

## Nd<sub>3-x</sub>Bi<sub>x</sub>Fe<sub>4</sub>GaO<sub>12</sub> (x = 2, 2.5) films on glass substrates prepared by MOD method

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**Abstract.** We studied Nd<sub>3-x</sub>Bi<sub>x</sub>Fe<sub>4</sub>GaO<sub>12</sub> films to obtain perpendicular magnetic anisotropy as well as large Faraday effect. NdBi<sub>2</sub>Fe<sub>4</sub>GaO<sub>12</sub> (Bi2:NIGG) and Nd<sub>0.5</sub>Bi<sub>2.5</sub>Fe<sub>4</sub>GaO<sub>12</sub> (Bi2.5:NIGG) films were obtained on Nd<sub>2</sub>BiFe<sub>4</sub>GaO<sub>12</sub> (Bi1:NIGG) layer prepared on glass substrates by metal-organic decomposition (MOD) method. Bi2:NIGG and Bi2.5:NIGG films showed large Faraday rotation angles of 7.5 and 10.5 degree/μm, at a wavelength of 520 nm, respectively. Those films have perpendicular magnetic anisotropy with a coercivity of 350 Oe and a saturation magnetic field of 730 Oe.

### Introduction

Bismuth substituted rare-earth iron garnets RE<sub>3-x</sub>Bi<sub>x</sub>Fe<sub>5-1</sub>NM<sub>y</sub>O<sub>12</sub> (RE : rare-earth element, NM : non-magnetic element such as Al and Ga) is known that have high transmittance in visible region and large magneto-optical (MO) effect which increases with amount of Bismuth substitution<sup>1-7</sup>. Therefore, bismuth-substituted rare-earth iron garnets have been used for applications such as optical isolators, spatial light modulators and magneto-optical indicator films<sup>8,9</sup>.

It is well known that the rare-earth iron garnets tend to have perpendicular magnetic anisotropy for the films prepared both on gadolinium gallium garnet (GGG) and glass substrates for low bismuth content  $x < 1$ . However, it is hard to obtain perpendicular magnetic anisotropy for higher  $x > 2$ , while MO effect becomes large with  $x$ . Grishin et al. reported Bi<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>/GGG multilayer films on GGG substrates with perpendicular magnetic anisotropy<sup>10</sup>. However, considering MO applications for large area such as MO indicator films, glass substrates are required. As far as we know, there is no report on highly bismuth substituted iron garnet with perpendicular magnetic anisotropy.

We have reported that metal-organic decomposition (MOD) method is promising to obtain high quality garnet films with high-bismuth content because they are advantageous not only for homogeneity of the thin film, the controllability of composition, and formation over large area but also for the good productivity and stability of the MOD solution for more than several years<sup>11-16</sup>. In previous work, we have also reported that Nd<sub>2</sub>BiFe<sub>4</sub>GaO<sub>12</sub> (Bi1:NIGG) layer is effective as a buffer layer to obtain Y<sub>2</sub>Bi<sub>2.5</sub>Fe<sub>5</sub>O<sub>12</sub>,  $x = 2.5$ , on glass substrates<sup>15</sup>.

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In order to achieve perpendicular magnetic anisotropy with higher bismuth substitution, we chose Nd<sub>3-x</sub>Bi<sub>x</sub>Fe<sub>4</sub>GaO<sub>12</sub>, because Nd<sup>3+</sup> has similar ionic radius with Bi<sup>3+</sup>. We expect that similar ionic radii between rare-earth elements and bismuth result in improving crystallinity. In addition, we substitute gallium for iron to reduce demagnetization field by reducing total magnetic moment, resulting in the perpendicular magnetic anisotropy. In this paper, we report on NdBi<sub>2</sub>Fe<sub>4</sub>GaO<sub>12</sub> (Bi2:NIGG) and Nd<sub>0.5</sub>Bi<sub>2.5</sub>Fe<sub>4</sub>GaO<sub>12</sub> (Bi2.5:NIGG) films with perpendicular anisotropy.

### 2 Experiments

Nd<sub>3-x</sub>Bi<sub>x</sub>Fe<sub>4</sub>GaO<sub>12</sub> (BiX:NIGG, X=1, 2, 2.5) films were prepared by MOD method using MOD solutions Bi1:NIGG (Nd : Bi : Fe : Ga = 2 : 1 : 4 : 1), Bi2:NIGG (Nd : Bi : Fe : Ga = 1 : 2 : 4 : 1) and Bi2.5:NIGG (Nd : Bi : Fe : Ga = 0.5 : 2.5 : 4 : 1) produced by Kojundo Chemical Laboratory Co., LTD The total concentration of carboxylates in those MOD solutions was fixed at 4%.

