

Preparation and Characterization of Bi substituted gadolinium iron garnet $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ films with $x = 1$ to 2.5 by Enhanced Metal Organic Decomposition method

D. A. Wahid, J. Sato, M. Hosoda, and H. Shimizu

Department of Electronic and Information Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-cho, Koganei-shi, Tokyo 184-8588, Japan

Bismuth substituted gadolinium iron garnet thin films ($\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$) were prepared with $x = 1, 2,$ and 2.5 on glass substrates by enhanced metal organic decomposition (EMOD) method. We mixed the solution containing Fe_2O_3 , Bi_2O_3 and Gd_2O_3 carboxylates so that we could obtain desired Bi content x . X-ray diffraction (XRD), optical transmittance / reflectivity, and Faraday rotation (FR) were measured for characterizations in order to examine their dependence on annealing temperatures and different amount of Bismuth substitution (x). When $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films were directly prepared on glass substrates, Bi_2O_3 phase were observed by XRD measurements and with increasing Bi content x from 1 to 2, the FR increased from 1.2 to 5.8 deg./ μm at the wavelength of 530 nm. FR of $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin films prepared directly on glass substrates were smaller (0.35 deg./ μm) than those with $x = 2$. When $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin films were prepared with annealing temperature of 620°C with $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer on glass substrates, the films showed garnet crystal structure and FR, which is comparable with that of $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin films prepared on (111) $(\text{GdCa})_3(\text{GaMgZr})_5\text{O}_{12}$ (SGGG) single crystal substrates. These results demonstrate that $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films can be prepared on glass substrates with controlled Bi content and that FR as high as that prepared on the SGGG substrate can be obtained by the EMOD method.

Key words: magnetic garnet, enhanced metal organic decomposition method, Faraday effect.

1. Introduction

Bismuth substituted rare-earth iron garnets have a considerable interest owing to their large magneto optic effect. Large FR with high transparency in the visible to near infrared range¹⁾ are key properties which made the magnetic garnet materials suitable for various applications for magneto-optical device elements such as in magnetoplasmonic structure²⁾, optical isolators³⁾, circulators^{4,5)}, and magnet photonic crystals (MPCs) used in magneto-optic spatial light modulators (MOSLM)⁶⁻⁹⁾.

Bismuth substituted gadolinium iron garnet ($\text{Bi}:\text{GdIG}$) is a ferrimagnetic material and shows perpendicular magnetic anisotropy, which is one of the most desirable materials for magneto optical devices owing to its high optical transmittance and extremely high magneto optical activity in the visible and near infrared regions^{10,11)}, which enable this material to have high frequency application. FR can be controlled by Bi substitution of Gd. Therefore, it is very important to control the amount of Bi substitution in order to control and increase the FR. There are several methods to prepare the bismuth substituted rare-earth iron garnet thin films such as a laser ablation¹²⁾, a liquid phase epitaxy¹³⁾, RF magnetron sputtering¹⁴⁾, etc. Among them,

metal organic decomposition (MOD) method is a promising one to prepare magnetic garnet film, because it is a simple fabrication method which is composed of spin coating of the MOD solution and annealing, and guarantees high uniformity in chemical composition and purity combined with chemical stability. It was reported that $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$, $\text{Bi}_x\text{Y}_{3-x}\text{Fe}_5\text{O}_{12}$, and $\text{Bi}_x\text{Y}_{3-x}(\text{FeGa})_5\text{O}_{12}$ thin films were prepared on gadolinium gallium garnet (GGG)¹²⁻¹⁷⁾ and glass substrates¹⁸⁾. We have prepared $\text{Bi}:\text{GdIG}$ thin films on GGG substrates by annealing with and without O_2 gas and investigated the crystal growth process and magnetic anisotropy¹⁹⁾. The fabrication of magnetic garnet such as $\text{Bi}_{2.5}\text{Y}_{0.5}\text{Fe}_5\text{O}_{12}$ films was reported by using $\text{Nd}_2\text{Bi}_1\text{Fe}_4\text{Ga}_1\text{O}_{12}$ buffer layers on glass substrate which was fabricated by the MOD method, and FR of 13.8 deg./ μm at $\lambda = 520$ nm was reported for the $\text{Bi}_{2.5}\text{Y}_{0.5}\text{Fe}_5\text{O}_{12}$ films¹⁸⁾. It is important to obtain $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films having higher Bi content x and FR. However, it is reported that preparation of $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ with high Bi content on glass substrates is difficult¹²⁻¹⁷⁾. Therefore, fabrication of $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films with various Bi content x and characterization of FR are important. In order to investigate the effect of changing the Bi content x on FR of $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films by increasing the Bi content x systematically, we fabricated the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin

films on glass substrates by the EMOD method. Furthermore, we used the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer in order to fabricate the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films with higher x of 2.5 showing larger FR by the EMOD method.

