Magnetic Properties of R-YIG (R = La, Nd, and Gd) Derived by a Sol-gel Method

Young Rang Uhm[1]*, Jae Cheong Lim[1], Sang Mu Choi[1], and Chul Sung Kim[2]

[1]*Radioisotope Research Division, Korea Atomic Energy Research institute (KAERI), Daejeon 34057, Korea*
[2]*Department of nano-electro physics, Kookmin University, Seoul 02707, Korea*

$Y_{3-x}R_xFe_5O_{12}$ (R = La, Nd, and Gd) powder were fabricated using a sol-gel pyrolysis method. Their magnetic properties and crystalline structures were investigated using x-ray diffraction (XRD), a vibrating sample magnetometer (VSM), and Mössbauer Spectrometer. The Mössbauer spectra for the powders were taken at various temperatures ranging from 12 K to Curie temperature (Tc). The isomer shifts indicated that the valence states of Fe ions for the 16(a) and 24(d) sites have a ferric character. The saturation magnetization (Ms) increases from 32 to 34 (emu/g) for the YIG, and Nd-YIG, respectively. However, Ms decreases to 27 (emu/g) at Gd-YIG.

Keywords : sol-gel method, Mössbauer spectroscopy, R-YIG (R = La, Nd, and Gd), garnet structure

1. Introduction

Yttrium iron garnet (YIG) has attracted significant attention as a microwave device material and magneto-optical recording medium [1-3]. YIG belongs to space group O_h^{10} –I_a3_d with the overall symmetry being cubic [3]. The substitution of rare earth (R = La, Nd, and Gd) ions exhibits very similar magnetic properties with Y ions. In a previous study, a single phased garnet can be fabricated below x = 0.75 of La substituted with $Y_{3-x}La_x$-Fe_5O_{12} because of the lager ionic radius of La than that of Y ion [4]. However, a single phased garnet can be formed at x = 1.0 of Nd and Gd substituted to $Y_{3-x}R_xFe_5O_{12}$. Rare earth (R = La, Nd and Gd) ions in a ferrite powder have high magnetization and can be easily substituted with Y in R-YIG. In ferrimagnetic rare earth iron garnet, the magnetic ions are distributed over three crystallographic sites. The ferrimagnetic models of the sub-lattice magnetization M_a (octahedral-16(a)) and M_d (tetrahedral-24(d)) are coupled antiferromagnetically, while the R^+ sub-lattice magnetization M_c (dodecahehedral-24(c)) are parallel at low temperatures [5, 6]. A magnetic coupling between M_a and M_d is antiparallel, when the temperature is going through the crossover point T_0 [5, 6]. The Fe^{3+}(a)-O-Fe^{3+}(d) super-exchange is the strongest interaction and it determine the Curie temperature. The saturation magnetization (M_s), Cure temperature (T_c) and Coercivity (H_c) are very important for practical applications. The small resonance line width decreases as an amount of R ions increases [7].

A number of wet chemical methods have been developed to prepare fine particles [8, 9], one of which is a sol-gel pyrolysis method, which is used to fabricate ultra-fine ferrite powders in our laboratory [10]. The sol-gel pyrolysis method is known as a technique for the low temperature synthesis of ceramics [11-13]. In this article, we substituted the rare earth ions such as Gd^{3+}, Nd^{3+}, and La^{3+} for some non-magnetic ions Y^{3+} in YIG, and prepared $Y_{3-x}R_xFe_5O_{12}$ powders using a sol-gel method. The Gd^{3+} and Nd^{3+} are magnetic heavy rare earth ion, and light rare earth ion, respectively. While La^{3+} is non-magnetic ion. The saturation magnetization was decreased, when the Gd^{3+} ion was doped, and increase after Nd^{3+} and La^{3+} ions were doped [14].

