

Magneto-optical enhancement in sputtered epitaxial films of praseodymium-substituted yttrium iron garnet

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Faraday rotation and ellipticity were measured at room temperature in the photon energy range of 1.5–4.2 eV on $Y_{3-x}Pr_xFe_5O_{12}$ ($x=0-2.0$) epitaxial films grown by rf sputtering. The Pr^{3+} substitution induced negative rotation and ellipticity which satisfy a paramagnetic dispersion relation caused by an electronic transition centered at 3.0 eV. The maximum value of the Pr^{3+} contribution was -2.5×10^4 deg/cm in rotation and -4.1×10^4 deg/cm in ellipticity for $x=2.0$. Optical absorption measurements showed that this is a new transition induced by the coexistence of Pr^{3+} and Fe^{3+} , and it is neither $4f-5d$ intra-atomic transition nor $4f-4f$ transition originating from Pr ions as previously supposed. © 1997 American Institute of Physics. [S0021-8979(97)01315-7]

I. INTRODUCTION

Praseodymium substitution to iron garnet is well known to induce large negative Faraday rotation in the visible. The origin has been investigated by many researchers so far, since the knowledge about the enhancement mechanism brings us a useful criterion for finding new materials exhibiting large magneto-optical (MO) effect.¹⁻⁹ Visnovsky *et al.* reported from Faraday rotation measurements for liquid-phase epitaxial films of $Pr_xY_{3-x}Fe_{5-y}Ga_yO_{12}$ that the induced Faraday rotation is attributed to a diamagnetic electronic transition associated with $4f-5d$ transition of Pr^{3+} around photon energies of $h\nu=3.1-3.3$ eV, rather than any enhancement of Fe^{3+} transitions as is known to be the case for Bi^{3+} (Ref. 2). They also showed that induced structures are observed at 2.9, 4.3, and 4.5 eV in polar Kerr rotation spectra. Leyculas *et al.* concluded, on the basis of temperature dependence of Faraday rotation induced by one Pr^{3+} ion for various Pr concentrations, that the Pr^{3+} contribution to the rotation is attributed to a newly observed paramagnetic transition located close to 2.25 eV.⁵ However, the origin of Pr contribution, i.e., type of MO dispersion and assignments of related electronic transitions has been not yet established.

To clarify the Pr contribution, we have examined the Faraday rotation and ellipticity in the photon energy range of 1.5–4.2 eV for yttrium iron garnet (YIG) thin films containing different amounts of Pr. In this article, the Pr contribution to MO properties and optical absorption of the films are described and the origin through comparison between them is discussed.

II. EXPERIMENT

The films were grown onto (111)-oriented $Gd_3Ga_5O_{12}$ (GGG) single crystal substrates by conventional rf diode sputtering using ceramic targets of $Y_{3-x}Pr_xFe_5O_{12}$ ($x=0, 1.0, 1.5, 2.0$). Typical sputtering conditions were as follows; substrate temperature=400 °C, argon pressure=50 mTorr, incident rf power density=5.6 W/cm², and deposition rate=5 nm/min. Film thickness was adjusted to be less than

150 nm, which allows transmission optical measurement even in the ultraviolet. Epitaxial films of $Y_3Al_{4.9}Fe_{0.1}O_{12}$ (Fe:YAG) and $Y_2Pr_1Al_{4.9}Fe_{0.1}O_{12}$ (Fe:PrYAG) for optical absorption measurements were also grown by the same procedure except that the growth temperature was 550 °C.

Chemical composition of the prepared films was analyzed by x-ray photoelectron spectroscopy. Faraday rotation and ellipticity angles were measured at room temperature by a polarization modulation method using a photoelastic modulator in the range of 1.5–4.2 eV (Ref. 10).

III. RESULTS AND DISCUSSION

A. Film quality

The films showed only x-ray reflection from a (111) plane as seen in Fig. 1. It was confirmed from x-ray pole figure analysis that the single crystalline films are *in situ* grown on GGG substrates, with the (111) plane parallel to the surface. However, the film for $x=2.0$ was double layered and poor in crystalline quality, which resulted from too large lattice mismatch between the film and the substrate.¹¹ The lattice constant a of the film calculated using the relation $a = a_s - [(1 - \mu_{111}) / (1 + \mu_{111})] (a_s - a_f)$ is shown in Table I, where a_s is the substrate lattice constant, a_f the measured perpendicular lattice constant of the film and μ_{111} is the Poisson constant for (111) oriented film. The Poisson constant of YIG, 0.30 was used for the calculation.⁸ The measured lattice constants are larger by 0.8% than those of the liquid-phase epitaxial films, reflecting iron deficiency as described below.⁸

The chemical composition analysis showed that these films are iron deficient, except x of 2.0, as shown in Table I. The ratios of Pr to Y are close to those of the targets.

