

Study of the Cation Distribution of $Y_3Fe_{5-x}M_xO_{12}$ (M=Al and Cr, $x=0.25$ and 0.75) Using Mössbauer Spectroscopy

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Al^{3+} and Cr^{3+} -substituted garnet $Y_3Fe_{5-x}M_xO_{12}$ (M=Al and Cr, $x = 0.5$ and 1.0) was prepared using a sol-gel method. Mössbauer spectra of $Y_3Fe_{5-x}M_xO_{12}$ were taken at various absorber temperatures ranging from 12 to 700 K. As the temperature increased up to Néel temperature, a line broadening of the Mössbauer spectra was observed. Al ions prefer to occupy tetrahedral-sites. The octahedral occupied Fe^{3+} ions are linked to six tetrahedral sites containing a statistical distribution of Fe^{3+} and Al^{3+} ions. In this way, seven nonequivalent octahedral sites are expected. The probability for a Fe^{3+} ion with n nearest-neighbor sites occupied by Fe ions becomes $P(n,y) = {}_6C_n y^n (1-y)^{6-n}$, where y is the iron concentration in tetrahedral (T_d) site. On the contrary, Cr ions prefer to occupy octahedral-sites. So, five nonequivalent tetrahedral sites are expected. It results from the distribution (${}_4C_n$) of Fe^{3+} and Cr^{3+} at octahedral site.

Keywords : Al- and Cr doped YIG, cation distribution, and Mössbauer spectroscopy

$Y_3Fe_{5-x}M_xO_{12}$ (M=Al, Cr, $x = 0.25, 0.75$)의 뫼스바우어분광학을 이용한 양이온 분포 연구

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Al^{3+} 와 Cr^{3+} 이온이 치환된 가넷 $Y_3Fe_{5-x}M_xO_{12}$ (M=Al과 Cr, $x = 0.5, 1.0$)는 sol-gel 법으로 제조되었다. $Y_3Fe_{5-x}M_xO_{12}$ 의 Mössbauer 스펙트럼은 12~700 K의 다양한 온도에서 측정되었다. 측정 온도가 Néel 온도에 이르면 뫼스바우어 스펙트럼의 선폭이 넓어지는 것을 확인할 수 있다. Al 이온들은 사면체를 점유하는 것을 선호한다. 이 경우, 팔면체를 점유하고 있는 Fe^{3+} 이온은 Fe^{3+} 와 Al^{3+} 이온이 확률적으로 분포할 수 있는 6개의 사면체 부격자와 이웃하게 된다. 이 경우 팔면체는 사면체의 7가지 경우의 상호작용이 가능하다. Fe 이온에 의해 점유된 n 개의 가장 가깝게 이웃할 수 있는 Fe^{3+} 이온이 분포할 확률은 $P(n,y) = {}_6C_n y^n (1-y)^{6-n}$ 이 되며 여기서 y 는 사면체(T_d) 부격자의 철의 분포로 볼 수 있다. 반대로, Cr 이온은 팔면체를 점유하는 것을 선호한다. 그래서 이웃하는 사면체 부격자는 5종류의 이온분포를 보일 수 있다. 팔면체 내의 Fe^{3+} 와 Cr^{3+} 의 분포는 ${}_4C_n$ 이다.

