Journal of Korean Magnetics Society, Volume 5, Number 5, October 1995

LASER ABLATION OF Bi-SUBSTITUTED GADOLINIUM IRON GARNET FILMS WITH LARGE FARADAY ROTATION

N.Watanabe and K.Tsushima

Faculty of Computer Science & Systems Engineering, Kyushu Institute of Technology,
Kawazu 680-4, Iizuka, Fukuoka 820, Japan

Abstract- Bi-substituted gadolinium iron garnet films were deposited on GGG(111) and NGG(111) substrates by irradiating KrF excimer laser onto targets having compositions of $Bi_xGd_{3-x}Fe_5O_{12}$ ($2.0 \leq x \leq 3.0$) under substrate temperature of 580~620°C. Analysis on structure, composition and angle of Faraday rotation, θ_F, were carried out. The composition, the structure and the magneto-optical properties of the obtained films were found to be strongly dependent both on the compositions of the targets and on the pressure of oxygen. Before annealing in air, all films showed $\theta_F \geq 0$ at λ=6328Å, while several films showed $\theta_F \leq 0$ after the annealing. The highest value of Bi-substitution up to $x = 1.76$ with uniform composition was obtained.

I. INTRODUCTION

It was in 1972 and 1973, that Wittekoek *et al.*[1] and Takeuchi *et al.*[2] have found a substitution of bismuth in rare earth iron garnet crystals enhances greatly an angle of Faraday rotation. Unfortunately, the amount of substitution of bismuth in bulk garnet crystals has been limited experimentally to an unsatisfied amount at that time, until one of the authors (K.T.) has proved to be able to grow bulk crystals of $Bi_xGd_{3-x}Fe_5O_{12}$ (BiGdIG) with a maximum value of x=1.4 by using an improved flux method in 1984[3].

Almost at the same time, Hansen *et al.*[4] have found the angle of Faraday rotation increases quite proportionally to the amount of substituted bismuth in these garnets. They have used a liquid phase epitaxal method to grow thin crystals on a substrate of gadolinium gallium garnet. Followed by the above-mentioned publications, Okuda *et al.*[5] have written a paper to be able to grow thin films of totally bismuth substituted iron garnet, $Bi_3Fe_5O_{12}$, by using an ion beam sputtering technique. Surprisingly, the angle of Faraday rotation for the film of $Bi_3Fe_5O_{12}$ thus obtained has been proved to the expected value which is proportional to the substituted amount of bismuth.

All of these results have given a strong and sound basis of using a series of bismuth substitued rare earth iron garnets for magneto-optical device application such as an optical isolator[6] and a magneto-optical recording medium.

We have undertaken another possible technique to grow thin films of bismuth substituted rare earth iron garnets by a laser ablation method which has been proved to be suitable for growing thin films of superconducting oxides since a discovery of high temperature superconductors in 1986. We shall describe some of our results on growing the bismuth substituted rare earth iron garnets which should be non-equilibrium phase when the amount of substitution of bismuth exceeds almost two thirds of rare earth sites. Then, followed by our experimental results of the Faraday rotation and the optical absorption in a visible wave length region, we shall discuss a possible theoretical explanation for these results.

II. EXPERIMENTAL PROCEDURE

Targets with various compositions of $Bi_{x_{nom}}Gd_{3-x_{nom}}Fe_5O_{12}$ ($0 \leq x_{nom} \leq 3$, x_{nom} represents a nominal composition of Bi contents in a target) were prepared by an usual sintering method under temperature from 900°C to 1150°C, which was determined from thermal analysis (TG and DTA) on the targets. For the targets with $x_{nom} \leq 2.0$, lines of garnet phase were observed in X-ray diffraction patterns, while several oxides such as Bi_2O_3, $BiFeO_3$ and γ-Fe_2O_3 were found for $x_{nom} \geq 2.0$.

