Preparation of High Coercive-Force Al-Substituted Bi-DyIG Fine Particles and Coating Films

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In garnet coating films, higher coercive force H_c and lower absorption coefficient α are required to develop a practical magneto-optical recording media. One of the solutions can be found at a magnetic compensation composition of Al-substituted iron garnet particles. Since fine particles of Bi-DyAlIG ($\text{BiDy}_2\text{Al}_y\text{Fe}_{5-y}\text{O}_{12}$; $0 \leq y \leq 1.1$) exhibit a magnetic compensation at room temperature, we investigated the effect of magnetic compensation in Al-substituted Bi-DyIG fine particles.

The Bi-DyAlIG fine particles were prepared by coprecipitation and heat treatment. The heat treatment was carried out at 750°C for 4h. The fine particles were milled with an epoxy binder by a milling machine. The thin films were prepared with a coating technique. Nano-size fine particles of Bi-DyAlIG had been dispersed in the plastic binders on Corning #7059 glass sheets.

The fine particle ($y = 0.9$) has a high coercive force of about 450 Oe and only 0.4 emu/g. All the X-ray diffraction peaks of the fine particles were assigned to garnet. The Faraday rotation θ_F was decreased with increasing y . Near $y = 0.8$ the rotating direction of the θ_F was reversed. These results lead to a compensation of the magnetic moments. The size of fine particles in the coating films was about 10 nm which is much smaller than the wavelengths of the lights utilized in the optical devices.

Key words: *Bi-DyAlIG, coprecipitation, magnetic compensation, Faraday rotation, reverses, magneto-optical device.*

1. Introduction

The increase in the coercive force of magnetic particles and in the lower absorption coefficient have been one of the major objectives for applying the garnet particles to magneto-optical recording media. The fine particles of garnet require more effort to increase the coercive force than the thin films because of their low internal stresses [1][2]. In case the magnetic compensation occurs in Al-substituted iron garnet particles, the coercive force of the particles will have a huge value and the absorption coefficients of coating films will be improved. At present, $\text{BiDy}_2\text{Al}_y\text{Fe}_{5-y}\text{O}_{12}$ is one of the candidates, however, the substitution content

y for the magnetic compensation of the fine particles is not clear with different reported values of $y = 0.35$ [3] and $y = 1.2$ [4]. And any attempts to prepare the coating films with the fine particles with these composition have not been reported. Fine particles of the Bi-DyAlIG exhibit a magnetic compensation at room temperature, therefore we investigated the effect of the magnetic compensation in Al-substituted Bi-DyIG fine particles.

In this paper, we precisely determined the magnetic compensation composition of $\text{BiDy}_2\text{Al}_y\text{Fe}_{5-y}\text{O}_{12}$ ($0 \leq y \leq 1.1$) fine particles, and the structural and magneto-optical properties of the coating films made from the fine particles were also investigated.

2. Experimental

2.1 Preparation of garnet fine particles

The Al-substituted Bi-DyIG fine particles were prepared by coprecipitation [5][6] and a heat treatment. Aqueous nitrate solutions of Bi (Bismuth(III) Nitrate Pentahydrate), Dy (Dysprosium(III) Nitrate Pentahydrate) and Fe (Iron(III) Nitrate Enneahydrate) were mixed where the ratio of the cations corresponded to the composition of $\text{BiDy}_2\text{AlFe}_{5-y}\text{O}_{12}$. Then the aqueous solution of Al nitrate (Aluminium(III) Nitrate Enneahydrate) was added. The concentration of Al in the samples was from $y = 0.0$ to 1.1 in the formula unit. Then the solution was mixed with an NH_4OH solution with stirring at room temperature. The concentration of the alkaline solution was adjusted so that the pH of the mixed solution was 10.0 at the end of the coprecipitation reaction. The obtained slurry was washed, filtered in aspirator and dried at 120°C for 1.5h. Then the coprecipitates were heated in air at 750°C for 4h to form fine garnet particles. The crystal phases in the particles were examined by X-ray diffraction (XRD) (RINT2100V; Rigaku) analysis with a Cu-K α source. The measurement was made with standard high-purity silicon powder. Saturation magnetization M_s and coercive force H_c of the fine particles were measured with a vibrating sample magnetometer (VSM) (BHV-55; Riken Denshi) at room temperature. The contents of the cations in the coprecipitates were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) (SPS4000; Seiko Instruments).

