Mössbauer Spectroscopy Study on the Effect of Al–Cr Co-Substitution in Yttrium and Yttrium–Gadolinium Iron Garnets

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Abstract. Room-temperature Mössbauer spectra were recorded for two series of Al–Cr co-substituted rare-earth iron garnets: YIG (Y3AlxCrxFe5−2xO12) and Y–GdIG (Y1.5Gd1.5AlxCrxFe5−2xO12). All the spectra were fitted with two magnetic sextets, one sextet corresponds to the (a) octahedral site and the other corresponds to the (d) tetrahedral site. The hyperfine fields for all the samples show a reduction of (∼5 Tesla) per substituted atom with increasing x. The values of the hyperfine fields of the Y–GdIG samples are slightly higher than those of the YIG samples. The relative intensities of the two sextets show that upon substitution, the Al–Cr occupy the (a) site rather than the (d) site. Also, the line widths of the two sextets were found to increase systematically upon substitution, due to the increasing atomic disorder as the Al–Cr contents increase.

Key words: Mössbauer spectroscopy, garnet, hyperfine parameters, substituted YIG.

1. Introduction

Interests in the yttrium and rare earth (RE) iron garnets R3Fe5O12 and substituted garnets continue due to their wide range of applications [1–2]. Systems of aluminum substituted YIG have been studied by many investigators [2–5].

The rare earth (RE) iron garnet (RIG) have the formula unit R3Fe5O12, when the RE ions are paramagnetic, there are three magnetic sublattices, one containing 24 trivalent R3⁺ ions occupying the dodecahedral (c) sites, another containing 16 iron (Fe3⁺) ions occupying the octahedral (a) sites and the third containing 24 iron (Fe3⁺) ions occupying the tetrahedral (d) sites. The magnetic moments are antiferromagnetically coupled because of the superexchange angle.

Muramkar et al. [6] have studied the magnetic and electrical properties of aluminum and chromium co-substituted YIG (Y3AlxCrxFe5−2xO12). They found that the saturation magnetization of these systems decreases linearly with increasing x indicating a reduction in ferrimagnetic behaviour.

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Previously, studies of Al substituted YIG [2, 4], Al substituted RIG [7], and on Al–Cr co-substituted YIG [6] have shown that the Al and Cr ions preferentially occupy the tetrahedral (d) sites.

In this work we use Mössbauer spectroscopy to investigate the hyperfine parameters of the Al–Cr co-substituted YIG and Y–GdIG. This study is conducted in order to obtain more information about the distribution of aluminium and chromium atoms in the various sites of the garnets under investigation. Also, the effects of these substitutions on the hyperfine interactions are investigated.

2. Experimental

Systems of Al–Cr co-substituted YIG (Y₃AlₓCrₓFe₅₋₂ₓO₁₂) and Y–GdIG (Y₁.₅Gd₁.₅AlₓCrₓFe₅₋₂ₓO₁₂) with \( x = 0, 0.2, 0.4 \) and 0.6 were prepared as follows:

The Fe, Y, Gd and Al oxides powders were all from Bayer company (min purity of 99.9%), while Cr oxide powder was from a Hungarian company named Chemo-lab (min purity of 99.9%). The elemental powders weighed in proper ratio to get a homogeneous and wet mixed for 1 hour in acetone. These were then dried in air, the dried powders calcined for 10 hours at 1200°C in air. The calcined powders were milled for 1 hour to get a homogenous submicron powders. The powders were pressed in blocks with 2 tons/cm² using PVA as binder. The blocks were then sintered in oxygen atmosphere for 10 hours. The sintering temperature was 1360°C for the aluminum free samples and the samples with 0.2 mole ratio while for the rest it was 1480°C. The sintered blocks were then crushed in to powders and a final annealing at 700°C for 2 hours was performed to relieve possible strain defects from crushing.