The MOD process for all films is as follows; spin coating of the MOD solution at 3000 rpm for 60 sec drying at 100°C for 30 min, pre-annealing processes at 450°C for 30 min, and after repetition of the process from the spin coating and the pre-annealing several times the samples were annealed at 700°C for 3 hours in air. Prior to preparation of Bi2:NIGG and Bi2.5:NIGG Bi1:NIGG films were prepared on glass substrates (EAGLE2000, Corning). For Bi1:NIGG, the process from the spin coating and the pre-annealing was repeated 3 times. Bi2:NIGG and Bi2.5:NIGG films were prepared on the Bi1:NIGG films with the same

MOD procedure except for the repetition process of 5 times. The thickness of Bi1:NIGG was approximately 120 nm, and the thickness of Bi2:NIGG and Bi2.5:NIGG is approximately 200 nm.

Samples were characterized by the magneto-optic spectrometer, the spectrophotometer and the X-ray diffraction (XRD) method.

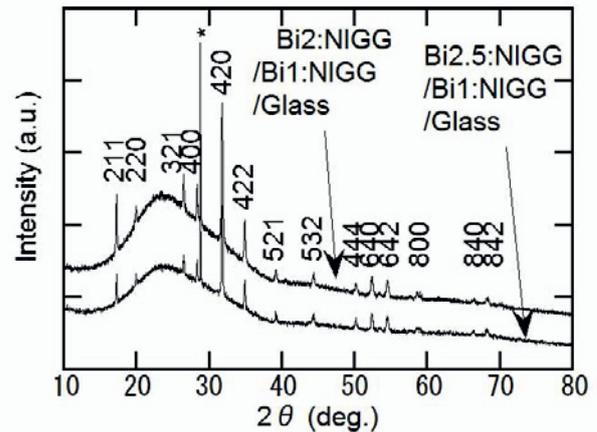
### 3 Results and Discussions

Figure 1 shows XRD patterns of Bi2:NIGG/Bi1:NIGG/glass and Bi2.5:NIGG/Bi1:NIGG/glass shown together with Miller indices of garnet structure. It is clearly observed that the garnet structure is obtained for both samples. Lattice constants of Bi2 : NIGG and Bi2.5 : NIGG are calculated from positions of 420 peaks and are determined to be 1.259nm and 1.260nm. The similar lattice constant is attributed to the similarity of ionic radii of  $\text{Bi}^{3+}$  and  $\text{Nd}^{3+}$ . These values are consistent with lattice constants of Bi2:NIGG and Bi2.5:NIGG expected from Vegard's law are 1.2597nm and 1.2601nm, respectively. On the other hand, additional peak due to an impurity phase (\*) is observed on the right side of 400 peaks as indicated by "\*". Although the impurity phase is unidentified, we found how to reduce it by shortening the pre-annealing time as described later.

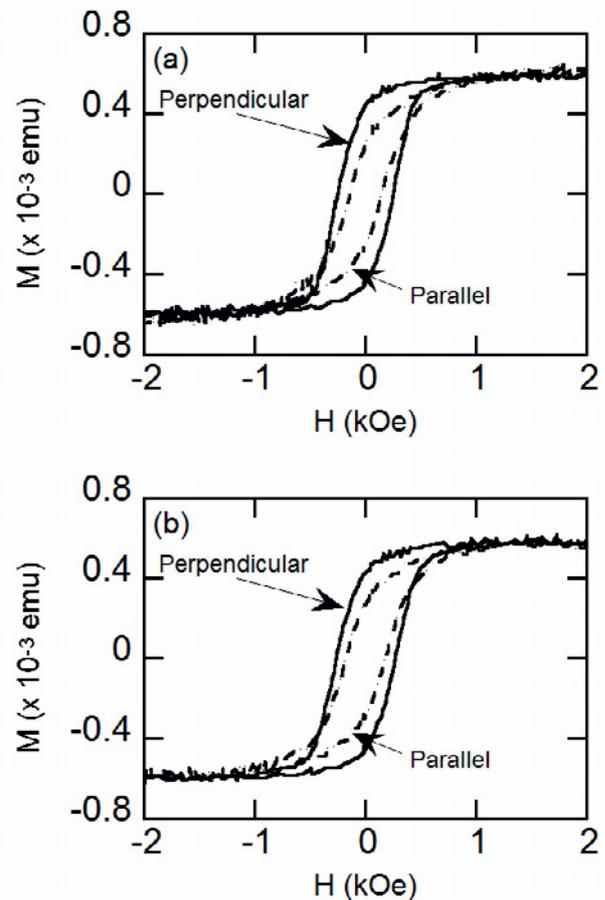
Magnetization curves of Bi2 : NIGG / Bi1 : NIGG / glass and Bi2.5 : NIGG / Bi1 : NIGG / glass films are shown in Fig.2. It is found that an easy axis magnetization is perpendicular to the sample surface, although coercivity is not zero for in-plane direction, and the magnetic properties of both samples are almost same.