2. Experiments

We fabricated $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films with $x = 1, 2$ and 2.5 at different annealing temperatures of 620°C , 650°C and 700°C on $15\text{ mm} \times 15\text{ mm}$ glass substrate, and $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin film with $x = 2.5$ on $12\text{ mm} \times 12\text{ mm}$ SGGG (111) single crystal substrate and $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer / glass substrate by the EMOD method. The EMOD liquids used in this experiment are SYM-FE05 containing Fe_2O_3 carboxylates, SYM-BI05 containing Bi_2O_3 carboxylates, and SYM-GD01 containing Gd_2O_3 carboxylates by Kojundo Chemical Laboratory so that we could obtain $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films with desired Bi content x . Kojundo Chemical Laboratory Ltd provides their own MOD solutions, as well as EMOD solutions developed by Symetrix corporation of the United States and Kojundo Chemical Laboratory Ltd²⁰. The MOD solution contains 2 – 3 kinds of metal oxides carboxylates such as Bi_2O_3 , Gd_2O_3 , and Fe_2O_3 carboxylates in acetic ester to prepare $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films. In case of preparation of $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films by the MOD method, Bi content x is fixed. On the other hand, the EMOD solution contains one metal oxide carboxylate in xylene and can be mixed with other EMOD solutions containing other metal oxide. Therefore it is possible to prepare the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films in any proportion of Bi content x , which enables greater degree of freedom and more precise control of composition in order to prepare $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films. When we prepare the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films with different Bi content x by the EMOD method, the EMOD solutions of Fe_2O_3 carboxylate (product name SYM-FE05), Bi_2O_3 carboxylate (product name SYM-BI05), and Gd_2O_3 carboxylate (product name SYM-GD05), are mixed and combined for different Bi content x , which is advantage compared with the MOD method. The selected components were mixed in the desired stoichiometric ratio of $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ with different value of $x = 1, 2$ and 2.5 and stirred well. The solution was then filtered by advantec filter paper. The solution was spin-coated in 2 steps process of 500 rpm for 10 s and 2000 rpm for 20 s, followed by drying on a hot plate at 120°C for 10 min and the solvent are evaporated. In order to decompose the organic materials and obtain the amorphous metal oxide films, the

samples were pre-annealed at 550°C for 10 min. The thickness by single spin coating step is typically 20 - 30 nm. The conditions for spin coating, drying, and pre-annealing were fixed. We changed the mixing ratio of the SYM-BI05 and SYM-GD01 solutions in order to change the Bi substitution x in $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films, and changed the final-annealing temperature. The thickness of the samples slightly changes with the spin coating speed, time and viscosity of the solutions. Spin coating, drying and pre-annealing were repeated for 11 times to obtain an appropriate thickness. Spin coating, drying and pre-annealing, were repeated 6 times for the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ films on the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer / glass substrate. Also, we prepared a $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ film on SGGG (111) single crystal substrate for a reference sample to compare the FR. The amorphous $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ films prepared by pre-annealing process were then annealed at 620, 650 and 700°C for 2 hours for crystallization (final annealing). The pressure during the annealing was atmospheric pressure. Bi:GdIG thin films prepared in this study were characterized by x-ray diffraction (XRD), optical transmittance, optical reflectivity, and FR spectra. All the measurement was done at room temperature. We measured the XRD from the central part of the samples. The diameter d of the x-ray beam is about 0.4 mm. Therefore, the measurement results of the XRD show average crystallinity of the samples over $d = 0.4\text{ mm}$. We estimated the thickness of the samples from the optical reflectivity spectra, and discussed the relationship between XRD and FR spectra.

3. Results and Discussion

Figure 1 shows the optical reflectivity spectra (wavelength $\lambda = 250 - 2600\text{ nm}$) of the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ samples annealed at 620, 650 and 700°C , with the Bi content $x = 0, 1, 2$ and 2.5 on glass substrates. The incident direction of the light was normal to the sample. In order to estimate the thickness of the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ films, we fitted the measured optical reflectivity spectra to reproduce the experimental results by the calculated reflectivity spectra. We calculated the reflectivity spectra by considering the multiple reflection inside the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ films by interfaces between air / film (af) and film / glass substrate (fs). We assumed that the film thickness is uniform and the glass substrate is non-absorbing and incoherent material. The reflectivity R is calculated by the following formula (1)^{21,22}.

$$R = R_{afs} + \frac{R_{sa}(T_{afs})^2}{1 - R_{sa}R_{sfa}} \quad (1)$$

where R_{afs} , is the reflectivity within the interface between air (a), film (f), and the interface between film (f) and substrate (s), R_{sfa} is the reflectivity within the interface between substrate (s), film (f), and the interface between film (f) and air (a), and T_{afs} is the transmission within the interface between air (a), film (f), and the interface between film (f) and substrate (s). R_{afs} , R_{sfa} and T_{afs} include the effect of multiple reflections inside the film and can be expressed by the following formulas (2), (3) and (4). They are related to the film thickness d , wavelength λ , and refractive index $n - ik$ of the film. Since the refractive index has wavelength dependence, we divided the optical reflectivity spectra to two regions ($\lambda < 1000$ nm and $\lambda > 1000$ nm), and changed the refractive index and thickness to reproduce the experimentally obtained optical transmission spectra²³. In the final stage of the fitting, the films thickness d is obtained.

