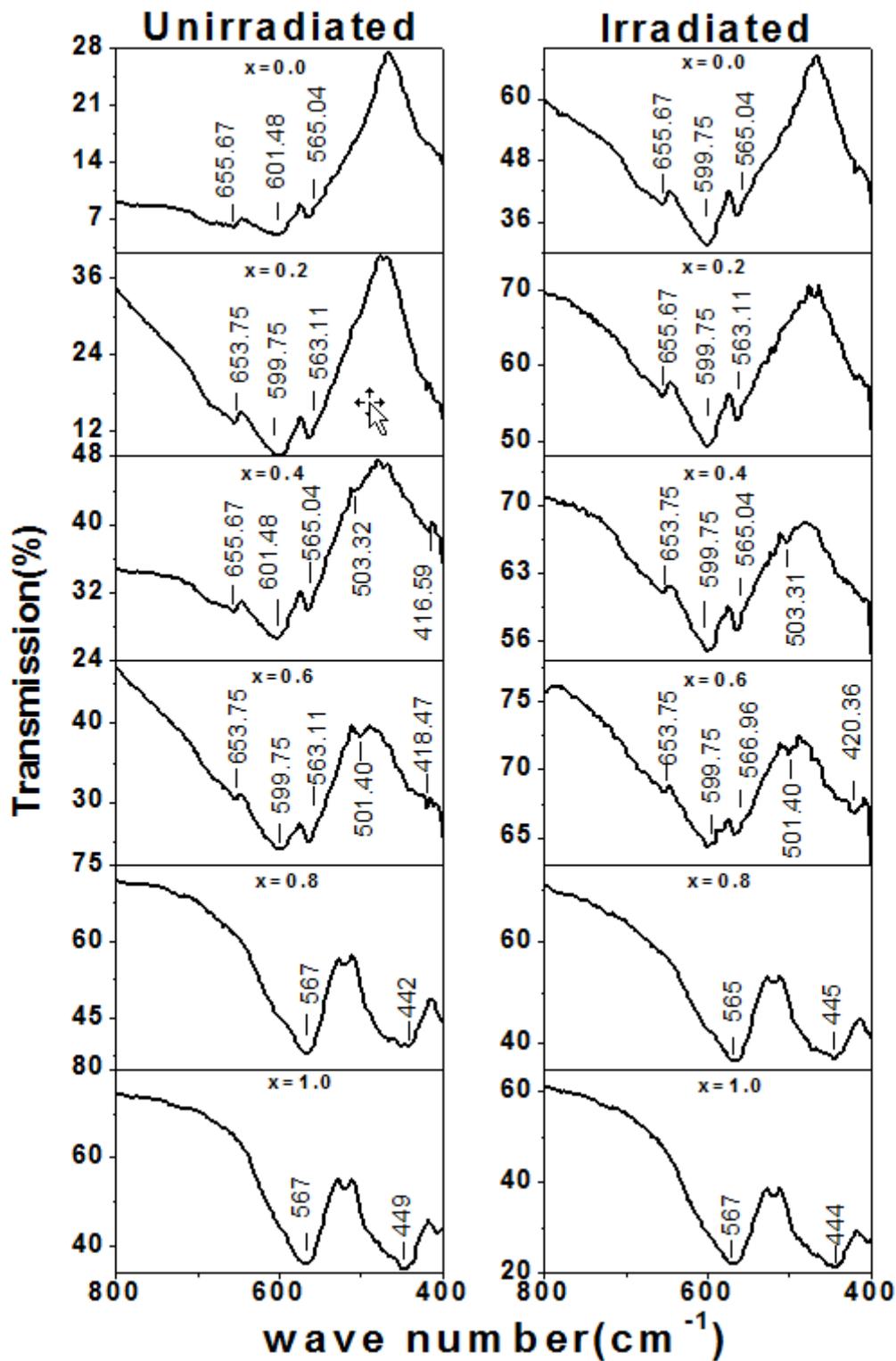
Fig. 2. Infrared spectra for different compositions of $Y_{3+x}Fe_{5-x}O_{12}$ system before and after irradiation at 300 K.

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