Mössbauer absorber was prepared as a thin layer of the sample powder on a transparent tape. The Mössbauer spectra were collected at room temperature (RT) using a constant acceleration Mössbauer spectrometer with \(^{57}\text{Co/Pd} source. The isomer shifts were measured in mm/s with respect to \(\alpha\)-iron at RT. The spectra were then fitted with Lorentzian lines using fitting routines based on least square analysis.

3. Results and discussion

Mössbauer spectra of the two Al–Cr co-substituted systems, YIG (Y₃AlₓCrₓFe₅₋₂ₓO₁₂) and Y–GdIG (Y₁.₅Gd₁.₅AlₓCrₓFe₅₋₂ₓO₁₂) with \( x = 0, 0.2, 0.4 \) and 0.6, were recorded at RT and plotted in Figure 1. The spectra show a well-defined hyperfine magnetic splitting, each spectrum is fitted with two magnetic sextets with variable width and free line widths ratios. The fitting parameters are listed in Table I. The first magnetic sextet corresponds to iron at the octahedral (a) site while the second sextet corresponds to the iron at tetrahedral (d) site.

The values of the hyperfine magnetic fields and isomer shifts are found to be similar to those reported in other studies [4, 5, 8].
Figure 1. Room-temperature Mössbauer spectra of Al–Cr co-substituted YIG system ($\text{Y}_3\text{Al}_x\text{Cr}_x\text{Fe}_{5-x/2}\text{O}_{12}$ with $x = 0, 0.2, 0.4$ and 0.6) and Al–Cr co-substituted Y–GdIG system ($\text{Y}_{1.5}\text{Gd}_{1.5}\text{Al}_x\text{Cr}_x\text{Fe}_{5-x/2}\text{O}_{12}$ with $x = 0, 0.2, 0.4$ and 0.6).

The data in Table I and Figure 2 show that the values of the hyperfine magnetic field ($B_{hf}$) at the iron nucleus in both (a) and (d) sites of both systems are found to decrease as the Al–Cr contents ($x$) increase. The reduction in $B_{hf}$ is ($\sim$5 Tesla) per substituted atom. This reduction agrees with the reduction in the saturation magnetization of $\text{Y}_3\text{Al}_x\text{Cr}_x\text{Fe}_{5-x/2}\text{O}_{12}$ with increasing $x$ [6].

As seen from Table I, the values of $B_{hf}$ corresponding to both (a) and (d) sites for the YIG system is ($\sim$0.5 Tesla) higher than those for the Y–GdIG. This could
Table I. Mössbauer hyperfine parameters for Al–Cr substituted YIG \((\text{Y}_3\text{Al}_x\text{Cr}_x\text{Fe}_{5-2x}\text{O}_{12})\) and Al–Cr substituted Y–GdIG \((\text{Y}_3\text{Al}_x\text{Cr}_x\text{Fe}_{5-2x}\text{O}_{12})\) with \(x = 0.0, 0.2, 0.4\) and 0.6; \(IS\): isomer shift in mm/s relative to \(\alpha\)-iron, \(B_{hf}\): hyperfine magnetic field in Tesla, \(W\): line width in mm/s and \(I\%\): the relative intensity

