Strong magneto-optical enhancement in highly Ce-substituted iron garnet films prepared by sputtering

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Faraday rotation and ellipticity spectra were measured at photon energies $hv = 0.9$–4.0 eV for $R_{3-x}Ce_xFe_5O_{12}$ ($R = $ Y, Gd, Yb) films with substitutions up to $x = 2.5$, epitaxially grown by rf sputtering. The Ce substitution prominently enhances the Faraday effect not only in the IR region at $hv = 1.4$ eV but also in the UV region at $hv = 3.1$ eV. Both transitions have a paramagnetic dispersion relation, which are nearly equal in magnitude but opposite in sign. Optical absorption is also induced by a new transition due to Ce^{3+} at $hv = 2.1$ eV, which does not enhance Faraday rotation. These electronic transitions may be attributed to charge transfer transition Ce^{3+} $(4f)$-Fe^{3+} (tet.).

I. INTRODUCTION

Recently we succeeded in growing epitaxial films of Ce-substituted iron garnet ($Y_{3-x}Ce_xFe_5O_{12}$) by rf sputtering[1-3] with substitutions up to $x = 1.5$. The magneto-optical (MO) effect and optical absorption in these films are strongly enhanced in the near infrared (IR) region around $hv = 1.4$ eV.[1,4] The enhanced Faraday rotation at room temperature is as large as 1.3×10^4 deg/cm per Ce ion at wavelengths of 1150 nm. This rotation surpasses, by a factor of 6, that found with Bi^{3+} ions, the champion of the MO enhancement for the past 20 years. However, origin of the MO enhancement with Ce ions is not clear at present.

In this paper we describe the Faraday rotation, ellipticity and optical absorption of $R_{3-x}Ce_xFe_5O_{12}$ (Ce:RIG, $R = $ Y, Gd, Yb) films in an extended photon energy range of $hv = 1$–4 eV, and discuss assignments of the observed electronic transitions. The detailed changes of MO and absorption spectra with Ce substitution give an important clue to the understanding of the origin of the MO enhancement.

II. EXPERIMENT

The films were deposited on (111)-oriented $Gd_3Ga_5O_{12}$ (GGG) and $Nd_3Ga_5O_{12}$ (NGG) single-crystal substrates by conventional rf diode sputtering in pure Ar or reduced atmosphere of Ar + H_2 (the total gas pressure = 50 mTorr, H_2/Ar = 0–5%). The substrates were heated to 500 °C. The deposition rate was 6 nm/min. We used ceramic targets with stoichiometric garnet compositions of $R_{3-x}Ce_xFe_5O_{12}$ ($x = 0$–3.0 for $R = $ Y, $x = 1.0$ for $R = $ Gd, $x = 1.5$ for $R = $ Yb).

The chemical compositions of the films were analyzed by an induction-coupled plasma (ICP) method. X-ray photospectroscopy (XPS) was used for determining the valence of the Ce ions. Faraday rotation and ellipticity angles were measured at room temperature by the polarization modulation method using a monochromatic light source ($hv = 0.9$–4.0 eV). The optical absorption coefficient was determined by comparing the intensity of light transmitted through the sample with that transmitted through the substrate.

III. RESULTS AND DISCUSSION

The single-crystalline garnet films were epitaxially grown *in situ* on GGG and NGG substrates. The composition ratios Ce/R in the epitaxial films were close to those in the targets, while the ratios Fe/Y were a bit smaller than the values in the targets. We could successfully extend the amount of Ce substitution to $x = 2.5$ for $R = $ Y by sputtering under the reduced atmosphere of Ar + H_2. This may be because the reduced atmosphere prevents Ce ions from changing valence $3+$ to $4+$, facilitating the incorporation of Ce into the garnet structure. The XPS showed that the Ce ions in the films are almost all trivalent.

Figure 1 shows Faraday rotation spectra for $Y_{3-x}Ce_xFe_5O_{12}$ ($x = 0$, 1.0, 2.0, 2.5) films. They exhibit paramagnetic type dispersion centered around 1.4 eV in agreement with those in the previous reports.[1,4] The zero-cross points of the spectra shift a bit toward higher photon energy with increasing Ce substitution. Faraday rotation of the film is prominently enhanced with increasing x, reaching 5.6×10^4 deg/cm for $x = 2.5$ at the wavelength $\lambda = 633$ nm ($hv = 1.96$ eV). This is also shown in Fig. 2 as specific Faraday rotation F at $\lambda = 1150$ nm ($hv = 1.08$ eV) plotted as a function of Ce content x. Faraday rotation for Bi-substituted YIG sputtered films is also shown for comparison. The enhancement factor per Ce ion is as large as 1.3×10^4 deg/cm. Faraday spectra and MO enhancement factors for $R = $ Gd and Yb were similar to the above for Y.