Figure 3 shows Faraday rotation spectra of Bi2 : NIGG / Bi1:NIGG / glass and Bi2.5:NIGG / Bi1:NIGG / glass films. The structures of the spectra are almost same with those of Bi-substituted iron garnet films. Negative peak position is around 520 nm for both films, while the peak around 500 nm shifts with Bi content for yttrium iron garnet, for example the peak position are at 520nm, 524 nm and 530 nm for  $x = 2, 2.5$  and 3, respectively. On the other hand, the sign of Faraday rotation of Bi2.5:NIGG changes at longer wavelength than that of Bi2:NIGG. The magnitude of Faraday rotation increases with bismuth content, 1.7 and 2.2 degree at a wavelength of 520 nm for Bi2:NIGG/Bi1:NIGG/glass and Bi2.5:NIGG/Bi1:NIGG/glass films. By considering an contribution from the Bi1:NIGG under layer and the glass substrate, whose Faraday rotation is 0.2 degrees, the Faraday rotation of Bi2:NIGG and Bi2.5:NIGG are determined to be 1.5 and 2.0 degrees, 7.5 and 10.5 degree/ $\mu\text{m}$ , respectively. Those values are 2-3 times larger than  $\text{Y}_2\text{BiFe}_5\text{O}_{12}$  grown on GGG substrate.

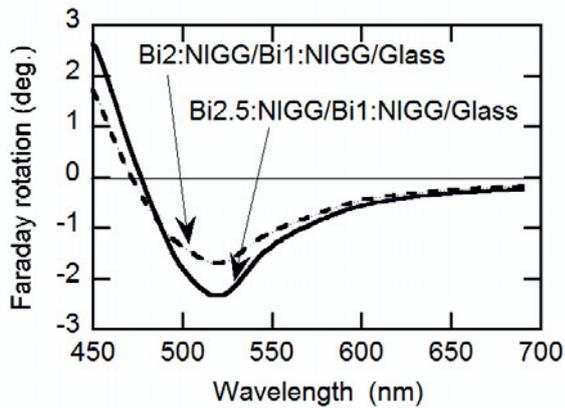
Faraday rotation hysteresis of Bi2:NIGG / Bi1: NIGG / glass and Bi2.5:NIGG / Bi1:NIGG / glass films has rectangular-shape as shown in Fig.4, indicating that both samples have the perpendicular anisotropy. Saturation magnetic field and ( $H_s$ ) coercivity ( $H_c$ ) are 730 and 350 Oe, respectively for both samples. We can conclude that



**Figure 1.** X-ray diffraction patterns of Bi2 : NIGG / Bi1 : NIGG / glass and Bi2.5 : NIGG / Bi1 : NIGG / glass films.

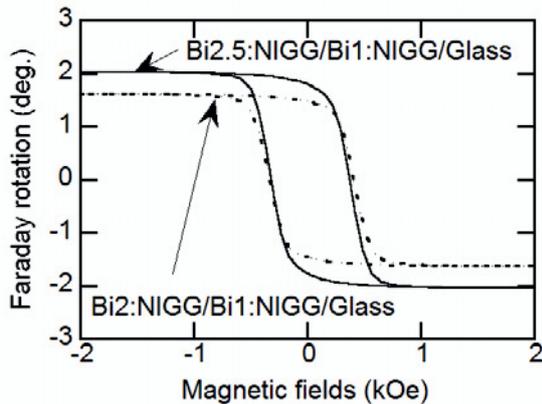


**Figure 2.** Magnetization curves of (a)Bi2:NIGG/Bi1: NIGG / glass and (b)Bi2.5:NIGG/Bi1:NIGG/glass films.



**Figure 3.** Faraday rotation spectra of Bi2:NIGG and Bi2.5:NIGG films prepared on Bi1:NIGG layer on glass substrates.

highly Bismuth substituted garnet films garnet films with perpendicular magnetization was successfully obtained by lowering the magnetic moments by gallium substitution.

