磁気特性の温度安定化のための Gd、In, Ti 置換磁性ガーネット薄膜の合成

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Growth of Gd, In and Ti substituted Magnetic Garnet Single Crystal Film with Temperature Stabilized Magnetic Properties

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The Gadolinium, Indium and Titanium substituted garnet films were synthesized in order to investigate the magnetostatic wave devices with the temperature stabilized magnetic and microwave properties. The single crystal films were grown by the liquid phase epitaxy technique. In the saturation magnetization v.s. temperature curve between the magnetic compensation temperature and the Curie temperature, the flat area appears where magnetization does not change. The optimized substitution of Gd ions for Y ions and In orTi ions for Fe ions realized the flat area around the room temperature. In addition, the In and Ti substitution show the tendency of decreasing the line width of the ferromagnetic resonance spectrum.

[Received February 10, Accepted February 22,2005]

1. Introduction

Rare earth magnetic garnet have been attracting materials as microwave and magneto-optical applications. Since the internet communication was wide spread in 1990's, the communication system including the optical and the wireless system has been rapidly improved. At the present stage, the ubiquitous network system requires more capacity and quick response of the information transportation. The optical isolator utilizing non-reciprocal property of Faraday effect is an essential device for the optical communication system and the rare earth magnetic garnet materials have been practically used as the optical isolators because they have large Faraday effects between visible and infrared light region. [1-3] The recent wireless communication technology requests higher microwave frequency from MHz to GHz band. The rare earth magnetic garnets are also attractive for the microwave device by using magnetostatic wave (MSW) because the MSW is well effective up to Q band (30 GHz) region. [4] The yttrium iron garnet (YIG) is a most famous garnet material due to extremely sharp ferromagnetic resonance absorption at microwave region. [5] In addition, the recent developments of the thin film technology enabled to synthesize homogeneous and good quality single crystal without defects. However, the saturation magnetization ($4\pi M_s$) of YIG strongly depends on temperature, [6] which leads the instability of microwave properties of the YIG film around room temperature. In order to realize the temperature stability of the magnetic and microwave properties of the garnet, one of the ideas is proposed to utilize the magnetic compensation point (T_{comp}) and Curie temperature (T_c) of rare earth garnet materials. [7] In the saturation magnetization v.s. temperature curve, a flat area appears between the T_{comp} and the T_c. According to the ferromagnetic resonance theory, the resonance frequency depends on the change of the $4\pi M_s$. [8] Thus for the stabilized microwave properties of the garnet films, it is necessary to realize the stabilized magnetic properties. Such attempts were studied in the form of polycrystalline bulk materials at the beginning of the research for the magnetic garnet in 1960's. [7] Thin film technology of the magnetic garnet was developed during the study for the magnetic bubble memory in 1970's and 1980's. It is obvious that single crystal with good homogeneous and quality has a great advantage for the practical application. We have reported the synthesis of the single crystal films of the $Y_{3-x}Gd_xFe_{5-y}Al_yO_{12}$ garnet with temperature stability of the magnetic properties. [9] In this paper, the optimized composition ratio of the Gd and Al substitutions for the magnetization stability around room temperature was reported, however, the ferromagnetic resonance line width increased with increasing the Al substitution. According to the report by Tanno et.al, [10] the line width of the ferromagnetic resonance extremely increased when the value of the $4\pi M_s$ becomes less than 500 gauss. The Al substitution induce the reduction of the saturation magnetization. In order to disturb the decrease of the saturation magnetization, Ti or In substitution are effective because the In or Ti ions are considered to be preferentially substituted with octahedral Fe ions. [11] The net magnetization of the iron garnet come from the magnetic moment of the tetrahedral Fe ions which are not cancelled out by the octahedral Fe ions. In addition, there is a report that the In substitution decreased the resonance line width. [12] In this paper, we report the Gd-In and Gd-Ti substituted garnet films for the temperature stabilized magnetic properties.

