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Mössbauer spectroscopic studies of $Y_{3-x}Gd_xFe_5O_{12}$($x = 0$, 0.5 and 3.0) prepared by an amorphous citrate process

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The system $Y_{3-x}Gd_xFe_5O_{12}$($x = 0$, 0.5 and 3.0) synthesized through an amorphous citrate gel process has been investigated by Mössbauer and EPR spectroscopy. These studies delineate the co-ordination, symmetry, valence and relaxation phenomena which in turn give information on the growth of garnet and other phases in the above system. Furthermore these studies help in finding the optimum growth conditions for the garnet phase.

1. Introduction

In recent years, several methods have been developed to synthesize non-crystalline magnetic oxides [1–7]. Of these, the citrate gel process appears to be suitable for preparing bulk amorphous powder, which on controlled heating provides useful magnetic properties [1, 6–7]. We have recently reported [6, 7] investigations of the system $Y_{3-x}Gd_xFe_5O_{12}$($x = 0$, 0.5 and 3.0) in which the emphasis was on synthesis, magnetic and microstructural studies and transformation behaviour in going from the amorphous to the crystalline state. We present here further detailed studies of the same system using Mössbauer and electron paramagnetic resonance (EPR) spectroscopy. These studies have provided a better understanding of the various phases present and helped us to investigate the effect of heat treatment schedule on the phases present. In addition, it has also helped to find the optimum heat schedule for the growth of the garnet phase.

2. Experimental details

The amorphous $Y_{3-x}Gd_xFe_5O_{12}$ garnet systems ($x = 0.0$, 0.5 and 3.0) were prepared by a citrate gel process as reported by us earlier [6]. The dried precursors were processed through two different heating schedules: (a) the precursor was heated at 400° C for 24 h in an atmosphere of 95% nitrogen and 5% oxygen followed by heating at 400° C for 24 h in air; and (b) the precursor was heated for 400° C for 24 h in air. These two heating schedules will be referred to as N and A, respectively. These samples were further heat treated in air at various temperatures for 4 h as described in Table I. The Mössbauer spectra of these samples were recorded at room temperature with a constant acceleration Mössbauer spectrometer. The source used in these measurements was ^{57}Co (strength 10 mCi) in a rhodium matrix obtained from New England Nuclear Inc, USA. EPR spectra were recorded using Varian Associates Spectrometer (Model V4502-12) in the X-band frequency using 100 kHz modulation.

3. Results and discussion

The results of the present Mössbauer spectroscopic studies are presented in Figs. 1 to 3. The system $Y_{3-x}Gd_xFe_5O_{12}$ is amorphous when heated below 650, 600 and 500° C for $x = 0$, 0.5 and 3.0, respectively [6]. The Mössbauer spectra of the samples heated below the crystallization temperature (see Figs. 1 to 3) consist of quadrupole-split broad peaks characteristic of the paramagnetic and amorphous nature of the samples. The Mössbauer spectra of samples heat treated above the crystallization temperature (see Figs. 1 to 3) consist of magnetically split six-finger patterns. The intensity of the components in the magnetically split spectra increases with higher heat treatment temperature, indicating growth of the magnetic phases. We shall first discuss the system with $x = 0.5$ in detail and follow it with a discussion of the system with $x = 3.0$. For $x = 0$, we have briefly discussed the Mössbauer results in our earlier paper [7].

3.1 $Y_{3-x}Gd_xFe_5O_{12}$ with $x = 0.5$

The samples heat treated below 600° C are amorphous, as indicated by the X-ray diffraction results [6]. The samples heat treated above 600° C show the presence of the garnet phase. Some other phases such as α-Fe_2O_3 and γ-Fe_2O_3 are also present. The volume fraction of garnet phase increases in samples heat treated at higher temperatures. Compared to the heat treatment schedule N, schedule A is observed to be more favourable for the development of the garnet phase.

Mössbauer spectra of $Y_{3-x}Gd_xFe_5O_{12}$($x = 0.5$) precursor samples heat treated at temperatures $T = 400$, 600, 650, 700, and 800° C are shown in Fig. 1 for heat treatment schedule A and in Fig. 2 for schedule N. Mössbauer spectra were analysed and Mössbauer parameters were obtained by conventional least-squares fitting. Electric field gradient (EFG) distributions were calculated using Window's method [8]. These results are summarized in Tables II and III.