B. Magneto-optical properties and optical absorption

Figure 2 shows Faraday rotation (F) and ellipticity (χ) spectra of Pr-substituted YIG films at room temperature. The spectra of nonsubstituted film have complicated structures above 2.5 eV arising from electronic pair transitions between neighboring octahedral and tetrahedral Fe^{3+} ions and

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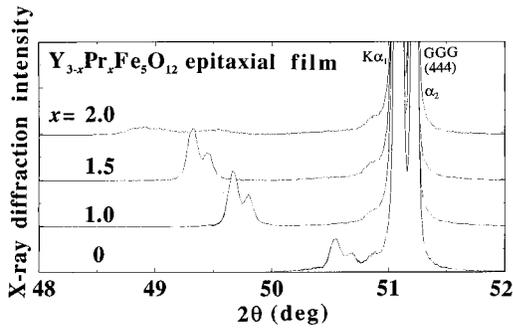


FIG. 1. X-ray diffraction spectra of Pr-substituted YIG films grown on (111) GGG.

oxygen-to-iron charge transfer transitions. These have been assigned by Scott *et al.*¹² When the Pr substitution is increased, the Faraday rotation spectrum changes sign around 3.1 eV. On the other hand, the ellipticity shows the remarkable increase in negative sign around 3 eV. It should be noted here that the fine structures seen in the spectrum for $x=0$ remain even after the spectral change. This suggests some contribution of the Pr substitution overlapping on the spectrum of YIG film. Therefore, it was evaluated by subtracting the spectrum of nonsubstituted film from those of Pr-substituted films, assuming that Fe contribution itself is unchanged by the Pr substitution. The results are shown in Fig. 3. The subtracted spectra of Faraday rotation (F_{Pr}) and ellipticity (χ_{Pr}) show approximately a paramagnetic dispersion relation centered at 3.0 eV, though some structures are also seen above 3.8 eV in both spectra. The maximum values increase with increased Pr concentration, reaching $F_{Pr} = -2.5 \times 10^4$ deg/cm at 2.8 eV and $\chi_{Pr} = -4.1 \times 10^4$ deg/cm at 3.0 eV for $x=2$. The least-squares curves calculated using the following dispersion relations for a paramagnetic transition with transition energy $h\nu_0$ and half-linewidth $h\Gamma_0$ roughly fit the measured spectra as shown in Fig. 4.

$$F \propto \epsilon''_{xy} \propto -\nu(\nu^2 - \nu_0^2 + \Gamma_0^2) / \nu_0 [(\nu^2 - \nu_0^2 + \Gamma_0^2)^2 + 4\Gamma_0^2\nu^2], \quad (1)$$

$$\chi \propto \epsilon'_{xy} \propto \Gamma_0(\nu^2 + \nu_0^2 + \Gamma_0^2) / \nu_0 [(\nu^2 - \nu_0^2 + \Gamma_0^2)^2 + 4\Gamma_0^2\nu^2], \quad (2)$$

where ϵ''_{xy} and ϵ'_{xy} denote imaginary and real parts of the off-diagonal dielectric tensor elements and ν is the frequency of the incident light. The deviation above 3.5 eV may be due

TABLE I. Lattice constant a and chemical composition per formula unit in the films. Composition values were obtained, assuming that the sum of rare earth ions is 3.

Target	Film a (nm)	Film composition		
		Y	Pr	Fe
$Y_3Fe_5O_{12}$	1.245	3.00	0	4.11
$Y_2Pr_1Fe_5O_{12}$	1.256	1.96	1.04	4.91
$Y_{1.5}Pr_{1.5}Fe_5O_{12}$	1.261	1.40	1.60	4.36
$Y_1Pr_2Fe_5O_{12}$...	0.93	2.07	6.29

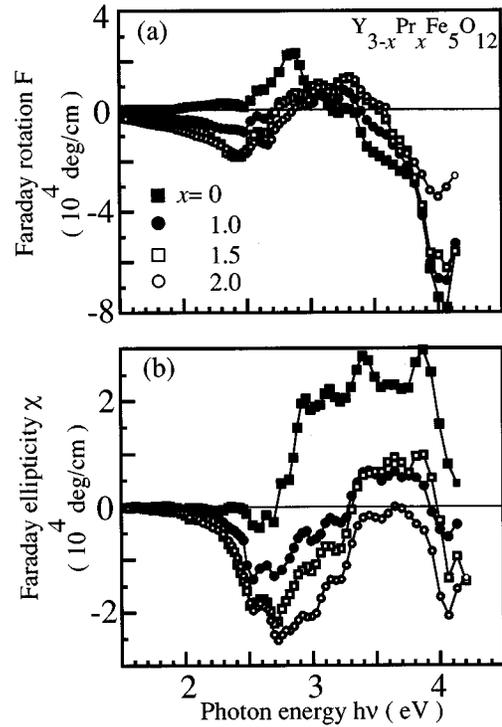


FIG. 2. Spectra of (a) Faraday rotation F and (b) Faraday ellipticity χ for epitaxial films of Pr-substituted YIG at room temperature.