주제어 : Al-과 Cr- 치환 YIG, 양이온분포, 뫼스바우어분광학

I. Introduction

Yttrium iron garnet (YIG, Y₃Fe₅O₁₂) is versatile materials for a microwave device application and magneto-optical recording media [1-3]. YIG belongs to space group O_h¹⁰-I_a3_d with the overall symmetry being cubic [3]. YIG filters with low loss, wideband tuning and excellent linearity characteristics make them ideal for commercial test equipment applications for several decades. In YIG, iron trivalent ions are positioned in both octahedral (16a) and tetrahedral (24d) sites [1]. The strongest magnetic interactions are the inter-lattice exchange between the Fe³⁺ ions in a and d sub-sites [2], although the intra-sublattice exchange interaction (a-a and d-d) can also be important. Exchange integrals, J_{a-d}; J_{a-a} and J_{d-d}; of super-exchange interaction in the garnet-related compound of composition Y₃Fe_{4.75}M_{0.25}O₁₂ (M=Al and Cr) were reported using ⁵⁷Fe- Mössbauer spectroscopy [3-5]. However, the substitution of Al and Cr at Fe site leads to negative properties such as decreasing both saturation magnetization (Ms) and dielectric constant. Recently, significantly enhanced both the dielectric constant and the Ms are reported in nano-sized Cr- doped YIG due to hoping of charge carrier across Fe²⁺-Fe³⁺ center [4]. To analyze electron hoping between sub-sites, the cations distribution depending on particle size from few nanometers to micrometers should be clarified. Also, the valence state of irons should be confirmed using ⁵⁷Fe- Mössbauer spectroscopy. In this study, the cations distribution in Cr-doped YIG and Al- substituted YIG with submicron particle size was analyzed using ⁵⁷Fe- Mössbauer spectroscopy.

II. Theory

The Cr ion prefers to occupy 16a sites. Each octahedral Fe is linked through oxygen to six tetrahedral coordinated Fe such that all the octahedral sites have identical environments. However, the tetrahedral coordinated Fe ions are connected to four octahedral sites with a statistical distribution of Fe and Cr ions. In this way, five non-equivalent tetrahedral sites are required, relevant to the configurations of neighboring octahedral such as 4Fe³⁺, 3Fe³⁺+1Cr³⁺, 2Fe³⁺+2Cr³⁺, 1Fe³⁺+4Fe³⁺ and 4Cr³⁺. The probability for a Fe ion with nearest-neighbor sites occupied by Fe ions was calculated using the binomial formula, $P(n,y) = {}_4C_n y^n (1-y)^{4-n}$, where y is the iron concentration in a-site [6]. In contrast to, the aluminum ions in the elements of the Y₃Fe_{5-x}Al_xO₁₂ are occupied at tetrahedral sites. The Mössbauer spectra can be fitted using from 3 to 6 sets of six Lorentzians with an increasing

Table I. The results of binominal formulas of $P(n, y) = N_{(n)} y^n (1-y)^{6-n}$ and $P(n, y) = N_{(n)} y^n (1-y)^{4-n}$ for Y₃Fe_{5-x}Al_xO₁₂ and Y₃Fe_{5-x}Cr_xO₁₂, respectively. The n means number of iron ions. The y is concentration of iron in sublattice (Doping ratio: x = 0.25 and 0.75).

	n	N(n)	x = 0.25	x = 0.75
Al-YIG	0	1	0.000	0.000
	1	6	0.000	0.004
	2	15	0.001	0.033
	3	20	0.009	0.132
	4	15	0.073	0.297
	5	6	0.318	0.356
Cr-YIG	6	1	0.593	0.178
	0	1	0.000	0.020
	1	4	0.007	0.132
	2	6	0.071	0.330
	3	4	0.335	0.366
	4	1	0.586	0.152

Al³⁺ ions in these garnet compounds. This results from the distribution ₆C_n of Fe³⁺ and Al³⁺ at tetrahedral site. the probability for a Fe³⁺ ion with n nearest-neighbor sub-sites filled with Fe ions is $P(n, y) = N_{(n)} y^n (1-y)^{6-n}$ where y is the amount of irons in d site. The strongest magnetic interactions are the inter-lattice exchange between the Fe ions in the and sublattices, although the intra-sublattice exchange interaction can also be important. The results of binominal formulas of P(n,y) are listed in Table I.