Mössbauer spectra of samples heat treated below

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TABLE I Details of the $Y_{3-x}Gd_xFe_5O_{12}$ samples studied

System	Heating schedule A (° C)								Heating schedule N (° C)			
	400	500	550	600	650	700	800	900	600	650	700	800
$x = 0$	YA4	–	–	YA6	YA6.5	YA7	YA8	YA9	YN6	–	YN7	YN8
$x = 0.5$	YGA4	–	–	YGA6	YGA6.5	YGA7	YGA8	–	YGN6	YGN6.5	YGN7	YGN8
$x = 3.0$	GA4	GA5	GA5.5	GA6	GA6.5	GA7	–	–	–	–	–	–

600° C (YGA4, YGA6, YGN6) consist of broad quadrupole-split peaks characteristic of an amorphous paramagnetic nature. The quadrupole splitting $\Delta E = 1.10$, 1.11 and 1.05 mm sec^{-1} obtained for YGA4, YGA6 and YGN6, respectively, by conventional least-squares fitting from the ΔE values obtained by EFG distribution. The observed values of isomer shift (IS) for these samples are intermediate between those for octahedral and tetrahedral co-ordinated Fe^{3+}. This behaviour indicates that both co-ordinations do exist in these samples but are not resolved due to the amorphous nature of the samples. Similar behaviour was also observed in the $x = 0$ system [7].

The Mössbauer spectra of samples heat treated at 650° C for 4 h (YGA6.5 and YGN6.5) consist of two quadrupole-split peaks and magnetically split components, while for the sample heat-treated at 650° C for 40 h (YGN6.5*) only magnetically split components are observed. It is noteworthy that Mössbauer parameters of samples given heat schedule A and N differ substantially. The quadrupole-split component vanishes in samples heat treated above 650° C and two hyperfine-split spectra appear, indicating the onset of magnetic ordering. From IS and H_{int} values the intense hyperfine field (having higher IS values) could be attributed to a combination of α-Fe_2O_3, γ-Fe_2O_3 and the octahedral site of the garnet phase. Since the strengths of the internal magnetic fields for these phases are close, they are not resolved in Mössbauer spectra. The weak six-finger pattern (lower IS values) is due to the tetrahedral site of garnet phase. Hence, the magnetic components are identified as being due to α-Fe_2O_3, γ-Fe_2O_3 and garnet phase. From the area under the resonance a qualitative estimation of the volume fraction of garnet phase in the samples has been made and this agrees with the X-ray data. These results show that heat schedule A and longer heat treatment time is more favourable for the development of garnet phase. The Mössbauer spectra

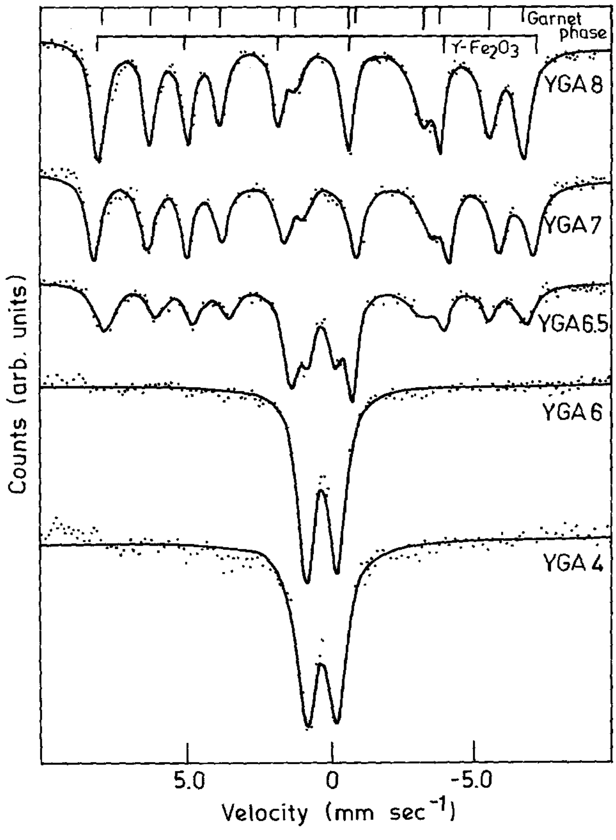

Figure 1 Mössbauer spectra of $Y_{3-x}Gd_xFe_5O_{12}(x = 0.5)$ samples heated as per schedule A. Peak positions observed for the garnet phase and γ-Fe_2O_3 are also shown. See Table I for a description of the labels assigned to the various samples.