$$R_{afs} = \frac{R_{af} - (2R_{af}R_{fs} - R_{fs})e^{-\frac{4\pi}{\lambda}(n-ik)d}}{1 - R_{af}R_{fs}e^{-\frac{4\pi}{\lambda}(n-ik)d}} \quad (2)$$

$$T_{afs} = \frac{(1 - R_{af})(1 - R_{fs})e^{-\frac{2\pi}{\lambda}(n-ik)d}}{1 - R_{af}R_{fs}e^{-\frac{4\pi}{\lambda}(n-ik)d}} \quad (3)$$

$$R_{sfa} = \frac{R_{fs} - (2R_{af}R_{fs} - R_{af})e^{-\frac{4\pi}{\lambda}(n-ik)d}}{1 - R_{af}R_{fs}e^{-\frac{4\pi}{\lambda}(n-ik)d}} \quad (4)$$

The simulated reflectivity spectra showed by the dotted lines in figure 1. The thicknesses were estimated to 170 - 210 nm for the samples with $x = 1$, 200 - 260 nm for the samples with $x = 2$, and 330 - 360 nm for the samples with $x = 2.5$. The viscosity of the solution was increased with increasing the Bi content x . Therefore the film thickness increased with increasing the Bi content x .

Figure 2 shows the XRD spectra of the fabricated samples on glass substrates. The XRD spectra of samples shows some peaks associated with (420) plane of $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$, (104) plane of Fe_2O_3 , (112) plane of Gd_2O_3 , (008) plane of $\epsilon\text{-Bi}_2\text{O}_3$, (200) plane of BiO_3 , (222) plane of $\beta\text{-Fe}_2\text{O}_3$, and (130) plane of $\epsilon\text{-Fe}_2\text{O}_3$ phases.

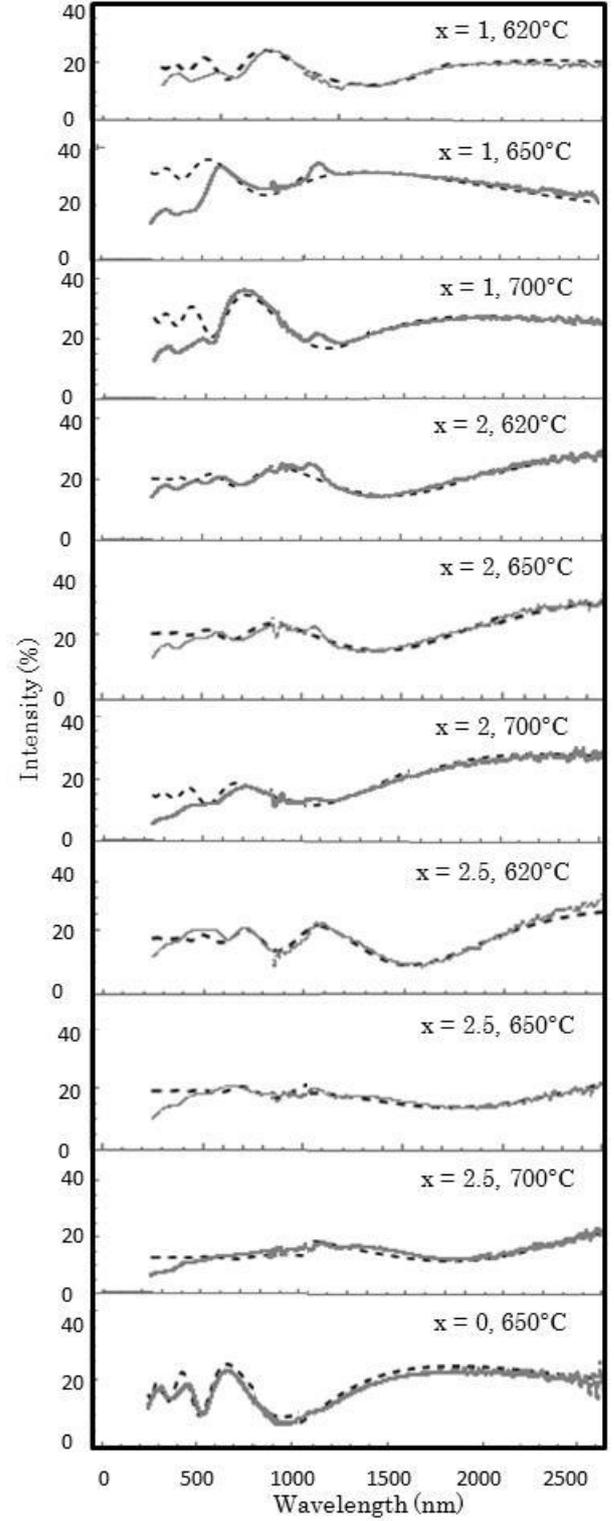


Fig. 1 Optical reflectivity spectra (solid lines) of the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ samples annealed at 620, 650 and 700 °C, with bismuth content $x = 0, 1, 2$ and 2.5 on glass substrates. The fitted spectra are shown by dashed lines.