Also, a detail investigation of the bond angle ($\angle$ Fe_a-O-Fe_d) affected by 24(c) site was carried out using Mössbauer spectroscopy. Especially, it is well known that the Gd is used as contrast agent for the magnetic resonance imaging. A. Satter *et al.* reported that $GdY_2Fe_5O_{12}$ could be used as multifunction material for diagnostic and therapeutic purpose [15]. So, we carried out detail analyses of Mössbauer spectra for the Gd-YIG powder, also.

*Corresponding author: Tel: +82-42-868-4835
Fax: +82-42-866-6217, e-mail: uyrang@kaeri.re.kr

2. Experimental Technique

Polycrystalline rare earth substituted YIG powders were prepared using a sol-gel pyrolysis method. Appropriate portions of $R(NO_3)_3 \cdot xH_2O$ (R = La, Nd, and Gd), $Y(NO_3)_3 \cdot 6H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved into ethylene glycol. A small amount of distilled H_2O was added for hydrolysis. The solution was refluxed at 80 °C for 12 hours and dried in vacuum oven at 60 °C. The dried powders were annealed at 1000 °C in air. The information of the magnetic properties of garnet powders was obtained using a VSM, whereas an external field was applied at up to 10 kOe. A Mössbauer spectrometer of the electromechanical type was used in the constant-acceleration mode [16]. A ^{57}Co single-line source in a rhodium matrix was used and low-temperature spectra were obtained using an APD CS-202 duplex closed-cycled refrigeration system with a DMX-20 Mössbauer vacuum shroud interface [17]. The magnetization curves were measured by a vibrating sample magnetometer (VSM).

3. Results and Discussion

X-ray diffraction patterns of R–doped YIG (R = $La_{0.75}$, Nd_1, and Gd_1) show that rare earth substituted garnet has only a single phase of the garnet structure. Figure 1(a) shows that the R-YIG powders anneals at up to 1,000 °C 3 hours. The unit cell parameter (a_0) shows a constant value from 12.380, 12.405, and 12.472 Å for pure YIG, Gd-YIG, and Nd-YIG, respectively. The lattice parameter is increased as the ionic radius of the substituted R ions in to Y becomes large in R-YIG. The ionic radii are 0.892, 0.938, 1.01, and 1.14 Å for Y^{3+}, Gd^{3+}, Nd^{3+}, and La^{3+}, respectively. Figure 1(b) shows SEM micrographs of $Y_3Fe_5O_{12}$, $Nd_1Y_2Fe_5O_{12}$, and $La_{0.75}Y_{2.25}Fe_5O_{12}$. The submicron sized particles were observed. The spherical shaped and agglomerated particles due to annealing were measured.