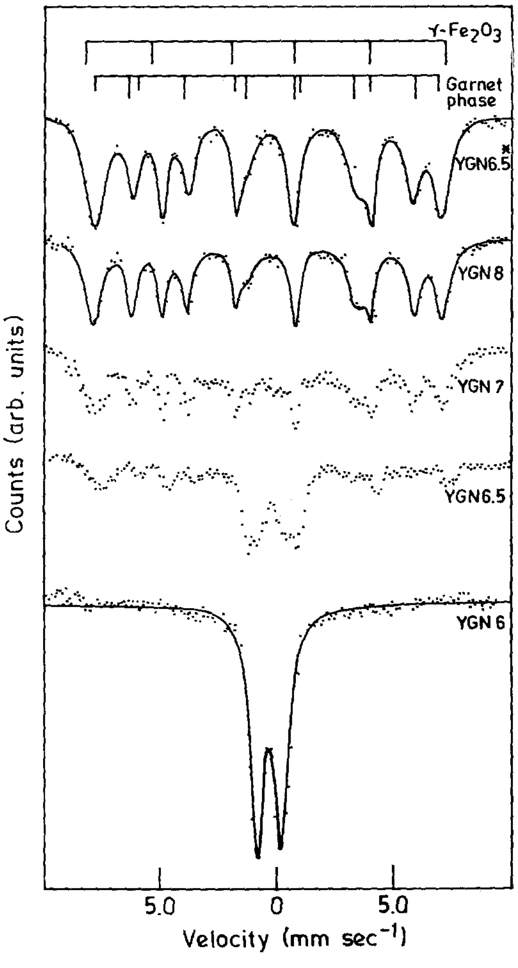

Figure 2 Mössbauer spectra of $Y_{3-x}Gd_xFe_5O_{12}(x = 0.5)$ samples heat treated as per schedule N. Peak positions observed for the garnet phase and γ-Fe_2O_3 are also shown. See Table I for a description of the labels assigned to the various samples.

*Indicates final heating in air for 40 h.

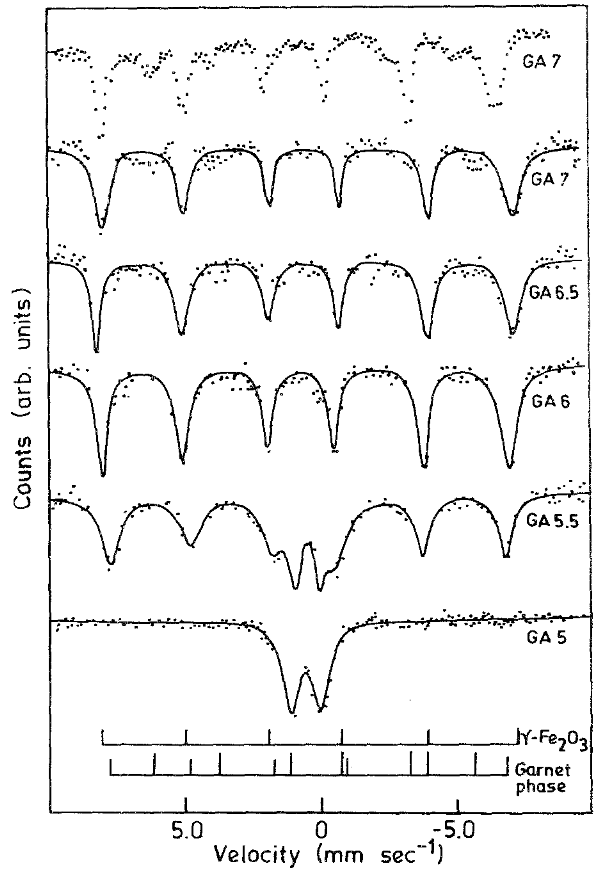

Figure 3 Mössbauer spectra of $Y_{3-x}Gd_xFe_5O_{12}(x = 3.0)$ samples recorded at room temperature. Peak positions observed for polycrystalline YIG and γ-Fe_2O_3 are shown at the bottom. The top most spectra is for GA7 run for a longer period.

of samples heat treated at 700° C (YGA7 and YGN7) and 800° C (YGA8 and YGN8) show only magnetically split components. However, the Mössbauer data show significant changes between heat schedule A and N. The volume fraction of garnet phase is more in samples given heat schedule A compared to samples given schedule N. A similar observation was made from X-ray and magnetic measurements [6]. The maximum volume fraction of garnet phase in samples given heat schedule A was 80%, whereas for heat schedule N it was 45%.