A KrF excimer laser (Questek 2560vβ: λ=248nm, pulse energy=210mJ, pulse duration=28ns) was used for the pulsed laser deposition (PLD). The laser beam was focused onto a surface of a target with the incident angle of 70 degree to the surface normal. Particles vaporized from the target were deposited onto two substrates of gadolinium gallium garnet (GGG+Ca,Mg,Zr,(111)plane, lattice constant a=12.494Å) and neodimium gallium garnet (NGG,(111)plane, lattice constant a=12.501Å) with a size of $10\times10mm^2$. These two substrates were placed just above the target with distance of 50mm so that the center of the film thickness is located at the corner of each substrate. A computer was used to monitor the temperature of the substrates (T_{sub}) which were heated up to 580~620°C with a nichrome heater. The pulse energy of the laser was controlled to be 200±10mJ on the surface of the target with fluence of $2J/cm^2$. The laser deposition was carried out for 30 minutes under repetition rate of 10Hz. The total pressure P_{Total} in the chamber was controlled to be 5mTorr (base pressure, without oxygen

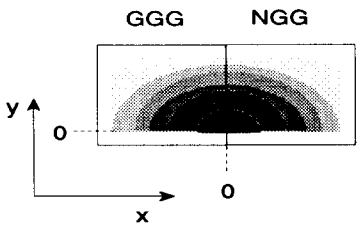

Figure 1: Directions of the x- and y-axis on the substrates. The thickness is measured at the edges of the film.

flow), 25mTorr and 55mTorr. After the deposition, the films were quenched to the room temperature in the same oxygenic flow. In the paper, five films will be discussed which were grown under condition of Table I.

Table I.Condition of PLD for several films.

	No.				
	1	2	3	4	5
Bi-contents	2.5	2.75	3.0	3.0	3.0
Substrate	GGG+Ca,Mg,Zr(111) and NGG(111)				
$T_{sub}(°C)$	600			580	620
$P_{Total}(mTorr)$	25				

After the film preparation, the thickness of the films was measured on the edges of the films by a step of 1mm along the x- and y-direction shown in Fig.1. Using the set of data, the thickness was approximated by least square fitting to a cone shape with the center being on the edges of two films. An experimental error on the thickness of the film is less than 5%.

Small specimens with size of $6\times4mm^2$ were cut from the films so that they contain the center of thickness, then they were analyzed using an X-ray diffractometer, an electron probe micro-analyzer (EPMA) and a magneto-optics analyzer which can measure the angle of Faraday rotation with an accuracy of $1mdeg$. Faraday loop at λ=6328Åand Faraday spectra were measured at the center of thickness using a slit with an aparture of $1mm\phi$. After these analyses, several films were annealed at 630°C in air for 3 hours. The heating and cooling rate was 10°C/hour. The same measurements were carried out after the annealing.

It is known that a lattice constant of a BiGdIG film can

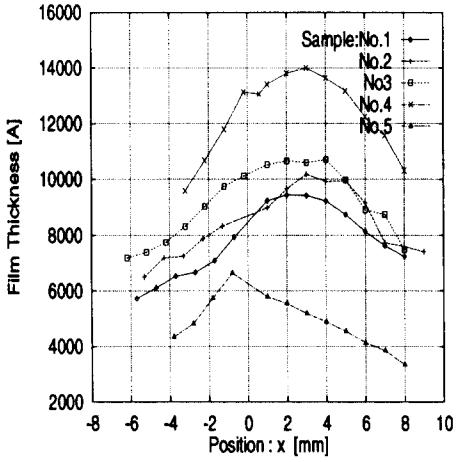

Figure 2: Thickness of the films along the x-direction.

be calculated by a simple formula of

$$a(x) = 0.05x + 12.475(\AA) \quad (1)$$

from an X-ray analyses, where x is Bi content in the film. Also, from the angle of Faraday rotation, we can obtain x by an equation

$$\theta_F(6328\AA) = -2.1448x + 3.45 \times 10^{-2}[deg./\mu m]. \quad (2)$$

Of course these equations are valid under assumption that whole film is made of single phase of BiGdIG.