III. Experimental

Compounds of composition Y₃Fe_{5-x}M_xO₁₂ (M=Al, and Cr, x = 0.0, 0.25, and 0.75) were prepared by a sol-gel method. Weighed amounts of Y(NO₃)₃·5H₂O, Cr(NO₃)₃·5H₂O, Al(NO₃)₃·6H₂O, and Fe(NO₃)₃·9H₂O are dissolved in ethylene glycol, firstly. The solution is refluxed at 70 °C for 6 h to change gel formation and then dried at 250 °C for 24 h. The dried powder is milled using a mortar and annealed at temperature 900 °C for 6 h in air. These compositions of samples fired were identified from X-Ray diffraction with CuK radiation. Magnetizations were measured with a vibrating sample magnetometer (VSM). Mössbauer spectra were recorded at temperatures ranging from 14 K to room temperature using a helium closed-cycle cryogenic system. A constant acceleration mode of Mössbauer spectrometer using a sealed source of ⁵⁷Co in Rh matrix is used for data collection [7].

IV. Results and Discussion

Single phases of cubic spinel structure were measured

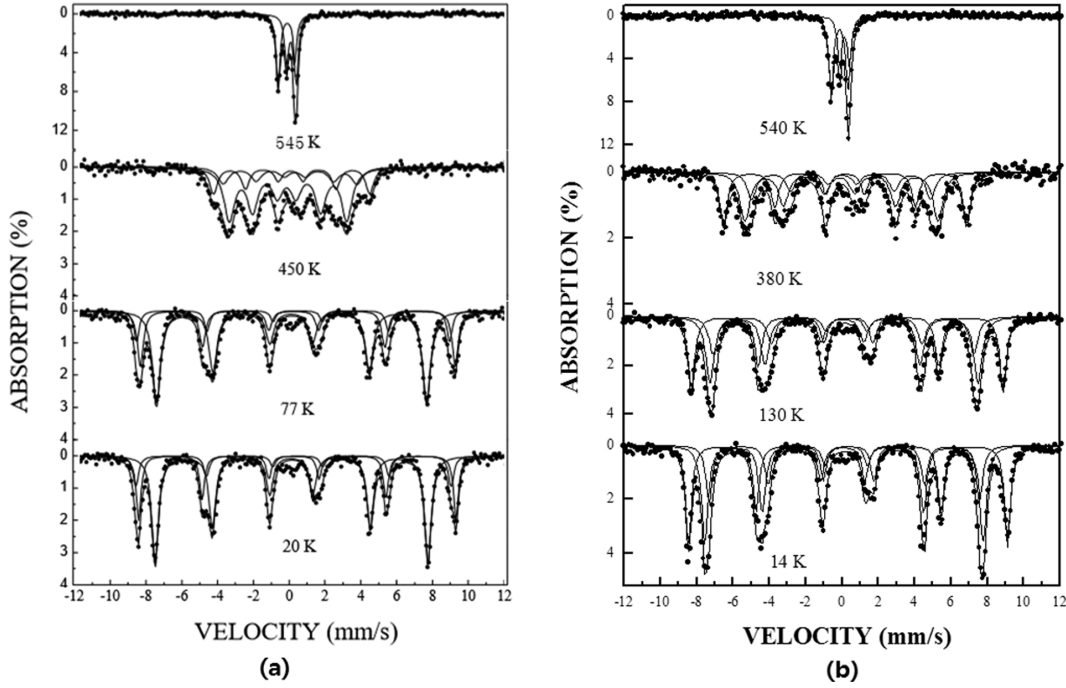


Fig. 1. Mössbauer spectra of $Y_3Fe_{4.75}M_{0.25}O_{12}$ ($M=Al$ and Cr) measured from 14 K to the Curie temperature.

in both Cr- and Al- doped YIG using X-ray diffraction. The determined lattice constants of $Y_3Fe_{5-x}Al_xO_{12}$ have shown decreasing tendency, which decreases linearly from 12.381 to 12.323 Å, with increasing Al ratio from $x=0.0$ to 0.75. These results are well matched to Vegard's law. Since ionic radius of Al^{3+} is 0.5 Å, while that of Fe^{3+} is 0.61 Å. The lattice constants of $Y_3Fe_{5-x}Cr_xO_{12}$ were decreased linearly from 12.381 to 12.357 Å, with increasing Cr concentration from $x=0.0$ to 0.75.