to contributions of other transitions which lie in higher energy. From the best fit, $h\nu_0$ and $h\Gamma_0$ were determined as 3.05 and 0.34 eV, respectively. These results tell us that there should be a paramagnetic electronic transition around 3 eV.

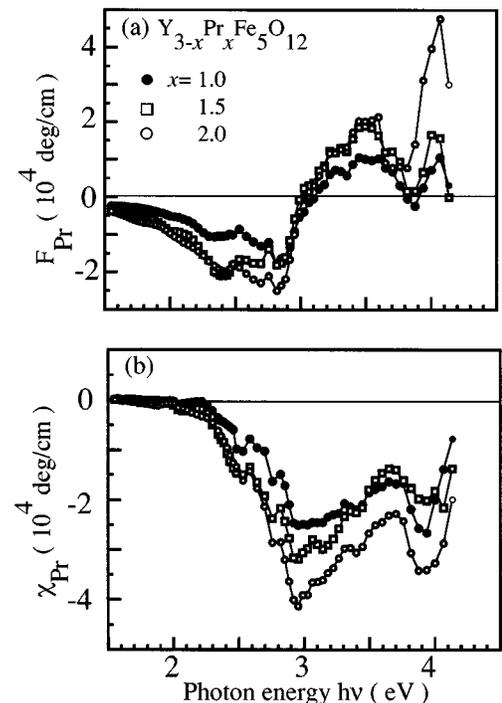


FIG. 3. Pr contribution to (a) Faraday rotation F_{Pr} and (b) Faraday ellipticity χ_{Pr} .

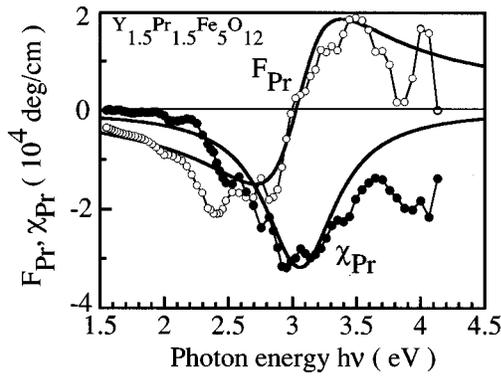


FIG. 4. Least-squares fit of paramagnetic dispersion curves to F_{Pr} and χ_{Pr} spectra of $Y_{1.5}Pr_{1.5}Fe_5O_{12}$ film; bold solid lines-calculated. Best fitting parameters are 3.05 eV for transition energy and 0.34 eV for half-linewidth.

In order to establish where electronic transitions associated with Pr ions are located, we examined the optical absorption spectrum for Fe: PrYAG film. The result is shown in Fig. 5. Prominent absorption peaks are observed at 4.2 and 5.2 eV. However, note that definitely no absorption appears at the energy position of 3.0 eV expected from the above result. The increase of absorption at higher energy including the broad shoulder around 3.6 eV is attributed to the doped Fe as understood from a comparison with the spectrum for Fe:YAG film presented together.¹³ Two peaks at 4.2 and 5.2 eV are identified with the $4f-5d$ transitions of Pr ion because they are not observed in the Fe:YAG film and are extremely strong in intensity, as well as large in half-linewidth. Taking account of so called “nephelauxetic” effect,¹⁴ the lowest $4f-5d$ transition energy in this film estimated from the reported value of 6.2 eV for PrF_3 is about 4.3 eV, is consistent with the above value.¹⁵ Figure 6 shows absorption spectra of YIG films with different Pr concentrations. In addition to the spectrum of YIG film which exhibits