Ⅲ. RESULTS AND DISCUSSIONS

3.1 Distribution of Thickness

The thickness of the obtained films on GGG substrates along the x direction is shown in Fig.2. As seen in the figure, each film have large distribution of the thickness with center nearby x=3(mm). The thickness decreases with increasing substrate temperature, T_{sub}.

3.2 Crystal Structure and Magneto-Optical Properties

Figure3 shows a dependence of an X-ray pattern on Bi-contents for films 1-3 prepared under 600°C. In the film of x_{nom}=2.5 (Fig.3(a)) we could find a diffraction peak of BiGdIG phase in the vicinity of 50deg, while no other peak can be seen except a sharp line at 24deg. Thus, BiGdIG phase is growing epitaxially on the GGG(111) substrate even though the peak is not so sharp. From eq.(1), Bi contents in these films are calculated under the assumption that whole films are made of single phase of BiGdIG. From Fig.3(a) and (b), we obtain $a(x)$=12.59Åand $a(x)$=12.66Å, resulting x=2.27 for

Journal of Korean Magnetics Society, Volume 5, Number 5, October 1995

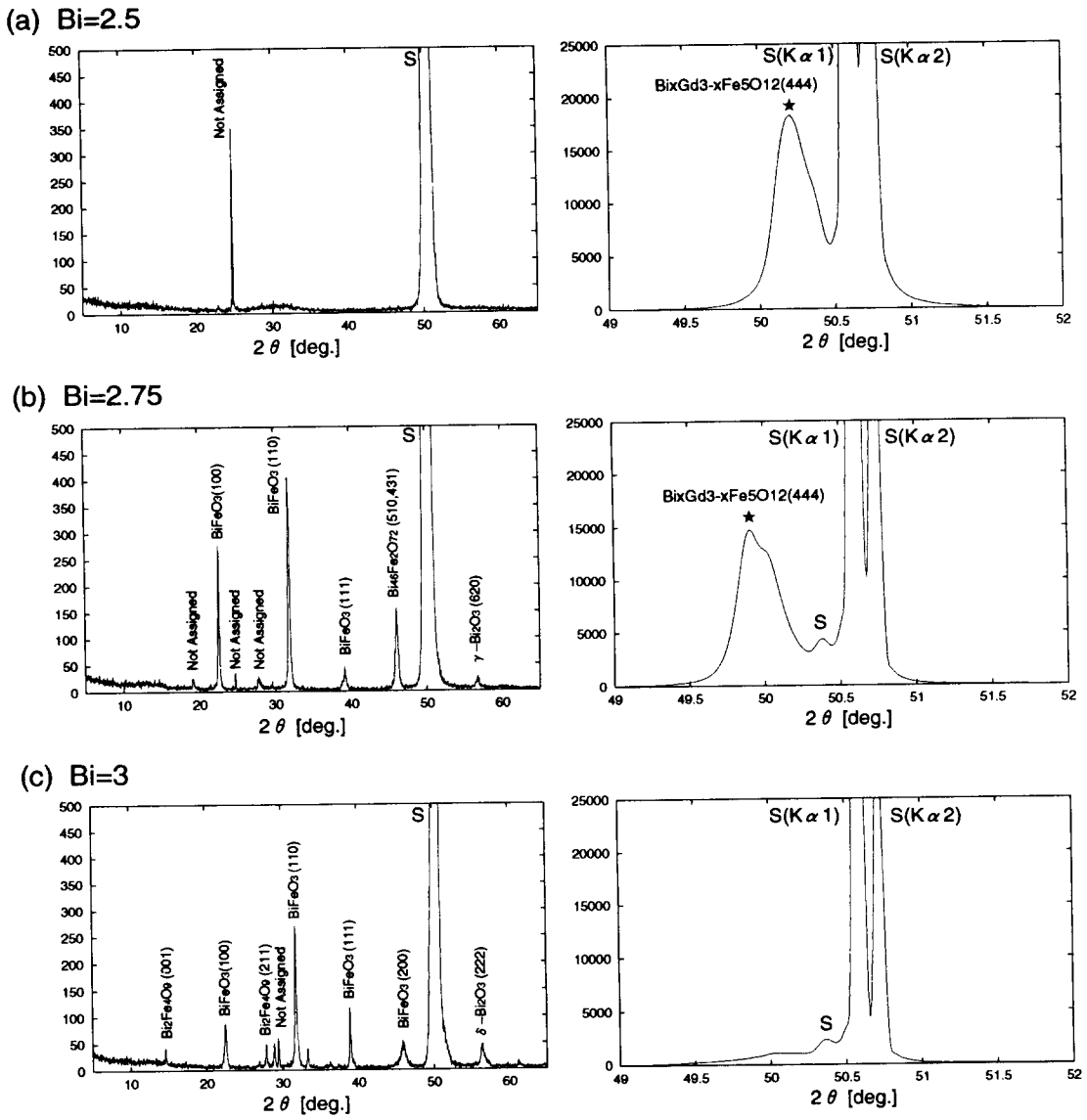

Figure 3: X-ray pattern of films for (a)x_{nom}=2.5, (b)x_{nom}=2.75 and (c)x_{nom}=3.0 in a formula of $Bi_xGd_{3-x}Fe_5O_{12}$

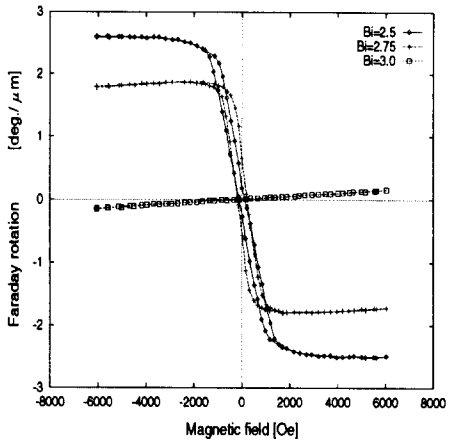

Figure 4: Faraday loops of films for (a) x_{nom}=2.5, (b) x_{nom}=2.75 and (c) x_{nom}=3.0 in a formula of $Bi_{x_{nom}}Gd_{3-x_{nom}}Fe_5O_{12}$ at 6328Å