The saturation magnetization (M_s) is dependent on the
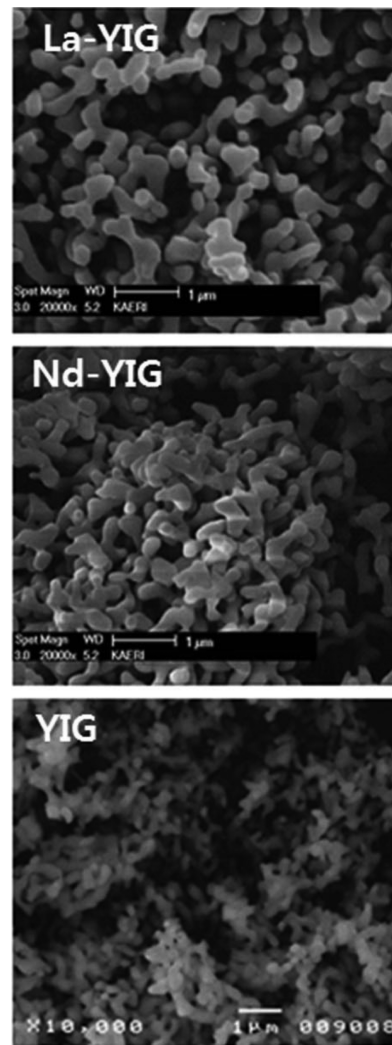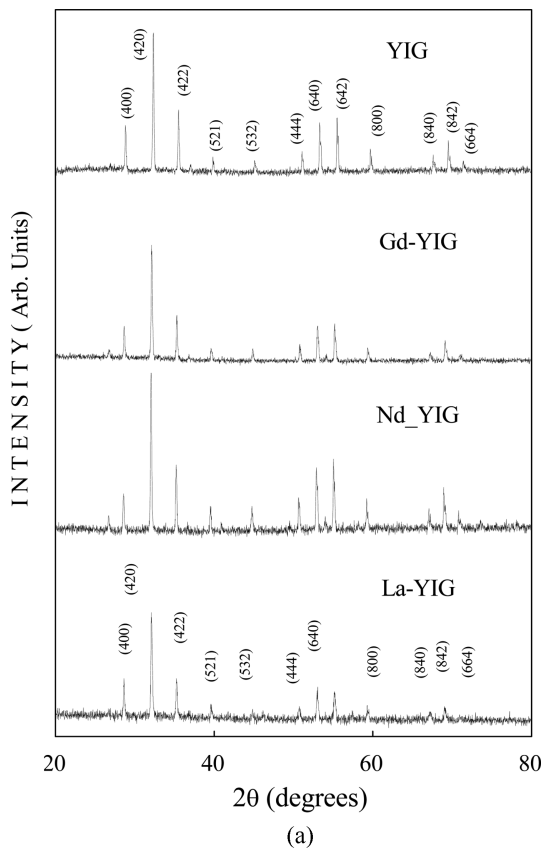
**Fig. 1.** (a) X-ray diffraction patterns of $Y_3Fe_5O_{12}$, $NdY_2Fe_5O_{12}$, and $GdY_2Fe_5O_{12}$, $NdY_2Fe_5O_{12}$, and $La_{0.75}Y_{2.25}Fe_5O_{12}$. (b) SEM images for $La_{0.75}Y_{2.25}Fe_5O_{12}$, $NdY_2Fe_5O_{12}$, and $Y_3Fe_5O_{12}$.

Table 1. Lattice parameter (a_0), magnetization (M_s), and coercivity (H_c) at room temperature for YIG, Gd-YIG, Nd-YIG, and La-YIG.

	a_0 (Å)	VSM (Powder)	
		M_s (emu/g)	H_c (Oe)
$Y_3Fe_5O_{12}$	12.380	32	54
$Gd_1Y_2Fe_5O_{12}$	12.405	27	70
$Nd_1Y_2Fe_5O_{12}$	12.472	34	78
$La_{0.75}Y_{2.25}Fe_5O_{12}$	12.432	22	58