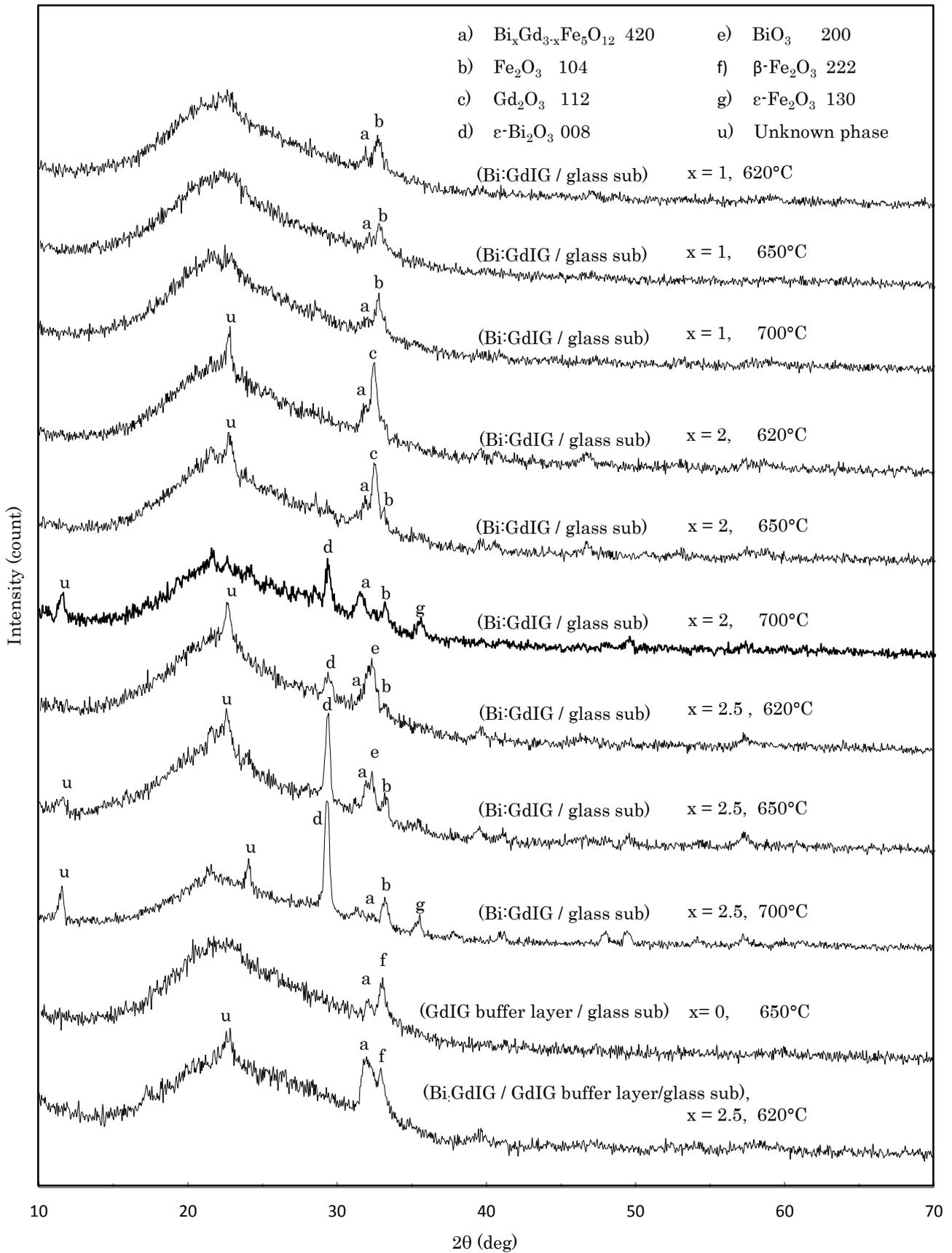


Fig. 2 X-ray diffraction spectra of the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films on glass substrates at annealing temperature of 620, 650 and 700 °C with Bismuth doped $x = 0, 1, 2$ and 2.5 on glass substrates and $\text{Bi}_{2.5}\text{GdIG}$ on GdIG buffer layer/glass substrate.