x_{nom}=2.5 and x=3.636 for x_{nom}=2.75, respectively. The latter value, x=3.636, is out of sense since even a full substitution is x=3.0. Thus the lattice of the film may be distorted significantly by the laser ablation. For the film with x_{nom}=2.75 many oxides such as $BiFeO_3$, $Bi_{46}Fe_2O_{72}$ and γ-Bi_2O_3 are found, though BiGdIG phase is growing as shown in the figure. For the film with x_{nom}=3.0, no trace of BiGdIG phase is seen, while we can see many bismuth-containing oxides.

Faraday loops of these films are plotted in Fig.4. In this figure films with x_{nom}=2.5 and 2.75 show relatively large θ_F with negative sign, while that is much smaller and positive for the film x_{nom}=3.0. From these values of θ_F, bismuth contents of these films are calculated using eq.(2) as x=1.2 for x_{nom}=2.5 and x=0.84 for x_{nom}=2.75. These values are remarkably different from those obtained by the X-ray analysis.

We also obtained several peculiar films on NGG(111) substrate for x_{nom}=2.75. Fig.5(a) shows an X-ray diffraction pattern of the film in the vicinity of NGG(444) peak. In this case, x can be calculated as 3.494, showing the lattice of the film also being distorted significantly. To confirm this, the film was annealed in air for 3 hours under 630°C. As shown in Fig.5(b), the lattice constant became smaller by the annealing showing the system was stabilized. Faraday loops of the film before and after the annealing are plotted in Fig.6. θ_F decreased from -3.56$deg./\mu m$(x=1.68) to -3.18$deg./\mu m$ by the annealing, though the shape of the loop became much better.