3.2. $Y_{3-x}Gd_xFe_5O_{12}$ with $x = 3.0$

The samples heat treated above 500° C show diffraction lines due to garnet (GdIG), hexagonal (α-Fe_2O_3) and spinel (γ-Fe_2O_3) phases [6]. However the volume fraction of hexagonal α-Fe_2O_3 phase is found to be more than that found for $x = 0.0$ and 0.5 samples. The volume fraction of garnet phase increases with higher heat treatment temperature.

Mössbauer spectra of $Y_{3-x}Gd_xFe_5O_{12}(x = 3.0)$ samples heat treated at temperatures $T = 500$, 550, 600, 650 and 700° C are shown in Fig. 3. The Mössbauer parameters evaluated from these spectra are given in Table IV. The Mössbauer spectrum of GA5 consists of broad (width = 0.8 mm sec^{-1}) quadrupole-split peaks characteristic of the amorphous paramagnetic nature of the sample. The observed isomer shift with respect to α-Fe (0.59 mm sec^{-1}) and quadrupole splitting (E = 1.17 mm sec^{-1}) suggest that Fe^{3+} exists mainly in octahedral co-ordination in GA5 and GA5.5. While GA5.5 shows an additional magnetically split component, the Mössbauer spectra of GA6, GA6.5 and GA7 consist of magnetically split components only. The magnetic component found in GA5.5, GA6, GA6.5 and GA7 is identified as being mainly due to α-Fe_2O_3 and γ-Fe_2O_3. The appearance of the garnet phase is not clear though there is an indication of extra hyperfine spectra appearing. The X-ray data, however, show a considerable amount of garnet phase. The Mössbauer spectra of GA7 were recorded for longer periods to confirm the presence of garnet phase. These spectra have also been included at the top of Fig. 3. The hyperfine spectrum due to the tetrahedral Fe^{3+} of the garnet phase is more clear in this figure and the spectrum due to the octahedral Fe^{3+} of the garnet phase overlaps with the other intense hyperfine spectrum as discussed for the previous sample.

The compensation temperature of GdIG is near room temperature (275 K) [9]. Therefore GdIG remains nearly in its magnetically disordered state at room temperature, which explains the absence of the corresponding hyperfine spectrum.

We have also carried out EPR measurements of these samples to obtain further insight into symmetry and relaxation phenomena of iron ions. Typical EPR spectra of $Y_{3-x}Gd_xFe_5O_{12}(x = 0)$ samples recorded at room temperature (295 K) and at liquid nitrogen temperature (78 K) are shown in Fig. 4. The Landau g-factor and linewidth ΔH for $Y_{3-x}Gd_xFe_5O_{12}$ samples are given in Table V.

TABLE II Mössbauer parameters† of $Y_{3-x}Gd_xFe_5O_{12}(x = 0.5)$ samples given heat treatment as per schedule A

Sample	Quadrupole-split components			Magnetic Zeeman-split components	
	IS* (mm sec^{-1})	Peak width (mm sec^{-1})	ΔE (mm sec^{-1})	IS* (mm sec^{-1})	H_{int} (kOe)
YGA4	0.38(2)	0.85(5)	1.10(3)		
YGA6	0.35(1)	0.70(2)	1.11(4)		
YGA6.5	0.33(2)	0.61(8)	1.02(4)	0.45(2)	471(7)
	0.31(2)	0.56(4)	1.99(2)	0.21(2)	386(9)
YGA7				0.50(8)	472(4)
				0.18(1)	393(5)
YGA8				0.58(1)	472(4)
				0.27(2)	373(4)

*With respect to α-Fe.

†Numbers in parenthesis indicate experimental error.