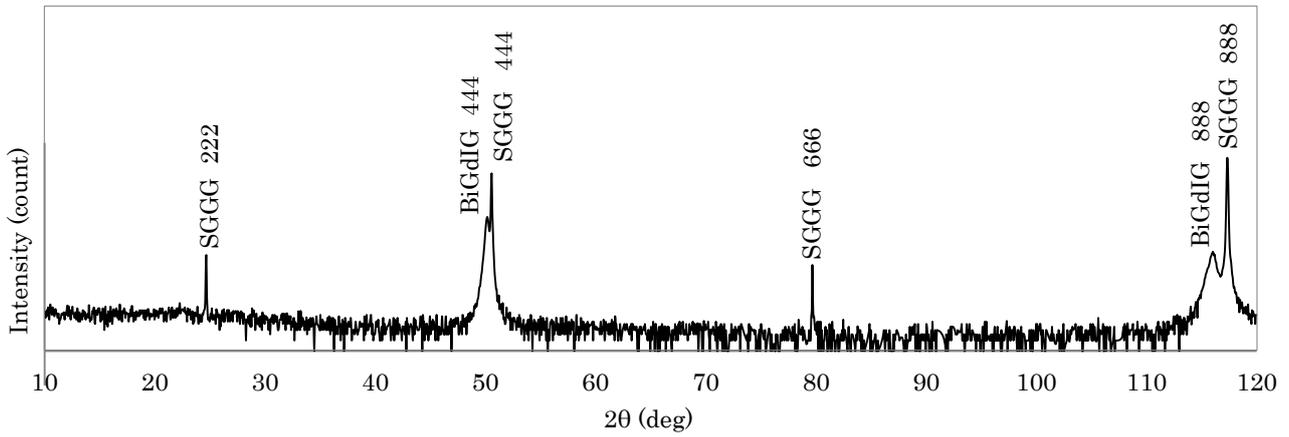


Fig. 3 X-ray diffraction spectra of the $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin film on SGGG (111) single crystal substrate at the annealing temperature of 620°C . Please note that the vertical axis is in logarithmic scale.

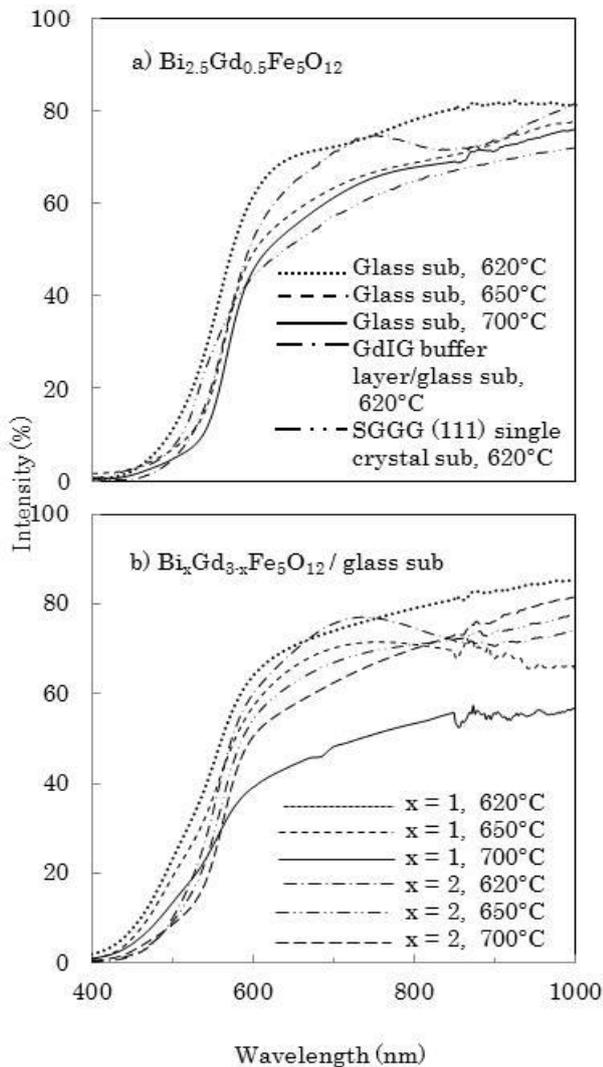


Fig. 4 Optical transmittance spectra of the Bi:GdIG samples annealed at 620, 650 and 700°C , with the bismuth content of a) $x = 2.5$ on glass, GdIG buffer layer / glass and SGGG (111) single crystal substrates, b) $x = 1$ and 2 on glass substrates.

When the Bi_2O_3 , Gd_2O_3 and Fe_2O_3 carboxylates are mixed with a ratio of 1 : 2 : 5, and the annealing temperature of $620 - 700^\circ\text{C}$ directly prepared on the glass substrates, the diffraction signal from Fe_2O_3 is larger than that from $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$. When the Bi_2O_3 , Gd_2O_3 and Fe_2O_3 carboxylates are mixed with a ratio of 2 : 1 : 5 and the annealing temperature of $620 - 650^\circ\text{C}$ directly prepared on the glass substrates, the diffraction signal from Gd_2O_3 is larger than that from $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$. When the annealing temperature is 700°C , the diffraction signal from Bi_2O_3 is increased. When the Bi_2O_3 , Gd_2O_3 and Fe_2O_3 carboxylates are mixed with a ratio of 2.5 : 0.5 : 5 and the annealing temperature of $620 - 700^\circ\text{C}$ directly prepared on glass substrates, the diffraction signals from Bi_2O_3 and $\epsilon\text{-Bi}_2\text{O}_3$ are much more dominant than that from $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$. The diffraction peak associated with $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ were the weakest with $x = 2.5$ among all the samples without the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer. With increasing the final annealing temperature, the diffraction peak associated with $\epsilon\text{-Bi}_2\text{O}_3$ increased. From the XRD spectra of the samples, it is difficult to fabricate Bi:GdIG thin films with high Bi content $x = 2.5$ directly on glass substrate. In order to solve this problem, we fabricated a gadolinium iron garnet (GdIG) thin film with composition of ($\text{Gd}_2\text{O}_3:\text{Fe}_2\text{O}_3 = 3:5$) as a buffer layer for preparation of $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films with higher Bi content x of 2.5, with the thickness of 150 nm on the glass substrate at final annealing temperature of 650°C by the EMOD method. When the Gd_2O_3 and Fe_2O_3 carboxylates are mixed with a ratio of 3 : 5, the diffraction signals from $\text{Gd}_3\text{Fe}_5\text{O}_{12}$, and $\beta\text{-Fe}_2\text{O}_3$ are dominant.