We could observe relatively large θ_F (-3.73$deg./\mu m$) for the film of x_{nom}=3.0 (Fig.7), and the film showed

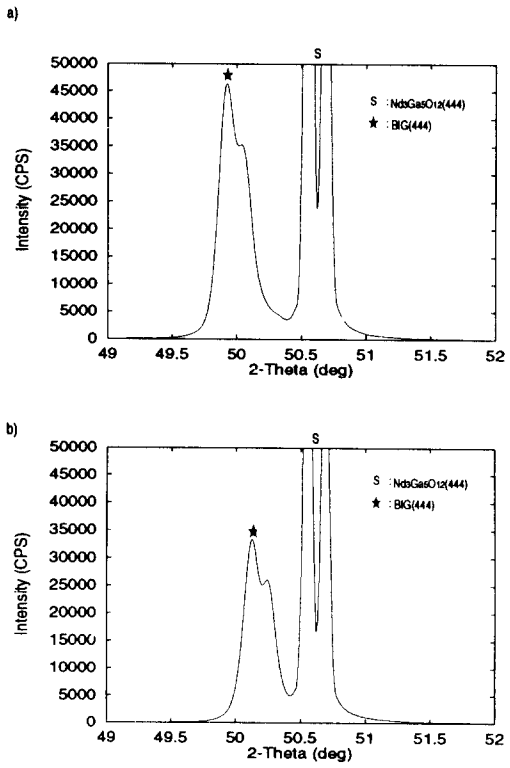

Figure 5: X-ray pattern of a film x_{nom}=2.75 nearby NGG(444). (a) $as-grown$, (b) after annealing.

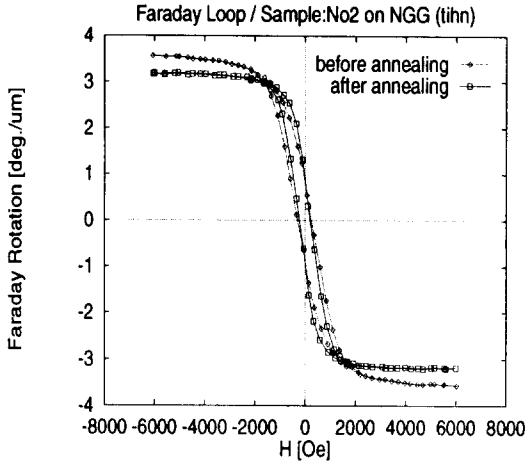

Figure 6: Faraday loops of a film x_{nom}=2.75. (a) $as-grown$, (b) after the annealing.

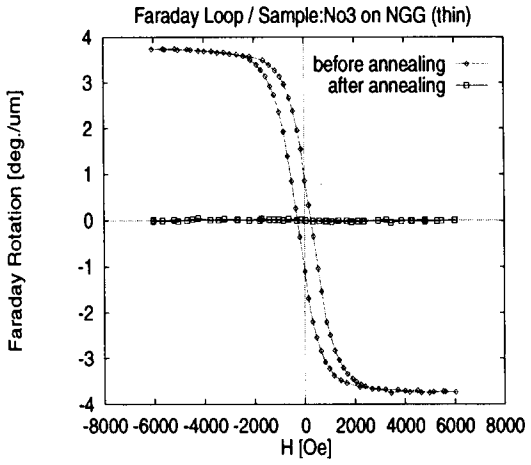

Figure 7: Faraday loop of a film x_{nom}=3.0. (a) $as-grown$, (b) after the annealing.

a=1.82Å(x=2.95) from the X-ray analysis. This result is more surprising, since the system has no Gd atoms in it. The rotation and the peak of BiIG in X-ray pattern thoroughly disappeared by the annealing. Therefore, BiIG may be growing at least locally in these films.