magnetic structure of rare earth materials. Table 1 shows M_s and H_c for powders at room temperature measured by VSM. The saturation magnetization was decreased, as Gd^{3+} ion was doped, and increase when Nd^{3+} and La^{3+} ions were substituted in YIG. In YIG, both 16(a) and 24(d) sub-sites are occupied by ferric ions and the 24(c) cavities are occupied for Y^{3+}. In this study, Nd^{3+} and Gd^{3+} are replaced into Y^{3+} in 24(c) site. Y^{3+} ion is a non-magnetic. It is known that Y^{3+} cation consists of inert krypton core with the 4p (no f-electron) layer fully filled with six electrons of paired spin. So, it has no permanent magnetic moment (0 μ_B). However, both Nd^{3+} and Gd^{3+} ions have a magnetic moment. A magnetic moment of Gd^{3+} ions in $Gd_1Y_2Fe_5O_{12}$ is 7.94 μ_B. The 24(c) sub-site is occupied antiferromagnetically with the two irons in the sub lattices. At room temperature, the three sub-lattices are aligned along the [111] direction [15]. Therefore, the net magnetic moment is 2.94 μ_B as following equation of M = Mc-|Md-Ma|. A magnetic moment of Nd^{3+} ions in $Nd_1Y_2Fe_5O_{12}$ is 3.62 μ_B. So, the net magnetic moment is 1.62 μ_B. The magnetic moments of R^{3+} ions align oppositely as the effective moments formed by Fe^{3+} ions. The H_c is increased as rare earth materials with a large ionic radius are substituted in garnet. The maximum M_s and H_c for the Nd-YIG powders with an applied field of up to 10 kOe are 34 emu/g, and 78 Oe, respectively. The M_s decreases to 27 emu/g, as the heavy rare earth ion of Gd is replaced into YIG. In YIG, both 16(a) and 24(d) sub-sites are occupied by ferric ions and the 24(c) cavities are occupied for Y^{3+}. It is well known that the La^{3+} ion is non-magnetic
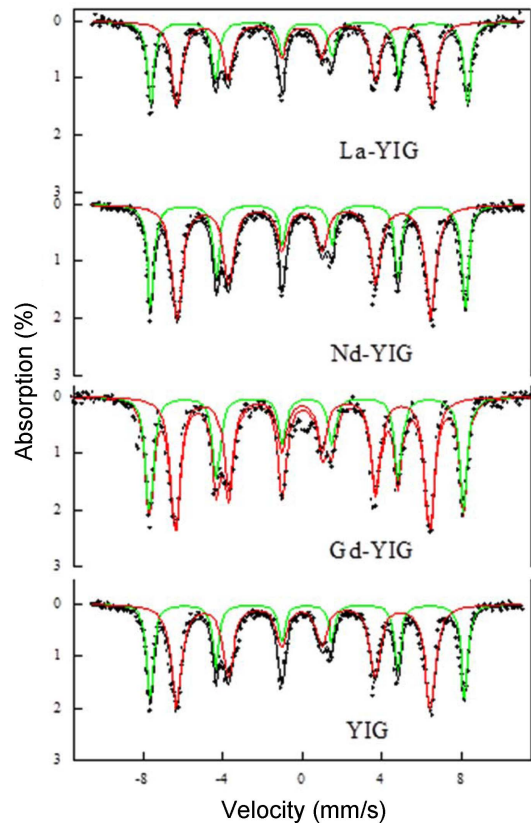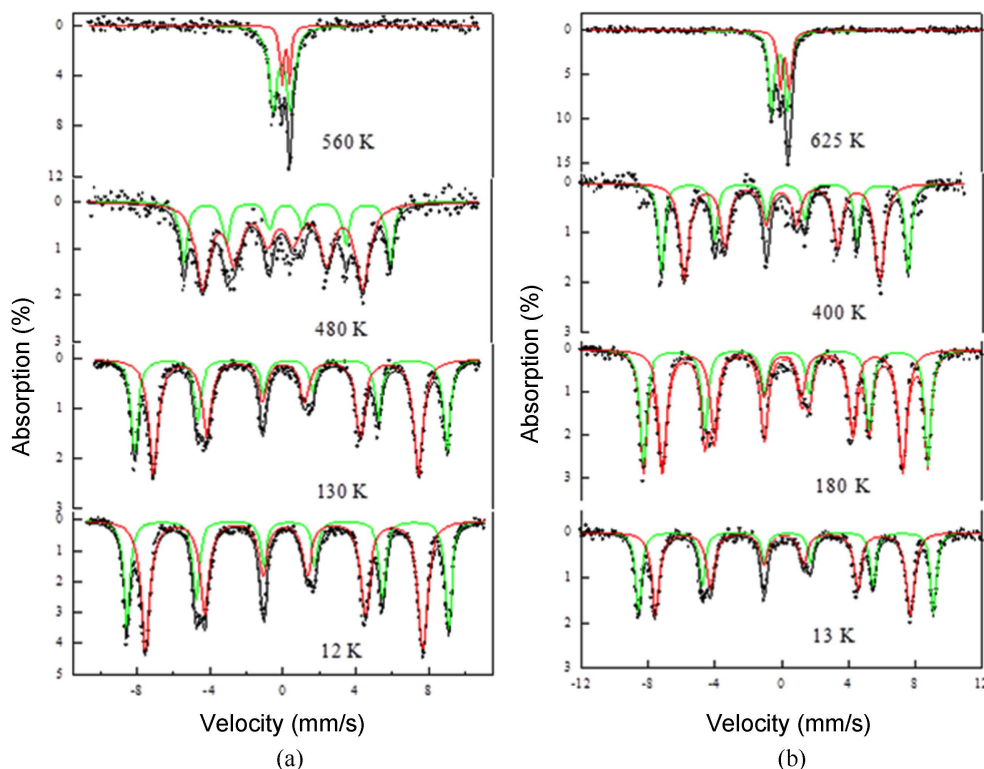