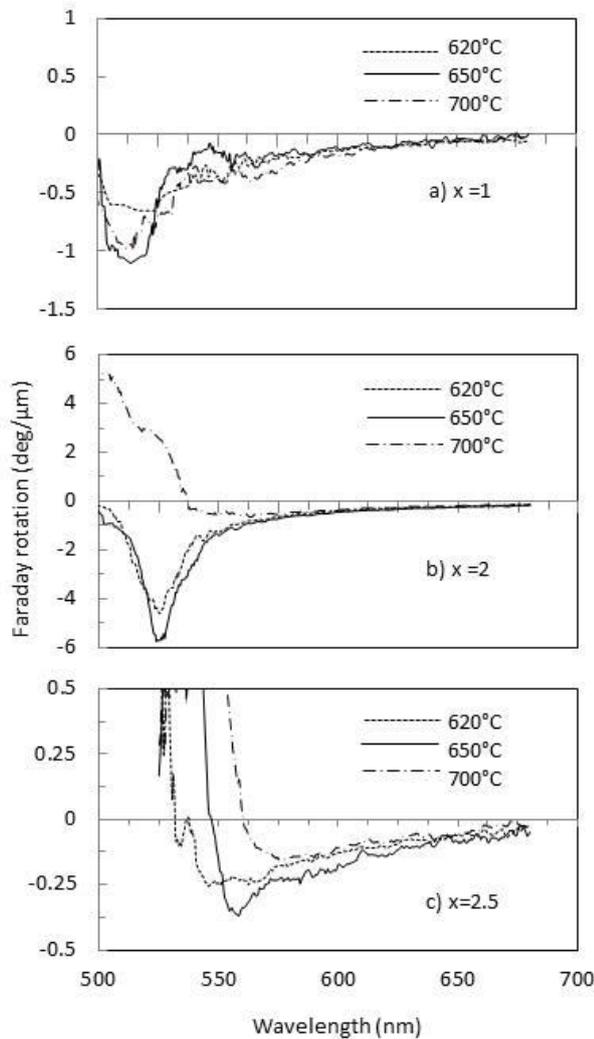


Fig. 5 Faraday rotation spectra of the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ samples with different annealing temperatures and bismuth content (a) $x = 1$, (b) $x = 2$ and (c) $x = 2.5$.

Then we tried to fabricate a $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin film on the GdIG buffer layer / glass substrate. The final annealing temperature for $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin film was set at 620°C instead of the annealing temperature of 650°C shown in figure 2. This is because when the final annealing temperature of the $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ film is the same or higher than the final annealing temperature for the GdIG buffer layer/glass sub., the part of crystal structure of the GdIG buffer layer can be destroyed²⁵. Therefore, we set the final annealing temperature at 620°C for the $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ film on the GdIG buffer layer/glass sub.

When the Bi_2O_3 , Gd_2O_3 and Fe_2O_3 carboxylates are mixed with a ratio of $2.5 : 0.5 : 5$ and the annealing temperature of 620°C with the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer on glass substrate, the diffraction signal from $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ is the most dominant and the formation of other

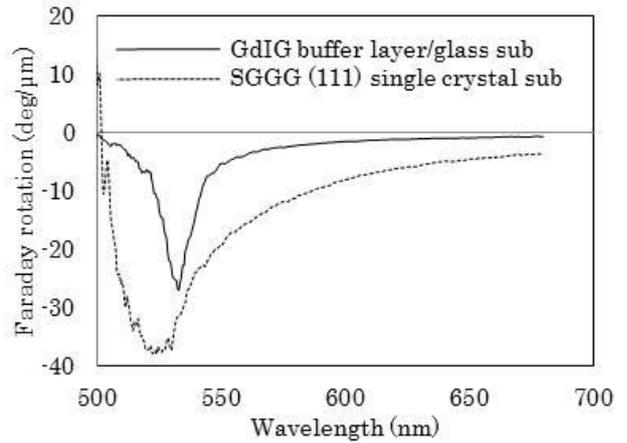


Fig. 6 Faraday rotation spectra of the $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ samples annealed at 620°C with the bismuth content $x = 2.5$ on gadolinium iron garnet buffer layer / glass sub and SGGG (111) single crystal substrates.

phases such as $\epsilon\text{-Bi}_2\text{O}_3$, BiO_3 and Gd_2O_3 are suppressed. The diffraction peak associated with $\beta\text{-Fe}_2\text{O}_3$ at the right side of the Bi:GdIG diffraction peak is associated with the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer. From figure 2, it was confirmed that the $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin film having garnet crystal structure was prepared with the buffer layer on glass substrate by the EMOD method.