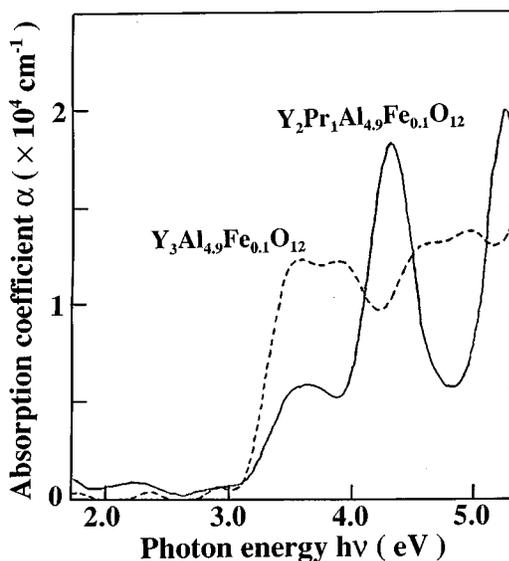


FIG. 5. Optical absorption spectrum of $Y_2Pr_1Al_{4.9}Fe_{0.1}O_{12}$ film at room temperature. The spectrum of $Y_3Al_{4.9}Fe_{0.1}O_{12}$ film is also shown for comparison.

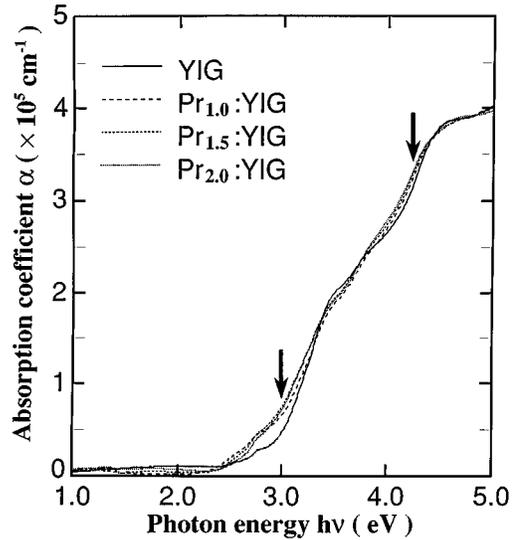


FIG. 6. Optical absorption spectra of Pr-substituted YIG films at room temperature. Arrows show energy positions at which absorption increases with Pr substitution.

shoulders around 2.8, 3.4, 3.8, and 4.4 eV, the increase of the absorption coefficient with the Pr substitution is clearly observed around 3.0 and 4.2 eV. The induced magnitude is on the order of 10^4 cm^{-1} . The absorption at 4.2 eV corresponds to the $4f-5d$ transition of Pr ion assigned in Fig. 5. While, the absorption enhancement at 3.0 eV which is not seen in Fig. 5 but obviously seen in Fig. 6, is induced by the coexistence of Pr and Fe ions. This transition energy is in good agreement with that at which MO enhancement occurs.

This situation is similar to the MO enhancement observed in cerium-substituted iron garnet films; the coexistence of Ce and Fe ions induces a new electronic transition at a photon energy as low as 1.4 eV which shows strong absorption and paramagnetic MO dispersion having the $\hbar\Gamma_0 = 0.26 \text{ eV}$.¹⁶ In this case, it was reported that the new transition is most likely a charge-transfer type from Ce^{3+} to Fe^{3+} because Ce and Fe ions easily change their valence from 3+ to 4+ and from 3+ to 2+, respectively.^{16,17} The valence of Pr ion may change as well, though higher energy may be required for the valence change from 3+ to 4+ since Pr^{3+} is rather stable, compared to Ce^{3+} . These lend considerable support to the view that Pr-Fe charge transfer transition occurs at higher energy than that of Ce-Fe, being responsible for the observed enhancement of MO effect.

IV. CONCLUSIONS

We have epitaxially grown the $Y_{3-x}Pr_xFe_5O_{12}$ films on (111) GGG substrates by rf sputtering. The measurements of Faraday rotation and ellipticity in a photon energy range extended to 4.2 eV showed that the Pr substitution induces negative Faraday rotation and ellipticity with a paramagnetic dispersion relation caused by an electronic transition centered at 3.0 eV. The maximum value of Pr contribution is $-2.5 \times 10^4 \text{ deg/cm}$ in rotation and $-4.1 \times 10^4 \text{ deg/cm}$ in ellipticity for $x=2.0$. From the optical absorption measurement, the transition at 3.0 eV is suggested to be induced by

the coexistence of Pr^{3+} and Fe^{3+} such as a Pr-Fe charge transfer transition, and not a $4f-4f$ transition and $4f-5d$ intra-atomic transition, originating from the Pr ions as previously assumed.

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¹¹When the lattice mismatch between the film and the substrate is too large, a layer is formed with large internal stress from the substrate in the initial stage of film growth. However, after the layer was grown up to some critical thickness, the resultant lattice distortion is almost released by dislocations and defects. Further film growth is stress-free, resulting in a layer with a lattice constant inherent to the film. Thus, the double layered film shows two lattice constants, i.e., two x-ray reflection peaks.
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