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\begin{array}{ccccccccc}
\text{Al–Cr co-substituted YIG} & & & & & & & & \\
(\text{Y}_3\text{Al}_x\text{Cr}_x\text{Fe}_{5-2x}\text{O}_{12}) & & & & & & & & \\
\text{Al–Cr co-substituted Y–GdIG} & & & & & & & & \\
(\text{Y}_{1.5}\text{Gd}_{1.5}\text{Al}_x\text{Cr}_x\text{Fe}_{5-2x}\text{O}_{12}) & & & & & & & & \\
x & 0.0 & 0.2 & 0.4 & 0.6 & 0.0 & 0.2 & 0.4 & 0.6 \\
IS (1) & 0.37 & 0.34 & 0.38 & 0.38 & 0.36 & 0.36 & 0.38 & 0.37 \\
IS (2) & 0.13 & 0.11 & 0.14 & 0.14 & 0.11 & 0.11 & 0.15 & 0.17 \\
B_{hf} (1) & 49.6 & 48.2 & 45.0 & 42.2 & 50.1 & 48.4 & 46.0 & 43.0 \\
B_{hf} (2) & 40.0 & 38.6 & 35.8 & 33.4 & 40.4 & 39.0 & 36.7 & 34.0 \\
W11 & 0.43 & 0.54 & 0.79 & 0.80 & 0.41 & 0.52 & 0.66 & 0.76 \\
W12 & 0.40 & 0.49 & 0.59 & 0.60 & 0.40 & 0.50 & 0.48 & 0.55 \\
W13 & 0.37 & 0.38 & 0.37 & 0.35 & 0.39 & 0.37 & 0.33 & 0.32 \\
W21 & 0.44 & 0.66 & 0.99 & 1.28 & 0.46 & 0.56 & 0.95 & 1.24 \\
W22 & 0.41 & 0.59 & 0.73 & 0.95 & 0.45 & 0.53 & 0.70 & 0.90 \\
W23 & 0.38 & 0.47 & 0.46 & 0.55 & 0.43 & 0.40 & 0.48 & 0.52 \\
I\% (1) & 40 & 37 & 32 & 22 & 40 & 39 & 31 & 22 \\
I\% (2) & 60 & 63 & 68 & 78 & 60 & 61 & 69 & 78 \\
\end{array}
\]

Figure 2. The hyperfine magnetic fields \((B_{hf})\) in Tesla versus the Al–Cr contents \((x)\) for \(\text{Y}_3\text{Al}_x\text{Cr}_x\text{Fe}_{5-2x}\text{O}_{12}\) and \(\text{Y}_{1.5}\text{Gd}_{1.5}\text{Al}_x\text{Cr}_x\text{Fe}_{5-2x}\text{O}_{12}\) with \(x = 0, 0.2, 0.4\) and 0.6. fitted by linear regression lines.
be due to the dipolar effect of the magnetic Gd$^{3+}$ ions having a magnetic moment of $7 \mu_B$.

The rate at which $B_{hf}$ decreases with increasing $x$ for $Y_3Al_xCr_xFe_{5-x}O_{12}$ is faster than that for $Y_3Al_xFe_{5-x}O_{12}$ and is consistent with previously reported results [4]. Also, the estimated rate of decrease in $B_{hf}$ with increasing $x$ for the substituted YIG is found to be slightly larger than that for the substituted Y–GdIG. The relative intensity $I (1)$ of the (a) octahedral site clearly decreases with increasing $x$, as Table I shows. This indicates that the Al and Cr ions prefer to occupy the (a) octahedral sites. This preference is different than that found in previous studies [5–8], where the tetrahedral (d) sites were preferred.

The Mössbauer line widths of the two magnetic sextets are clearly increasing (for both systems) as the Al and Cr contents increase. The widths of the outer (1, 6) lines are shown in Table I. The rate of broadening is higher in the sextet of the tetrahedral (d) sites, which could be explained as a result of local fluctuations of the chemical environments of the iron atoms at these sites arising from the substitution of Al and Cr atoms at the (a) sites. This is further supporting evidence of the preferential occupation of the octahedral (a) sites by the Al and Cr atoms.

4. Conclusion

We conclude from this study that the Al–Cr ions in both garnet systems prefer to replace the Fe ions in the octahedral (a) sites rather than the Fe atoms in the tetrahedral (d) sites. Substituting Al–Cr in the YIG and Y–GdIG systems causes a broadening in the Mössbauer lines of the two iron sites. This broadening is greater in the lines corresponding to the tetrahedral (d) sites. Also, a reduction in the $B_{hf}$ at both sites is observed as the Al–Cr contents increase in both systems.

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