Fig. 2. (Color online) Mössbauer spectra for YIG, Gd-YIG, and Nd-YIG measured at room temperature.

same as Y^{3+} ion. However, the results of magnetic property show that the Ms is decreased. This is because the substitution of La^{3+} affects to a distortion of the 16(a) and 24(d) site to different degrees, and the length and angle of the Fe-O-Fe linkage are changed.

Figure 2 shows the Mössbauer absorption spectra for $Y_3Fe_5O_{12}$, $Gd_1Y_2Fe_5O_{12}$, $Nd_1Y_2Fe_5O_{12}$, and $La_{0.75}Y_{2.25}Fe_5O_{12}$ measured at room temperature. Table 2 shows Curie temperatures (T_C), magnetic hyperfine fields (H_{hf}), quadrupole splittings (ΔE_Q), and isomer shifts (δ) at room temperature for YIG, Gd-YIG, Nd-YIG, and La-YIG powders. The values of magnetic hyperfine fields for YIG, Gd-YIG, Nd-YIG and La-YIG are almost same, because Mössbauer

Table 2. Curie temperature (T_C), magnetic hyperfine field (H_{hf}), quadrupole splitting (ΔE_Q), and isomer shifts (δ) for YIG, Gd-YIG, Nd-YIG, and La-YIG powders measured at 293 K.

	T_C (K)	H_{hf} (kOe)		ΔE_Q (mm/s)		δ (mm/s)	
		16(a)	24(d)	16(a)	24(d)	16(a)	24(d)
YIG	560	491	398	0.04	0.01	0.28	0.05
Gd-YIG	575	490	397	−0.02	0.008	0.24	0.01
Nd-YIG	600	491	397	−0.03	0.00	0.25	0.03
La-YIG	625	490	397	−0.04	−0.02	0.30	0.02

Fig. 3. (Color online) (a) Mössbauer spectra for YIG from 12 K to Curie temperature, and (b) Mössbauer spectra for La-YIG from 13 K to Curie temperature.

absorption spectra reveal mainly iron states in garnet structure, though rare earth ions such as Nd^{3+}, Gd^{3+} in 24(c) site is anti-ferromagnetically coupled with Fe^{3+} in 16(a) and 24(d) sites. However, the values of quadrupole splitting are slightly affected by net magnetic moment, because this value includes symmetry of subsite. This implies that the bond angle ($\angle Fe_a$-O-Fe_d) is changed as the 24(c) site is substituted to rare-earth ions with large ionic radius.

Figure 3 shows Mössbauer spectra for YIG and La-YIG measured from 12 K to Curie temperature. The Curie temperatures are increased from 560 to 625 K, as the rare earth ions with a large radius are substituted. The absorption ratio for 16(a) versus 24(d) site is almost same as 2:3. This value is same as number of ferric ions

occupied in sub-sites. The magnetic hyperfine fields (H_{hf}) are slightly decreased as rare earth materials are substituted to R-YIG. At low temperature, heavy rare earth ion of Gd^{3+} doped YIG show the lowest values of H_{hf}. The two irons in sub-lattice are anti-ferromagnetically coupled by the super-exchange interaction acting via the intervening O^{2-} ions. The 24(c) sub-lattice is coupled anti-ferromagnetically with 24(d)-site. At low temperature, super-exchange link, Fe_a-O-Fe_d, is weaken due to Gd^{3+} ions in 24(c)-site. The magnetic ion in 24(c) –site is strongly coupled with 24(d) site at low temperature. So, the exchange interaction between 16(a) and 24(d) –site is weak at low temperature.