Recently, Kidoh *et al.*[7] have published a similar paper on a laser ablation of $Y_{3-x}Bi_xFe_5O_{12}$ with $x \sim 1.0$.

3.3 Faraday Spectra and Optical Absorption

Optical absorption spectra and Faraday spectra of films on GGG with x_{nom} of 2.5, 2.75 and 3.0 are shown in Fig.8(a) and (b), respectively. Optical absorption spectra of these films show similar behavior on wavenumber as seen in Fig.8(a), while the behavior of θ_F is dependent on each film. The films x_{nom}=2.50 and 2.75 show similar and large dependence of θ_F on wavenumber, though θ_F of the film x_{nom}=3.0 is much smaller.

Optical properties reflect the microscopic magnetic characteristics in magnetic materials. Rare earth iron garnet, $R_3Fe_5O_{12}$, has long been studied extensively because of relatively large angle of Faraday rotation at room temperature in the near infrared wave length region with small optical absorption. Faraday rotation is expressed in a macroscopic form as

$$\theta_F = \omega\, l\, (n_+ + n_-)/2c, \qquad (3)$$

where ω, l and c represent an angular frequency of incident light, an optical path length of a magneto-optical medium and the light velocity, respectively. n_+ and n_- are refractive indices for right and left circularly polarized light, respectively. From a microscopic viewpoint, spin-orbit splitting, Δ, in the optically excited level is very

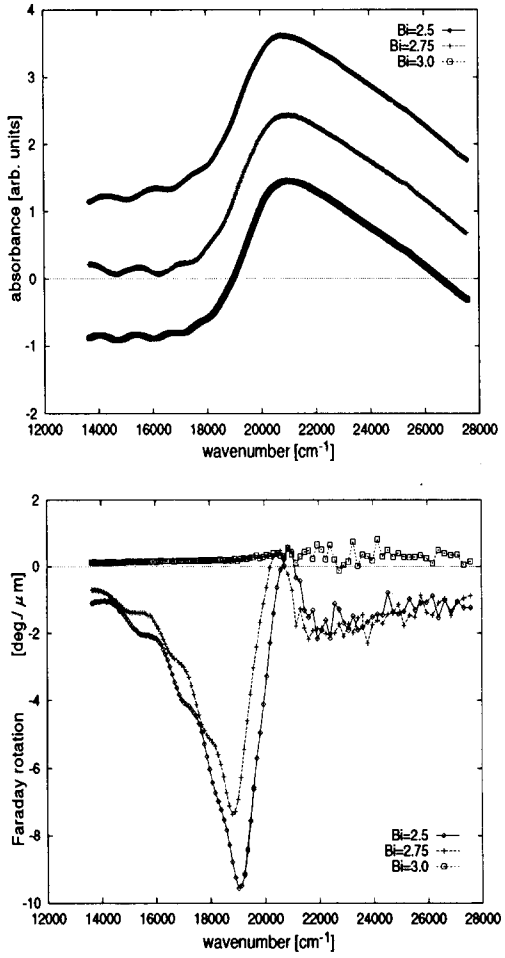

Figure 8: Optical absorption and Faraday spectra on films with x_{nom} of 2.5, 2.75 and 3.0.

important to give rise to the Faraday rotation. That is, an excited level is split by the spin-orbit interaction of the constituent atoms and the optical transition has different final states depending on the right and left circularly polarized light. This causes differences between n_+ and n_-.

The Faraday rotation is given in a microscopic term as

$$\theta_F = f\ \Delta\ l\ \frac{\pi N e^2 \omega}{m\ c\ n\ \omega_0}\ \frac{((\omega-\omega_0)^2-\gamma_0^2)}{((\omega-\omega_0)^2+\gamma_0^2)}\ . \qquad (4)$$

Here, f is an oscillator strength at the frequency ω. If we take p^2 as the transition probability at the same frequency, f is given as $f{=}2m\omega_0 p^2/e^2$, where ω_0 is the transition frequency with no spin-orbit splitting. γ_0, line width of the absorption, N, the number of magnetic ions, n, the average refractive index given by $n = (n_+ + n_-)/2$, m, electron mass and e, electronic charge. Faraday rotation, θ_F, is proportional to f and Δ. For a given f, therefore, θ_F becomes larger if the transition concerned has larger Δ.