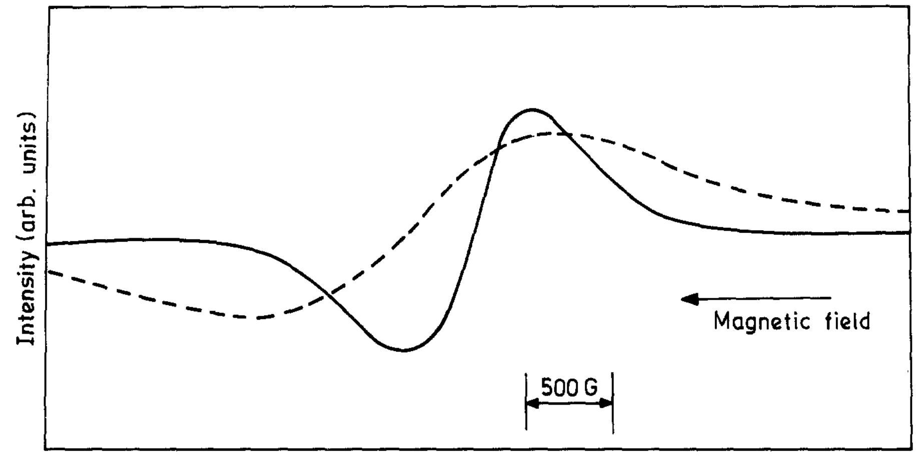

Figure 4 Typical EPR spectra for $Y_{3-x}G$
$Fe_5O_{12}(x = 0)$ sample (YA6) recorded
(——) room temperature (295 K) and (---
liquid nitrogen temperture (78 K).

The EPR spectra of all these samples show only one resonance with **g** values ranging from 2.0 to 2.2 at room temperature. This resonance could either be attributed to Fe^{3+}–Fe^{3+} or Fe^{3+}–O–Fe^{3+} interactions in these samples [10, 11]. It should be mentioned that resonance corresponding to **g** = 4.3 which usually occurs for paramagnetic Fe^{3+} ions [11] is not observed in any of the samples. This behaviour indicates the presence of some superexchange interaction in all the samples. It is observed that linewidths for YA4 and YA6.5 are nearly same. However, a sharp decrease is observed in the case of YA7. The linewidth further decreases for YA8 and YA9 in EPR spectra recorded at room temperature. The decrease in linewidth as a function of heat treatment temperature is indicative of the crystallization of magnetic phases which enhances the superexchange interaction. It is noteworthy that YA4 and YA6.5 are amorphous and they also exhibit large and broad quadrupole splitting. A similar explanation has been given by us for glass–ceramic systems with crystalline YIG phase [4] where we observe a large linewidth for the non-crystalline state. The linewidth decreased sharply for the crystallized samples. Mössbauer and EPR results in garnet delineate the optimum growth conditions for garnet and other phases.

TABLE III Mössbauer parameters of $Y_{3-x}Gd_xFe_5O_{12}(x = 0.5)$ samples given heat treatment as per schedule N

Sample	Quadrupole-split components			Magnetic Zeeman-split components	
	IS† (mm sec^{-1})	Peak width (mm sec^{-1})	ΔE (mm sec^{-1})	IS† (mm sec^{-1})	H_{int} (kOe)
YGN6	0.34(6)	0.71(1)	1.05(6)		
YGN6.5	0.12(4)	0.79(15)	1.12(8)	0.01(2)	477(3)
	0.35(2)	0.68(8)	2.12(5)	0.07(1)	331(3)
YGN6.5*				0.56(5)	475(4)
				0.45(3)	382(3)
YGN7				0.27(2)	476(3)
				0.08(2)	381(5)
YGN8				0.31(2)	478(5)
				0.24(2)	386(6)

*Indicates final heating in air for 40 h.
†With respect to α-Fe.

TABLE IV Mössbauer parameters of $Y_{3-x}Gd_xFe_5O_{12}(x = 3.0)$ samples

Sample	Quadrupole-split components			Magnetic Zeeman-split components		
	IS† (mm sec^{-1})	Peak width (mm sec^{-1})	ΔE (mm sec^{-1})	IS† (mm sec^{-1})	Average peak width (mm sec^{-1})	H_{int} (kOe)
GA5	0.59(3)	0.80(4)	1.17(2)			
GA5.5	0.48(5)	0.48(11)	0.96(5)	0.50(3)	0.88(11)	466(9)
GA6				0.58(3)	0.60(11)	472(4)
GA6.5				0.46	0.57	490(5)
				*	*	*
GA7				0.37	0.54	482(6)
				*	*	*

*Indicates presence of the hyperfine spectra but Mössbauer parameters could not be evaluated due to the very low intensity of the resonance lines.
†With respect to α-Fe.

TABLE V EPR results for $Y_{3-x}Gd_xFe_5O_{12}$ samples at room temperature (295 K)

Sample	ΔH (G)	g
YA4	700	2.08
YA6.5	725	2.09
YA7	550	2.09
YA8	538	2.08
YA9	475	2.08
YGA4	875	2.14
YGA6	725	2.09
YGA6.5	375	2.11
YGA8	363	2.14
GA6.5	475	2.29

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