Figure 3 shows the spectra after subtracting the Faraday effect in a $Y_3Fe_5O_{12}$ film from the effect in a $Y_2Ce_1Fe_5O_{12}$ film. These spectra express Ce contribution to the Faraday rotation F_{Ce} and ellipticity χ_{Ce}. The spectra of F_{Ce} and χ_{Ce} clearly show paramagnetic type dispersions centered not only at $hv = 1.4$ but also at 3.1 eV. They are nearly equal in magnitude but opposite in sign. Thus MO enhancement in the visible region may be ascribed to two electronic transitions associated with Ce^{3+}. The half-line-widths determined from the resonance lines of χ_{Ce} are 0.22
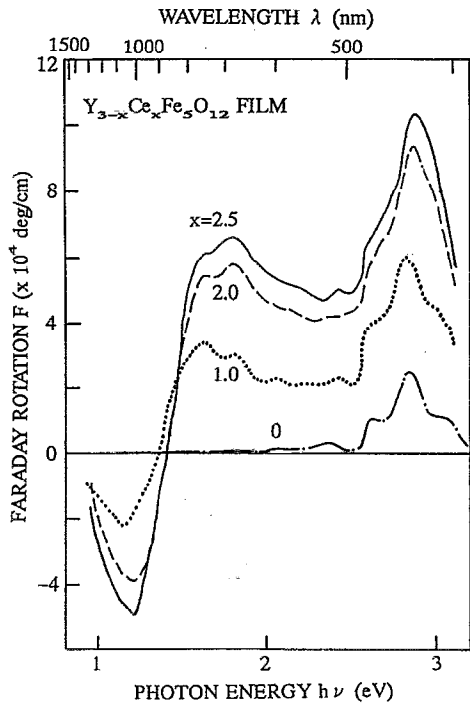
FIG. 1. Faraday rotation spectra for $Y_{3-x}Ce_xFe_5O_{12}$ films at room temperature.

FIG. 3. Ce contribution to Faraday rotation F_{Ce} and Faraday ellipticity X_{Ce}.

and 0.24 eV for the transitions at $h\nu = 1.4$ and 3.1 eV, respectively.

Figure 4 shows optical absorption spectra for $Y_{3-x}Ce_xFe_5O_{12}$ films. As x increases, the spectra show an increasing broad shoulder in the near IR region. However the spectrum induced with increasing x is too broad to be

attributed to an electronic transition. To estimate the Ce contribution to the optical absorption, we roughly fitted the following dispersion relation, which gives the absorption α due to a single transition,[5] to the measured absorption spectrum:

$$\alpha = A\Gamma\nu[(\nu_0^2 - \nu^2 + \Gamma^2)^2 + 4\Gamma^2\nu^2]^{-1}, \qquad (1)$$

where ν is the frequency of the incoming light, A is a constant, and Γ and ν_0 are the half-linewidth and the central frequency of the transition, respectively. Figure 5 shows the fitted curve (dotted line) for the absorption spectrum of $Y_1Ce_2Fe_5O_{12}$ film, together with components used to produce the fit. The fitting requires that the absorption of Ce:YIG films in the near IR region is ascribed to at least two electronic transitions, i.e., one ($h\Gamma = 0.26$ eV) centered at $h\nu = 1.5$ eV and the other ($h\Gamma = 0.42$ eV)
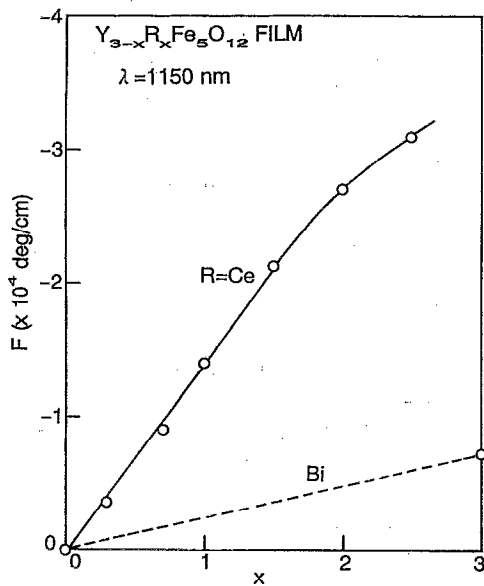