$$R_1 \equiv \frac{Fe_2O_3}{\sum R_2O_3} \qquad R_2 \equiv \frac{Fe_2O_3}{M_2O_3} \qquad R_3 \equiv \frac{PbO}{B_2O_3}$$

$$R_4 \equiv \frac{Fe_2O_3 + M_2O_3 + \sum R_2O_3}{Fe_2O_3 + M_2O_3 + \sum R_2O_3 + PbO + B_2O_3 + Bi_2O_3}$$

$$R_5 \equiv \frac{R_2O_3}{\sum R_2O_3} \qquad R_6 \equiv \frac{PbO}{Bi_2O_3}$$

R : Ion of the *c* cite (Y, Lu, Bi, Pr, Nd, Sm, Eu, Gd, etc.)
M : Ion of the *a*, *d* cite (Ga, Al, Ge, etc.)

2. Experimental

The $Y_{3-x}Gd_xFe_{5-y}In_yO_{12}$ and $Y_{3-x-y}Gd_xCa_yFe_{5-y}Ti_yO_{12}$ garnet films were prepared by liquid phase epitaxy (LPE) technique. PbO-B_2O_3 was used as flux melt in Pt crucible. The Ca^{2+} ion was used for the electric charge compensation of the Ti^{4+} ions in the Gd-Ti substituted garnet system. The single crystal (111) $Gd_3Ga_5O_{12}$ wafers (GGG: the lattice constant a_s=12.37 Å) were used for the substrates. The melt composition was calculated by using *R* parameters [13] which are the composition molar ratios of the raw materials given by

where the R_1, R_2, R_3, R_4 and R_5 were fixed to be 14, 15.6, 0.1 and 2.33, respectively. The value of the R_2 was varied from 60(50) to 19(3) for the In (Ti) substituted film. The films were prepared by horizontal dipping mode at 100 rpm rotation speed. The growth temperature was kept at the temperature between 910 ℃ and 950 ℃. The lattice mismatch between the film and substrate was measured by the X-ray diffractometer with Cu and the compositions of the film were determined by EDX analysis. The magnetization of the films were measured by the vibrating sample magnetometer (TOEI VSM-5) in the temperature range from –193 ℃ to 300 ℃. In the temperature range between –250 ℃ and -193 ℃, we measured the magnetization by SQUID magnetometer (Quantum Design MPMS-7). Ferromagnetic resonance (FMR) measurements were performed in X-band (9 GHz) region by conventional ESR magnetometer (JEOL FE1XG) at room temperature.

3. Results and Discussion

3.1 $Y_{3-x}Gd_xFe_{5-y}In_yO_{12}$

The lattice mismatch *Da* was calculated using the following relations[14];

$$\Delta a = a_f - a_s = -\frac{1-\nu}{1+\nu}\Delta a^{\perp}, \quad \Delta a^{\perp} = -\cot\theta_s \cdot \Delta\theta \cdot a_s$$

where, a_f and a_s are the lattice parameter of the film and the substrate, respectively. The *m* is the Poisson constant of the film (In this case, we use the value of 0.29. The *Dq* is $q_s - q_f$ and the q_s and q_f are the (888) diffraction angle from the substrate and the film, respectively.

With increasing the amount of the In substitution, the lattice parameter of the film increased and the lattice mismatch Δa between the film and the substrate exceed 0.04 Å, which was relatively large for the film prepared by the LPE growth. The characterization of the $Y_{3-x}Gd_xFe_{5-y}In_yO_{12}$ films are shown in Table I. The Gd ions also show a slight increase with the increasing the In ions. The $4\pi M_s$ v.s. temperature curves of the $Y_{3-x}Gd_xFe_{5-y}In_yO_{12}$ films are shown in Fig. 1. The magnetization of the film was calculated by subtracting the paramagnetic magnetization of the substrate from the total magnetization of the film and the substrate. The paramagnetic magnetization of the substrate was approximated by a straight line. The magnetization data of the film below –250 ℃ are not shown in Fig. 1

Table I. The characterization of the $Y_{3-x}Gd_xFe_{5-y}In_yO_{12}$ films.