Fig. 1 shows Mössbauer spectra for $Y_3Fe_{4.75}M_{0.25}O_{12}$ ($M=Cr$ and Al) at and below the Curie temperature. All spectra were fitted as one sextet for 16a site and two sextets for 24d site. The nonmagnetic Y^{3+} ion occupy dodecahedral (24c) site only. It means that Heisenberg Hamiltonian and molecular fields can be considered at 16a and 24d site. The magnetic hyperfine fields for the 16a and 24d sites are slowly reduced as a function of the decreasing temperature $t = T/T_c$.

In the Néel theory of ferrimagnetism, the temperature dependence of the magnetic moment per mole of each sublattice [9] may be expressed in terms of Brillouin functions as eq. (1)

$$\begin{aligned} M_a(T) &= M_a(0)B_{S_a}(x_a), \\ M_d(T) &= M_d(0)B_{S_d}(x_d), \end{aligned} \quad (1)$$

in which the subscript a and d refer to the a and the d sublattices these sublattices containing Fe^{3+} as a the magnetic ion, where

$$\begin{aligned} x_a &= (S_a g m_B / k_B T)(N_{a-d} M_d(T) + N_{a-a} M_a(T)), \\ x_d &= (S_d g m_B / k_B T)(N_{d-d} M_d(T) + N_{d-a} M_a(T)), \end{aligned} \quad (2)$$

In these equations N_{a-d} , $N_{d-a} = N_{a-d}$, and N_{d-d} are the molecular-field coefficients, S_a and S_d are the spin quantum numbers, g is the spectroscopic splitting factor, m_B is the Bohr magneton, and k_B is the Boltzmann constant ($= 1.3807 \times 10^{-23}$ J/K). Here, the molecular-field coefficients can be represented as $N_{ik} = (2Z_{ik}J_{ik}) / (n_k g_i g_k \mu_B^2)$, where Z_{ik} is the number of nearest neighbors, n_k is the number of ions per mole in the k th sublattice, J_{ik} is the exchange integral ($J_{a-d} = J_{d-a}$).

The reduced magnetic hyperfine fields should be equal to the reduced sub-lattice magnetization, because both the magnetic moment and the magnetic hyperfine field of the ferric ion are proportional to its spin [10]. In order to extract information on superexchange interaction, we applied the Néel theory of ferrite [10,11] to the two sublattice of $Y_3Fe_{0.75}M_{0.25}O_{12}$ ($M=Cr$ and Al) [12,13]. The inter-sublattice a-d, intra-sublattice a-a, and d-d interac-

Table II. The intersublattice J_{a-d} , intrasublattice J_{a-a} , and J_{d-d} interactions for YIG, Al-YIG and Cr-YIG. Doping ratio for Al and Cr is $x = 0.25$. Here, k_B is the Boltzmann constant.

	J_{a-d} (k_B)	J_{a-a} (k_B)	J_{d-d} (k_B)
YIG	-21.98	-13.18	-10.55
Al-YIG	-12.6	9.8	6.3
Cr-YIG	-18.73	11.08	9.33