FIG. 2. Specific Faraday rotation for $Y_{3-x}Ce_xFe_5O_{12}$ films at $\lambda = 1150$ nm. Faraday rotation for Bi-substituted YIG films are also shown for comparison.
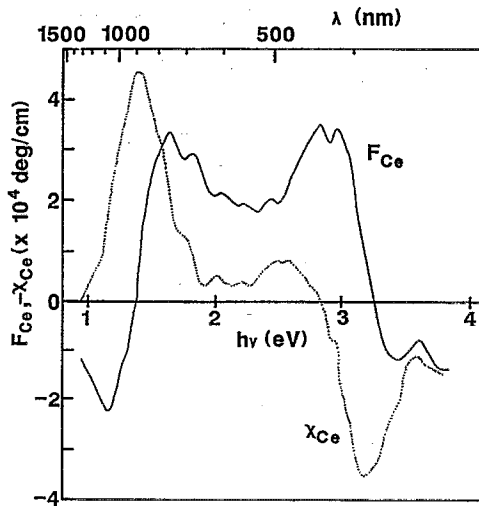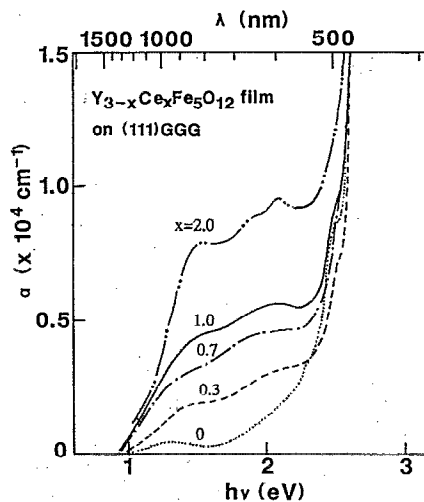

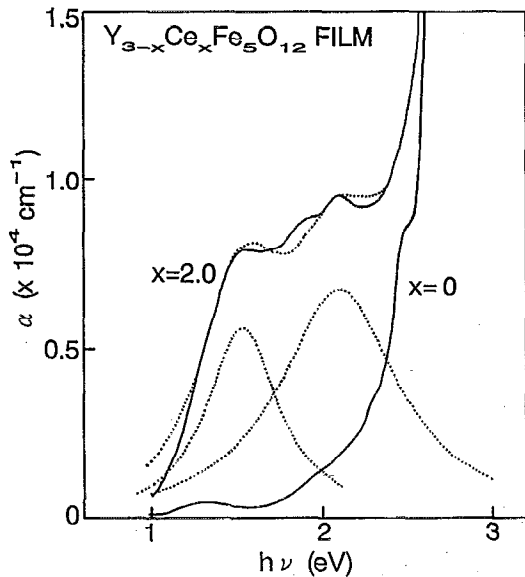FIG. 4. Optical absorption spectra for $Y_{3-x}Ce_xFe_5O_{12}$ films at room temperature.

FIG. 5. Fit using Eq. (1) to the absorption spectrum of $Y_1Ce_2Fe_5O_{12}$ film; solid line—experimental, dotted line—calculated.

FIG. 6. Energy-level scheme for Fe(tet.) and Ce(dodeca.) in iron garnets. Allows denote the charge transfer transitions.

centered at 2.1 eV. The first transition is identified with that inducing a pronounced Faraday effect as shown in Fig. 3, since the values of the transition energy and half-linewidth in both transitions are in good agreement. On the other hand, the second transition centered at 2.1 eV is new and shows no Faraday effect.