Sample	Gd(x /f.u.)	In (y /f.u.)	d (μm)	Δa(Å)	T_s(℃)	T_g (℃)
GYI-I	1.82	0	9.41	0.026	950	913
GYI-II	1.86	0.18	8.34	0.029	980	938
GYI-III	1.86	0.39	9.14	0.036	976	931
GYI-IV	1.87	0.57	7.87	0.040	970	929

Δa: a_f-a_s ,d: thickness, T_s, T_g and *DT* are the saturation temperature of the melt, growth temperature and supercooling temperature, respectively.

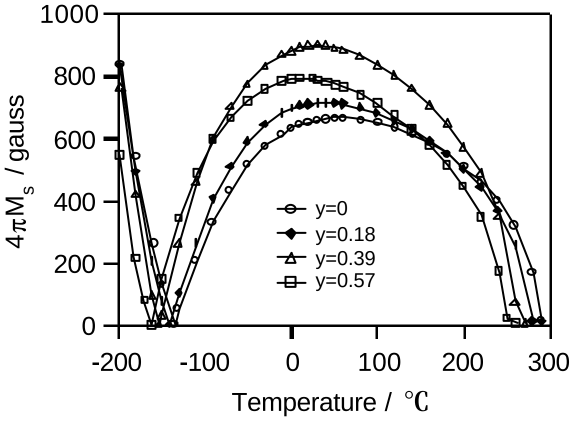

Fig.1 Temperature dependence of the saturation magnetization $4\pi M_s$ of the $Y_{3-x}Gd_xFe_{5-y}In_yO_{12}$ films

because of the difficulty to estimate the accurate magnetization value of the film. The paramagnetic moment of the GGG substrate was extremely enhanced below –250 ℃ and the magnetization curve deviate from the linear approximation. This makes difficulty to characterization of the film itself. With increasing the amount of the In ions, the maximum value of the saturation magnetization between T_{comp} and the T_c (we call $4\pi M_{s\_MAX}$ in this paper.) increased. The T_{comp} and the T_c slightly decrease with increasing the amount of In ions. The value of the $4\pi M_{s\_MAX}$ of the film with y=0.39 is 1.4 times as large as that of the film without In substitution. The magnetization of the Gd substituted YIG comes from the magnetic moments of the tetragonal Fe ions, the octahedral Fe ions Gd ions. Above T_{comp}, the increments of the Gd ions should affect the decreasing of the $4\pi M_{s\_MAX}$ value.[7] The reason of the increased $4\pi M_{s\_MAX}$ is considered to be the preferential In substitution with the octahedral Fe sites. However, the $4\pi M_{s\_MAX}$ of the film with y=0.57 becomes smaller than the value of the film with y=0.39. This might suggest that the In ions begin to be substituted with the tetragonal Fe ions.

The ferromagnetic resonance (FMR) linewidth decreases with increasing the amount of the In ions. Fig.2 shows the FMR spectra of the $Y_{3-x}Gd_xFe_{5-y}In_yO_{12}$ films in the magnetic field perpendicular to the film at room temperature. The value of the half width of the resonance line ΔH of the film without In ions is 170 Oe, however, the value of ΔH of the film with y=0.57 is 58 Oe, although the lattice mismatch between the film and the substrate becomes larger with increasing the In