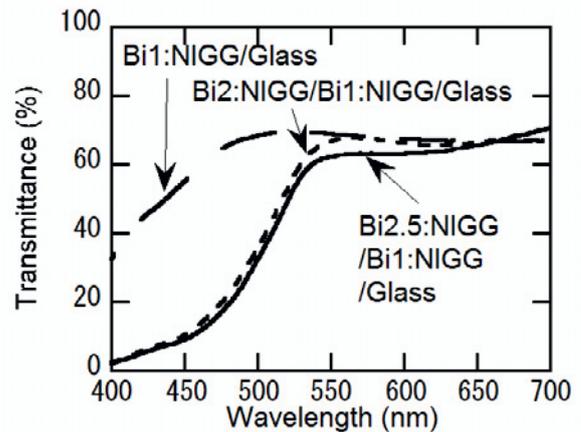


**Figure 4.** Faraday rotation hysteresis loops of Bi2:NIGG and Bi2.5:NIGG films prepared on Bi1:NIGG layer on glass substrates.

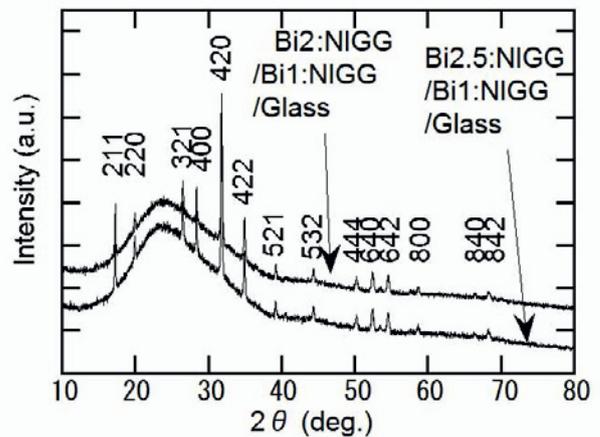
Figure 5 shows transmittances of Bi1:NIGG, Bi2:NIGG/Bi1:NIGG and Bi2.5:NIGG/Bi1:NIGG films. The Bi2:NIGG/Bi1:NIGG and the Bi2.5:NIGG/Bi1:NIGG have similar transmittance spectra. This is in contrast to the case of bismuth-substituted iron garnet that the transmittance decreases with bismuth content  $x$ . We need further investigation in order to understand this result.

We would like to discuss about the reason why Bi2:NIGG and Bi2.5:NIGG were obtained. In most of works reported earlier,  $Y^{3+}$  or  $Lu^{3+}$  is chosen for a rare-earth ion to make the lattice constant close to that of GGG substrate, because  $Bi^{3+}$ , large ion, is substituted. However, if we can use glass substrate, we do not need smaller rare-earth ion anymore. In this case, we consider that a large rare-earth ion with similar radius to  $Bi^{3+}$  is better to obtain garnet structures.

Finally, XRD patterns of Bi1:NIGG/Bi2:NIGG and Bi1:NIGG/ Bi2.5:NIGG films without the impurity phase are shown in Fig.1. We found that the peak due to the impurity phase has been almost disappears when the pre-annealing time is shortened to 10 min. This result indicates that the impurity phase is crystallized during the pre-annealing, and therefore, the crystallization can be suppressed by the short pre-annealing time. We assume that the impurity phase is neodymium compound, since the impurity phase can be observed only in the case of neodymium iron garnet films.



**Figure 5.** Transmittances of Bi1:NIGG prepared on glass substrates, Bi2:NIGG and Bi2.5:NIGG films prepared on Bi1:NIGG layer on glass substrates.



**Figure 6.** XRD patterns of of Bi2 : NIGG / Bi1 : NIGG / glass and Bi2.5 : NIGG / Bi1 : NIGG / glass films with shortening pre-annealing time, 10 min.

## 4 Conclusions

Perpendicular magnetization was successfully obtained for large Bi substitution by choosing neodymium as a rare-earth element in  $RE_{3-x}Bi_xFe_{3-y}NM_yO_{12}$ . Bi2:NIGG and Bi2.5:NIGG films were successfully obtained on Bi1:NIGG/glass substrates by MOD method. Faraday rotation angles of Bi2:NIGG and Bi2.5:NIGG films reaches 7.5 and 10.5 degree/ $\mu m$ , respectively. Magnetic anisotropy,  $H_s$  and  $H_c$ , of Bi2:NIGG and Bi2.5:NIGG

were 730 Oe and 350 Oe, respectively. Impurity phase was suppressed by shortening a pre-annealing time.

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