Figure 3 shows the XRD spectra of $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ prepared by the EMOD method on (111) SGGG single crystal substrate. 444 and 888 diffraction peaks are clearly observed and other peaks associated with polycrystalline or impurity phases were not observed. The lattice constant a was calculated to 1.2587 nm . It was reported that the lattice constant of $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ samples prepared by liquid phase epitaxy (LPE) was 1.259 nm ²⁴, and comparable to that of our $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin films on (111) SGGG substrate. By comparing the lattice constant of two materials and the results of figure 3, we estimated the composition of our single crystal film to $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ by the EMOD method. Also the diffraction peaks associated with Bi_2O_3 , Gd_2O_3 , Fe_2O_3 , GdIG and BiGdIG of the polycrystalline samples on the glass substrates were confirmed by comparing the lattice spacing d measured by the XRD to the powder diffraction files of international center for diffraction data (ICDD). Therefore, we estimated the fabricated crystal structure by the EMOD method to the garnet structure.

Figure 4 shows the optical transmittance spectra of the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films on the glass substrates with / without $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer and on (111)

SGGG single crystal substrate. The $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ on the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer / glass sub has high transparency in visible and near infrared region, higher than the $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ film on (111) SGGG substrate.

Figure 5 shows the FR spectra of the fabricated $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films crystallized at 620, 650, and 700 °C with $x = 1, 2$ and 2.5 on glass substrates. The magnetic field of 1 T was applied perpendicular to the samples in order to fully magnetize the samples.

The samples with the annealing temperature of 650°C show larger FR (negative) than the other samples with $x = 1, 2$, and 2.5 annealed at 620 and 700 °C. Therefore the annealing temperature of 650°C is the optimum condition for crystallization of the BiGdIG thin films on the glass substrate by the EMOD method. The FR of Bi:GdIG increased with increasing x to 2, and decreased in the sample with high Bi content of $x = 2.5$.

Figure 6 shows the FR spectra of the $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin films on the GdIG buffer layer / glass substrate and SGGG (111) single crystal substrate. $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin film on the GdIG buffer layer / glass substrate showed 27.5 deg./ μm at the wavelength of 533 nm, which is 8 times larger than that without the GdIG buffer layer. This is because the sample with the GdIG buffer layer showed the largest diffraction signal from the $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ and garnet structure, and the samples without garnet structure including other phases such as Bi_2O_3 and Gd_2O_3 showing little FR, as shown in figure 2.

Maximum FR (negative) angle of the $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin films on SGGG substrate is 32.5 deg./ μm at the wavelength of 533 nm. The maximum FR of the $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin films on the GdIG buffer layer / glass substrate is comparable with that on (111) SGGG single crystal substrate. The FR of $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin films on the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer / on glass substrate (27.5 deg./ μm at $\lambda = 533$ nm) is 3 time larger than that of the reported $\text{Bi}_{1.4}\text{Gd}_{1.6}\text{Fe}_5\text{O}_{12}$ sample (9.3 deg./ μm at $\lambda = 520$ nm.), which was fabricated by sintering, hot press and annealing method²⁶⁾. Also it was reported that $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ films on $\text{Nd}_2\text{Bi}_1\text{Fe}_4\text{Ga}_1\text{O}_{12}$ buffer layers on a glass substrate which was fabricated by the MOD method had FR of 13.8 deg./ μm at $\lambda = 520$ nm, which is half of the FR of our $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ thin films on the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer / on glass substrate¹⁸⁾. Therefore, our samples fabricated by the EMOD method showed 2 - 3 times larger FR compared with that of previously reported $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ samples.

4. Conclusion

We have prepared $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films on glass substrates, with and without $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer prepared on glass substrates and (111) SGGG single crystal substrate by the EMOD method. We characterized the XRD, FR and optical transmittance spectra of the samples. The FR shows that the annealing temperature of 650 °C is the optimum condition for crystallization of $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ on the glass substrate. From the XRD spectra, the $\text{Bi}_{2.5}\text{Gd}_{0.5}\text{Fe}_5\text{O}_{12}$ samples on the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer shows that the Bi:GdIG thin films were successfully fabricated on the glass substrates without forming Bi_2O_3 and Gd_2O_3 phases, which are observed in samples without $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer. Furthermore, larger Faraday rotation (27.9 deg./ μm at $\lambda = 533$ nm) was obtained on the sample with the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer than that without $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer, and the Faraday rotation is comparable with that prepared on SGGG (111) single crystal substrate. It is important to suppress the formation of the Bi_2O_3 and Gd_2O_3 phases by the $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ buffer layer in order to prepare $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films having higher Bi content x and FR, from the XRD spectra and measurement of the Faraday rotation. These findings are important to realize $\text{Bi}_x\text{Gd}_{3-x}\text{Fe}_5\text{O}_{12}$ thin films having large Faraday rotation for future applications to MOSLMs and optical isolators on the glass substrates.