These observed electronic transitions, especially the two transitions found in absorption spectra may be treated in terms of Ce^{3+}-Fe^{3+} charge transfer (Ce^{3+} + Fe^{3+}-Ce^{4+} + Fe^{2+}) rather than the $4f$-$5d$ intraorbital transition[1,4] in Ce^{3+} ions. This is because the $4f$-$5d$ transition energy assigned in Ce-doped $Y_3Al_5O_{12}$ (Ref. 6) is too high to explain the spectra in the IR region.[7] The Ce^{3+}-Fe^{3+} charge transfer transitions are expected at lower energy than the $4f$-$5d$ transition since the final states, i.e., the empty bands of Fe^{2+} are thought to be situated below the $5d$ level.[8,9] The lowest charge transfer transition within Ce^{3+}(dodecahedral)-Fe^{3+}(tetrahedral or octahedral) pair will be Ce^{3+} ($4f^1$)-Fe^{3+} (tet.)since the tetrahedral Fe^{3+} ions are the nearest-neighbor metal ions to the dodecahedral Ce ions (Fig. 6). It should be further noted that the final state of this transition consists of two subbands of the tetrahedral e (Fe^{2+}) and t_2 (Fe^{2+}) levels separated by 0.45 eV.[9] This value is fairly consistent with the energy separation (0.6 eV) between two transitions observed in the absorption spectra. The above charge transfer model is also supported by the fact that MO enhancement factor at $hv = 1.4$ eV is proportional to the sublattice magnetization of the tetrahedral sites, which was evaluated from the M concentration dependence of χ_{Ce} in $Y_2Ce_1Fe_{5-x}M_xO_{12}$ (M = Al, In).[10] However, we need to investigate further in order to derive exact conclusions on the origin of MO enhancement in Ce-substituted iron garnet.
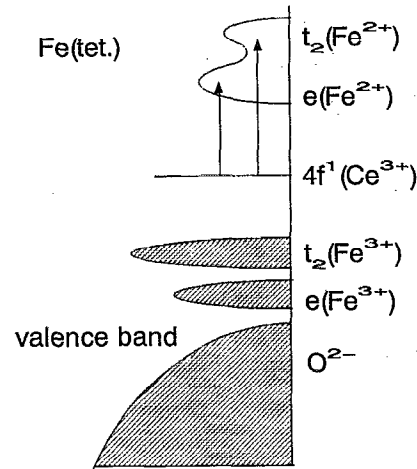
IV. CONCLUSIONS

We have successfully grown the $R_{3-x}Ce_xFe_5O_{12}$ epitaxial films containing a large amount of Ce up to $x = 2.5$ by rf sputtering. The Ce substitution prominently enhanced the Faraday effect not only in the IR region at $hv = 1.4$ eV but also in the UV region at $hv = 3.1$ eV. Both transitions have a paramagnetic dispersion relation, which are nearly equal in magnitude but opposite in sign. We also found a new optical absorption due to Ce^{3+} at $hv = 2.1$ eV which does not enhance the Faraday effect. The electronic transitions observed in the IR region may be attributed to the charge transfer transition from Ce^{3+} ($4f$) to Fe^{3+} (tet.) rather than the $4f$-$5d$ intraorbital transition in Ce^{3+} ions.

ACKNOWLEDGMENT

[1] M. Gomi, K. Satoh, and M. Abe, Jpn. J. Appl. Phys. **27**, L1536 (1988).
[2] M. Gomi, K. Satoh, and M. Abe, in "Proceedings of the 5th International Conference on Ferrites," Bombay, India, *Advances in Ferrites*, edited by C. M. Srivastava and M. J. Patni (Trans Tech, Switzerland, 1990), p. 919.
[3] M. Gomi and M. Abe, Mater. Res. Soc. Symp. Proc. **150**, 121 (1989).
[4] M. Kucera, J. Bok, and K. Nitsch, Solid State Commun. **69**, 1117 (1989).
[5] J. C. Suits, IEEE Trans. Magn. **MAG-8**, 95 (1972).
[6] M. J. Weber, Solid State Commun. **12**, 741 (1973).
[7] T. Tamanoi, M. Ariizumi, K. Shinagawa, T. Saito, and T. Tsushima, J. Magn. Soc. Jpn. **13**, 44 (1989) (in Japanese).
[8] S. H. Wemple, J. Electron. Mater. **3**, 243 (1974).
[9] G. B. Scott and J. L. Page, Phys. Status Solidi (b) **79**, 203 (1977).
[10] M. Gomi, H. Furuyama, and M. Abe, in Digests of The 13th Annual Conference on Magnetics, Yokohama, Japan, 1989, p. 148.