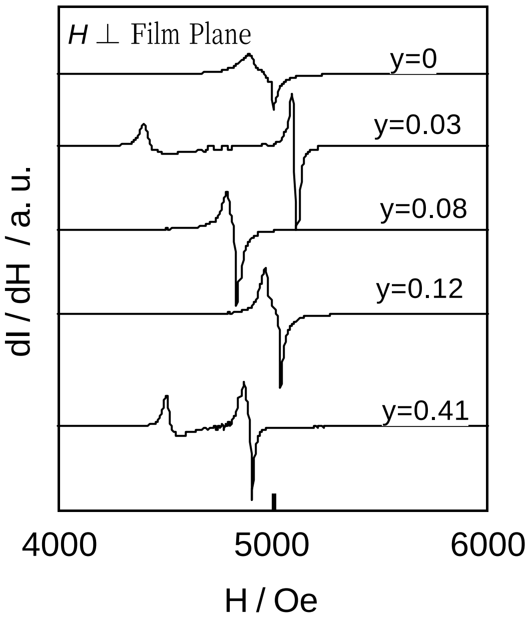

Fig.2. Ferromagnetic resonance spectra of the $Y_{3-x}Gd_xFe_{5-y}In_yO_{12}$ at X band (9 GHz) region in the magnetic field perpendicular to the film plane. The measurements were performed at room temperature.

Table II. The characterization of $Y_{3-x-y}Gd_xCa_yFe_{5-y}Ti_yO_{12}$ films.

Sample	Gd(x /f.u.)	Ti (y /f.u.)	d (μm)	Δa(Å)	T_s(℃)	T_g (℃)
GYT-I	1.05	0	9.02	0.027	1000	932
GYT -II	0.96	0.03	3.23	0.011	962	950
GYT -III	0.89	0.08	4.22	0.025	958	933
GYT -IV	0.87	0.12	3.60	0.025	954	924
GYT -IV	0.80	0.41	3.82	0.033	951	924

Δa : a_f-a_s , d : thickness, T_s, T_g and *DT* are the saturation temperature of the melt, growth temperature and supercooling temperature, respectively.

substitution. This tendency is qualitatively consistent with the past report .[12]

3.2. $Y_{3-x-y}Gd_xCa_yFe_{5-y}Ti_yO_{12}$

The Ti ions are also substituted with the octahedral Fe ions. The characterization of the grown films are shown in Table II. The content of the Gd ions of the films decreases with the increasing the Ti ions although we designed the constant value of the Gd content in the film. The saturation temperature of the melt changed from 1000 ℃ to 950 ℃ with increasing Ti substitution, which may induce the difficulty to control the segregation factor of all elements simultaneously. In order to realize

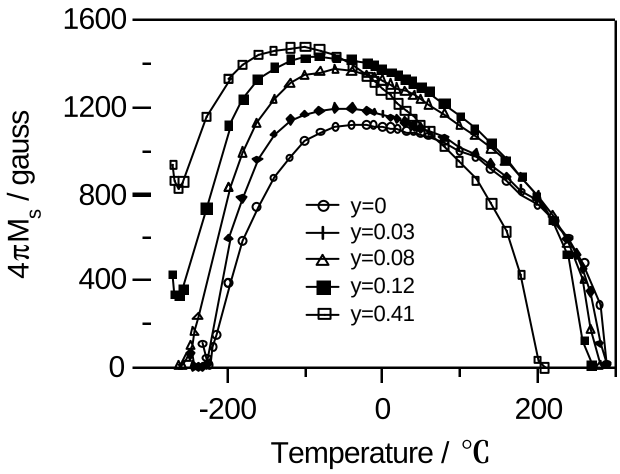

Fig.3. Temperature dependence of the saturation magnetization $4\pi M_s$ of the $Y_{3-x-y}Gd_xCa_yFe_{5-y}Ti_yO_{12}$ films.