Acknowledgements This work was partially supported by JSPS KAKENHI (Grant Number 24656010 and 15K13942) and Support Center for Advanced Telecommunications (SCAT) Technology Research, Foundation. The authors would like to thank Prof. T. Sameshima for the guidance of the optical reflectivity measurement.

References

- 1) P. Hansen, H. Heitmann, and K. Witter: *Phys. Rev. B.*, **23**, 6085 (1981).
- 2) L. Halagačka, K. Postava, M. Vanwolleghem, F. Vaurette, J. Ben Youssef, B. Dagens, and J. Pištora: *J. Opt. Soc. Am. A.*, **4**, 1903 (2014).
- 3) H. Ishikawa, K. Nakajima, K. Machida and A. Tanii: *Opt Quantum Electron.*, **22**, 517 (1990).
- 4) W. Smigaj, L. Magdenko, L. Magdenko, J. Romero, S. Guenneau, B. Dagens, B. Gralak and M. Vanwolleghem: *Phot. Nano. Fund. Appl.*, **10**, 83 (2012).
- 5) W. Smigaj, J. Romero, B. Gralak, L. Magdenk, B. Dagens and M. Vanwolleghem: *Opt. Lett.*, **35**, 568 (2010).
- 6) H. Kato, T. Matsushita, A. Takayama, M. Egawa, H. Uchida, K. Nishimaura, and M. Inoue: *Trans. Magn. Soc. Jpn.*, **4**, 289 (2004).
- 7) H. Takagi, J. Kim, K. H. Chung, S. Mito, H. Umezawa, and

- M. Inoue: *J. Magn. Soc. Jpn.*, **33**, 525 (2009).
- 8) S. Mito, K. Takahashi, F. Kawanishi, K. H. Chung, H. Takagi, J. Kim, P. B. Lim, and M. Inoue: *J. Magn. Soc. Jpn.*, **32**, 63 (2008).
 - 9) K. H. Chung, J. Heo, K. Takahashi, S. Mito, H. Takagi, J. Kim, P.B.Lim and M.Inoue: *J. Magn. Soc. Jpn.*, **32**, 114 (2008).
 - 10) M. Suzuki, T. Kotani, N. Yamaguchi, T. Miura, M. Yamaoka, M. Kobayashi, and A. Misu: *J. Electron. Spectrosc. Relat. Phenom.*, **78**, 291 (1996).
 - 11) W. Eppler, and M. H. Kryder: *IEEE Trans. Magn.*, **25**, 3743 (1989).
 - 12) M. Laulajainen, P. Paturi, J. Raittila, H. Huhtinen, A.B. Abrahamsen, N.H. Andersen and R. Laiho: *J. Magn. Magn. Mater.*, **279**, 218 (2004).
 - 13) J. M. Robertson, S. Wittekoek, Th. J. A. Popma, and P. F. Bongers: *Appl. Phys.*, **2**, 219 (1973).
 - 14) Y. H. Kim, J. S. Kim and S. I. Kim: *J. Korean Phys. Soc.*, **43**, 400 (2003).
 - 15) T. Ishibashi, A. Mizusawa, N. Togashi, T. Mogi, M. Houchido and K. Sato: *J. Cryst. Growth.*, **275**, 2427 (2005).
 - 16) T. Kosaka, M. Naganuma, M. Aoyagi, T. Kobayasi, S. Niratisairak, T. Nomura, and T. Ishibashi: *J. Magn. Soc. Jpn.*, **35**, 194 (2011).
 - 17) T. Ishibashi, A. Mizusawa, N. Togashi, T. Mogi, M. Houchico, and K. Sato: *J. Cryst. Growth.*, **275**, 2427 (2005).
 - 18) T. Ishibashi, T. Yoshida, S. Ikehara and T. Nishi: *J. Appl. Phys.*, **113**, 17A926 (2013).
 - 19) D. A. Wahid, T. Hattori, J. Sato, and H. Shimizu: *J. Magn. Soc. Jpn.*, **39**, 100-106, (2015).
 - 20) <http://www.kojundo.co.jp/English/Guide/material/csd.html>
 - 21) D. Pekker, and L. Pekker: *Thin Solid Films.*, **425**, 203 (2003).
 - 22) M. M. Gader: *Euro. Intl. J. Sci. Technol.*, **2**, 214 (2013).
 - 23) R. Kitamura, L. Pilon, and M. Jonasz: *Appl. Opt.*, **46**, 8118 (2007).
 - 24) P. Hansen, K. Witter, and W. Tolksdorf: *Phys. Rev.*, **27**, 4375 (1983).
 - 25) M. Hosoda, J. Sato, D. A. Wahid, H. Shimizu: Proc. the 63rd. spring meeting of Japan Society of Applied Physics., 20a-S621-2, Tokyo, (2016).
 - 26) H. Takeuchi: *Jpn. J. Appl. Phys.*, **14**, 1903 (1975).

Received Jan. 27, 2016; Accepted May. 12, 2016