Basically, the value of ΔE_Q shows almost same at measuring temperature from 4.2 K (at liquid He temper-

Table 3. Measuring temperature (T), Magnetic hyperfine field (H_{hf}), quadrupole splitting (ΔE_Q), and isomer shifts (δ) for YIG, Gd-YIG, Nd-YIG, and La-YIG powders measured at and below 13 K.

	T (K)	H_{hf} (kOe)		ΔE_Q (mm/s)		δ (mm/s)	
		16(a)	24(d)	16(a)	24(d)	16(a)	24(d)
YIG	12	553	475	0.04	0.01	0.40	0.2
Gd-YIG	13	549	474	0.007	−0.04	0.32	0.1
Nd-YIG	13	555	478	−0.03	0.00	0.32	0.1
La-YIG	13	550	473	−0.05	−0.03	0.31	0.1
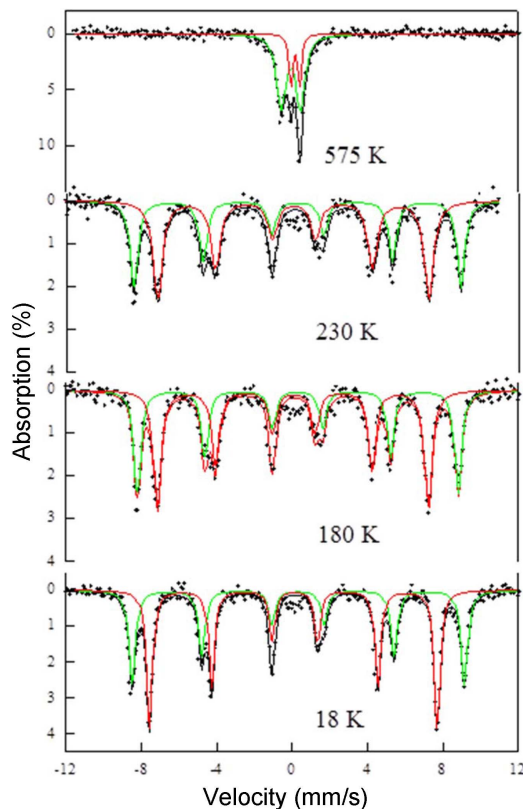
Fig. 4. (Color online) Mössbauer spectra for Gd-YIG measured from 13 K to Curie temperature.

ature) to Curie temperature in Mössbauer spectra, unless a distortion of sub-site is changed. The absolute value of ΔE_Q measured at 13 K for 16(a)-site in Gd-YIG is slightly decreased, whereas, those for 24(d) site is increased. As the measuring temperature is increased, the values of ΔE_Q s are recovery. The Gd-YIG powder with size of nanometer scale was prepared using sol-gel method. Recently, Neel's relaxation at submicron sized Gd-YIG was reported [15]. The different distribution of the surface atoms on the powder affect to quadrupole splitting at and below 13 K. It easily disappeared as increasing measuring temperature [18]. The spin rotation relative with particle size may affect to quadrupole splitting [19].

4. Conclusion

The crystallographic and magnetic properties of single phase garnet $Y_{3-x}R_xFe_5O_{12}$ (R = La, Nd, and Gd) were studied using x-ray diffraction, Mössbauer spectroscopy, and vibrating sample magnetometer (VSM). The lattice constants increase when substituting rare earth ions of Nd and Gd in YIG. The Curie temperature was slightly increased when substituting rare earth ions such as Gd, Nd and La, with a relatively larger ionic radius than those

of Y. The ionic radius doped in 24(c) site have a more immediate and vital influence on the magnetization, though super-exchange interaction between 16(a) and 24(d) site is weaken due to heavy rare earth Gd^{3+} ions substituted in 24(c) site.

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