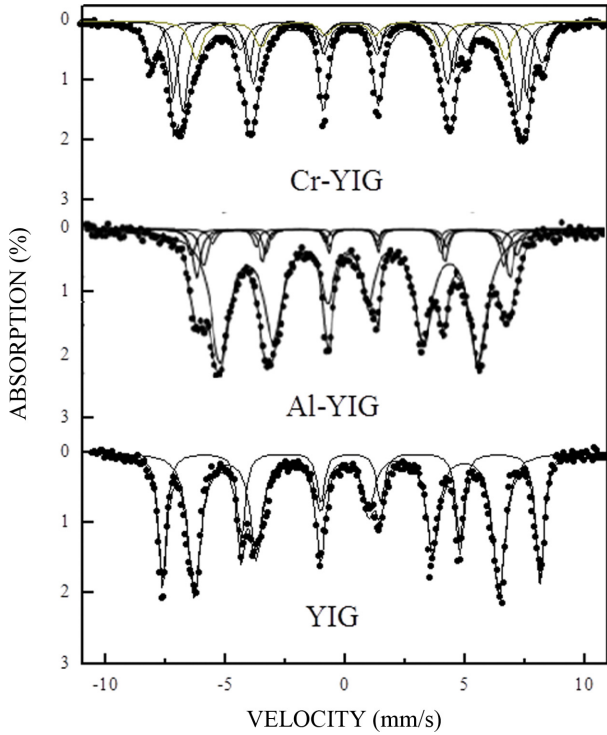


Fig. 2. (Color online) Mössbauer spectra of Y₃Fe₅O₁₂ and Y₃Fe_{4.25}M_{0.25}O₁₂ (M=Al and Cr) measured at room temperature.

tions were represented in Table II. The super-exchange interaction of a-d is much larger than a-a, and d-d interaction. The negative values of exchange integral mean antiferromagnetic coupling. It means the exchange interaction strength in pure garnet is stronger than that of Cr- and Al- doped garnet.

Fig. 2 shows Mössbauer spectra of Y₃Fe_{5-x}M_xO₁₂ (M=Cr and Al, x = 0.0, and 0.75) at room temperature. A spectrum for x = 0.0 is well reflected two sets of six line patterns. While as Al concentration increases, outer sextet pattern, which is originating from octahedral site,

broadens widely. In contrast to, as Cr concentration increases, inner sextet pattern, which is originating from tetrahedral site, broadens widely. In order to explain line broadening phenomena, we adapted a probability distribution model of cations. The Al ions of YIG systems are known to prefer to occupy tetrahedral 24d sites. The magnetic hyperfine field at Fe³⁺ with n Fe (24d) ions in Y₃Fe_{4.25}Al_{0.75}O₁₂ may be written as [6]

$$H(n) = H_0 + n\Delta H \quad (1)$$

According to these procedures, 3-6 suitable six Lorentzians of octahedral spectra and one set of tetrahedral spectrum were fitted to data. The analyzed magnetic hyperfine fields and areas of various samples are listed in Table III. Isomer shifts values of iron ions at room temperature are in the range of 0.35~0.40 mm/s relative to Fe metal, which means that the ionic state of iron ions in five sites is ferric (Fe³⁺) [14]. The Cr ion prefers to occupy octahedral (a)-sites. The tetrahedral coordinated Fe ions are linked to four octahedral sites containing a statistical distribution of Fe and Cr ions. The spectra were fitted to five sets for Y₃Fe_{4.25}Cr_{0.75}O₁₂ of Zeeman patterns. The probability that a Fe ion with nearest-neighbor sites occupied by Fe ions was calculated using the binomial formula. The spectra were fitted to minimum two sets for Y₃Fe₅O₁₂, and maximum five sets for Y₃Fe_{5-x}M_xO₁₂ (M=Al and Cr) of Zeeman patterns. These results of binominal distribution are represented in Table II.

V. Conclusions

The Al- and Cr-containing YIGs were prepared using a sol-gel process, and their exchange interactions and cation distribution in sub-site were studied using analyses Mössbauer spectra. The exchange integrals with negative value of J_{a-d}, and positive values of J_{a-a} and J_{d-d}, exhibit that the super-exchange interactions decrease

Table III. Results of Mössbauer spectra for Y₃Fe_{4.25}M_{0.75}O₁₂ (M=Al and Cr) at room temperature; magnetic hyperfine field (H_{hf}) and absorption area.

	YIG		Al-YIG		Cr-YIG	
	H _{hf} (kOe)	Area (%)	H _{hf} (kOe)	Area (%)	H _{hf} (kOe)	Area (%)
16(a)	491	40	463	16	510	43
	-	-	444	11	-	-
	-	-	425	8	-	-
	-	-	406	3	-	-
24(d)	398	60	365	62	461	8
	-	-	-	-	440	19
	-	-	-	-	414	21
	-	-	-	-	409	9

with Al- and Cr increases. The Mössbauer spectra reflect cation distribution of Cr at octahedral sites and Al at tetrahedral site.

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