From eq.(4) and Fig.8, it is concluded that spin-orbit coupling in this system plays most important role to θ_F than oscillator strength.

Then what is the reason for such linear enhancement of Faraday rotation with bismuth substitution? In a garnet system, there are three kinds of sites of cations, (a)octahedral, (d)tetrahedral and (c)dodecahedral sites. Applying an analysis by Crossley *et al.*[8], Faraday rotation can be written as

$$\begin{aligned}\theta_F &= -[A_e(\lambda)+A_m(\lambda)]M_a + [D_e(\lambda)+D_m(\lambda)]M_d \\ &\quad -[C_e(\lambda)+C_m(\lambda)]M_c, \qquad (5)\end{aligned}$$

where M_a, M_b, M_c are sublattice magnetization, A_e, D_e, C_e are magneto-optical coefficients for electrical dipole transitions and A_m, D_m, C_m are magneto-optical coefficients for magnetic dipole transitions. These coefficients can be written at 0.63μm as

$$\begin{aligned}A'(x) &= -300x - 350 \\ D'(x) &= -700x + 500 \\ C'(x) &= 35x + 10 \quad [deg/cm\mu_B], \qquad (6)\end{aligned}$$

where $A' = A_e + A_m$ etc. The dependence of coefficient D' on bismuth concentration is two times or more larger than A', and the sign changes from positive to negative at x=0.7. Therefore it is concluded that the large negative Faraday rotation mainly comes from iron atoms of tetrahedral sites[9]. These results are consistent with our experimental results.

IV. CONCLUSIONS

1. *as-grown* films of bismuth-substituted gadolinium gallium garnet are prepared by a pulsed laser deposition method.
2. The quality of the films for $x \leq 1.4$ is good from the viewpoint of crystallographical and magneto-optical properties.
3. For $x \geq 1.4$, we found several films which have unusually large lattice constants though the angle of Faraday rotation was small.
4. From optical absorption and Faraday spectra on these films, it was confirmed that spin-orbit coupling plays much important role for the rotation.

ACKNOWLEDGMENTS

This work has started in 1990 and needed many help by students in our laboratory. We would like to mention names of these students and express our thanks to all of them, B.Ishikawa, K.Hayashida, K.Higuchi and K.Kawano.

The work was supported in part by a Grant-Aid for Scientific Research 02402033 from the Japanese Ministry of Education, Science and Culture.

REFERENCES

[1] S.Wittekoek and D.E.Lacklison : Physical Rev.Lett., 28 (1972) 740

[2] H.Takeuchi, K.Shinagawa and S.Taniguchi : Jpn.J.Appl.Phys., 12 (1973) 465

[3] T.Tamaki and K.Tsushima : J.Mag.Soc.Japan, 8 (1984) 125

[4] P.Hansen, W.Torksdorf, K.Witter and J.M.RObertson : IEEE Trans.Magn.MAG-20 (1984) 1099

[5] T.Okuda, T.Katayama, H.Kobayashi and N.Kobayashi : J.Appl.Phys., 67 (1990) 4944

[6] T.Tamaki and K.Tsushima : Advances in Magneto-Optics II, Proc. 2nd Int. Symp. Magneto-Optics, 18 (1992) 415

[7] H.Kidoh, H.Yashima, A.Morimoto and T.Shimizu : Jpn.J.Appl.Phys. 33 (1994) 4094

[8] W.A.Crossley, R.W.Cooper, J.L.Page and R.P.van Stapele : Phys.Rev.181 (1969) 896

[9] P.Hansen, H.Heitmann and K.Witter : Phys.Rev.B23 (1981) 6085