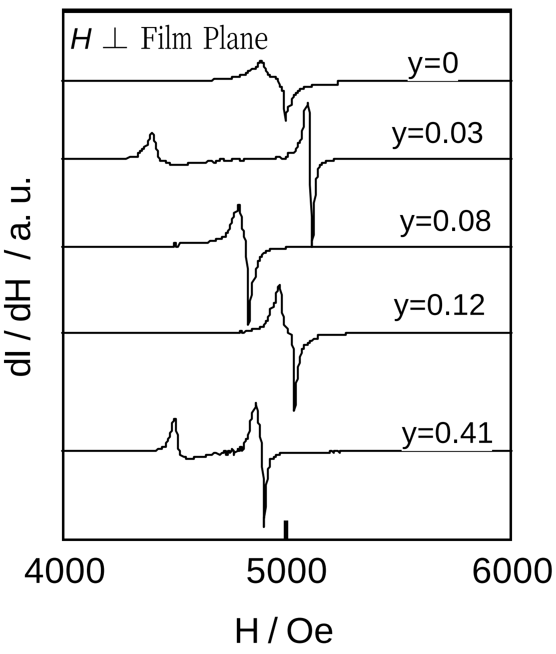

Fig.4. Ferromagnetic resonance spectra of the $Y_{3-x-y}Gd_xCa_yFe_{5-y}Ti_yO_{12}$ at X band (9 GHz) region in the magnetic field perpendicular to the film plane. The measurements were performed at room temperature.

the designed composition, the growth conditions should be optimized carefully. The magnetization curves of the $Y_{3-x-y}Gd_xCa_yFe_{5-y}Ti_yO_{12}$ are shown in Fig.3. The increments of the $4\pi M_{s\_MAX}$ are similarly observed with increasing the amount of the Ti ions with the case of the In substituted film. In this case, the increments of the $4\pi M_{s\_MAX}$ can be considered to come from both the decreasing the amount of Gd ions and the preferential Ti substitution with the octahedral Fe sites. The T_{comp} and T_c also decrease with increasing the Ti substitutions. The decreasing of the T_c is caused by the dilution of the Fe ions. The increment of the net magnetization needs larger magnetic moments of the Gd ions in order to compensate the magnetic moments of Fe ions. This is the reason of the T_{comp} shift to lower temperature. The magnetization of the film with y=0.33 near –270 ℃ does not decrease to zero, which confuses the position of the T_{comp}. According to the report by F. C. Rossol, [5] the bad quality of the crystallinity of the specimen induces such behavior of the magnetization. This might suggest the inhomogeneity of crystallinity of the film. The FMR spectra of the $Y_{3-x-y}Gd_xCa_yFe_{5-y}Ti_yO_{12}$ are shown in Fig.4. The ΔH of the resonance absorption near 5 kOe of the $Y_{3-x-y}Gd_xCa_yFe_{5-y}Ti_yO_{12}$ film is smaller than that of the film without Ti ions. The resonance fields depends on the specimens due to the different magnetic anisotropy filed in the film and the specimens with y=0.03 and y=0.41 shows the several 'branched' resonance peaks except for the 'main' resonance peak. Such resonance peaks were considered to be magneto-static mode which were often reported for the case of YIG film.[15,16] The appearance of the many magneto-static mode seems to be related with the single crystallinity of the film, however, the detail of this case is not clear at the present stage. The film with y=0.03 shows the smallest value of 20 Oe. This is a different tendency with the case of the $Y_{3-x}Gd_xFe_{5-y}In_yO_{12}$ films where the ΔH decrease with increasing the amount of In ions. The value of ΔH is also very sensitive to the crystallinity and the stress between the film and the substrate. At the present stage, it is difficult to conclude the reason, however, the substitution of In or Ti ions disturbs the decreasing of the saturation magnetization and it is effective for the small value of ΔH. As far as the lattice mismatch is concerned, the In and Ti substitution induce the large mismatch between the film and the substrate for the case of the GGG substrate. In order to clear the effect of the In and Ti substitution, the substrate with larger lattice parameters should be chosen.

4.Conclusion

The Gd-In (Ti) substituted garnet films have been synthesized for the temperature stability of the magnetic properties around room temperature. The substitution of the In and Ti ions increase the saturation magnetization between T_{com} and T_c of the film, which might be due to the preferential replacements of the octahedral Fe ions. The FMR spectra show the tendency of the decreasing of the ΔH with substitution of the In or Ti ions.

Acknowledgement
We gratefully thank to the staff members of the Research Center for Molecular-scale Nanoscience, Institute Molecular Sciences for the SQUID and FMR measurements.

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