2.2 Preparation of the coating films

The fine particles were mixed with an epoxy binder (Epo-tek 396; Epoxytechnology) dissolved in a cyclohexanone and milled with a planetary milling machine (Pulverisette 7; Fritsch) for 30h. They were then coated on Corning #7059 glass substrates using a rod coater. The coating films were dried at 80°C for 2h in an oven. The volume content of the fine particles in the coating films was about 0.35. The coating film thickness was measured with a surface step analyzer (DEKTA 3030; Sloan) and the coating film surface was

observed with a scanning electron microscope (SEM) (S-4000; Hitachi). The thickness of the coating films was about $1.2\sim 1.7\mu\text{m}$. It was controlled by the viscosity of the ink and the mesh of the rod coater. The magnetic properties of the coating films were measured with the VSM. The fine particles in the coating films were observed with an atomic force microscope (AFM) (SPI3700; Seiko Instruments). Faraday rotation θ_F was measured by the polarization modulation method (MOE-7; Jasco). The absorption coefficient α was measured with a spectrophotometer (U-2000A; Hitachi). The optical measurements were carried out in the visible wavelength region from 450 nm to 700 nm.

3. Results and discussion

3.1 Properties of the garnet fine particles

The X-ray diffraction patterns of the Bi-DyAlIG fine particles are shown in Figure 1. We investigated the X-ray diffraction patterns with the JCPDS data, when the patterns were identified to garnet. The phase of the fine particles from $y = 0.0$ to 1.1 is assigned to garnet.

Fig. 1. X-ray diffraction patterns of $\text{BiDy}_2\text{AlFe}_{5-y}\text{O}_{12}$ fine particles after heat treatment in 750°C for 4h.

Figure 2 shows the M - H curves of the Bi-DyAlIG fine particles at room temperature under the magnetic field up to 20 kOe. All the particles showed unsaturated magnetization curves. The thickness of magnetic domain walls is about 20 nm [7]. This value is much larger than that of our observation of about 10 nm which is described in the following section. The size of about 15 nm for Bi-YIG particles was also reported [8]. Therefore the size of the particles is much smaller than the thickness of domain walls. We presume that the presence of superparamagnetic particles as a mixture is the reason for the unsaturated M - H curves.

Fig. 2. M - H curves of the $\text{BiDy}_2\text{AlFe}_{5-y}\text{O}_{12}$ fine particles at room temperature under the magnetic field up to 20 kOe.

Figures 3 and 4 show the magnetization and coercive force H_C of the Bi-DyAlIG fine particles at $H = 3$ kOe ($M_{3\text{kOe}}$) as a function of y . The $M_{3\text{kOe}}$ decreased with increasing y , and became less than 1 emu/g in the composition range of $0.8 < y < 1.0$, which is indicative of the magnetic compensation of the Bi-DyAlIG fine particles. We determined the contents of Al ions occupied on the $16a$ site (x_a) and $24d$ site (x_d) using the saturation magnetizations M_s of bulk DyIG and YIG [9] on the basis of the Neel model. The estimated values of x_a and x_d are 0.18 and 0.72,

Fig. 3. Hysteresis loops of the $\text{BiDy}_2\text{AlFe}_{5-y}\text{O}_{12}$ fine particles.

Fig. 4. Magnetization at $H = 3$ kOe ($M_{3\text{kOe}}$) and coercive force (H_C) of $\text{BiDy}_2\text{AlFe}_{5-y}\text{O}_{12}$ fine particles as a function of Al substitution.

respectively. Moreover, the H_C of the fine particles was increased at this composition. The fine particles with $y = 0.9$ has a high coercive force of about 450 Oe which is a factor of 3 larger than the previously reported value [10]. We should shortly comment on the magnetic compensation in Bi-DyAlIG fine particles. There are some reports showing the different compensation compositions, e.g., $y = 1.2$ [4] and $y = 0.35$ [3]. We reliably attribute this discrepancy to the different contents of the Al atoms on each site. However, the magnetic compensation composition

of $y = 0.35$ cannot be explained in terms of the saturation magnetizations of the bulk. This requires novel spin structure in the particle systems. It was previously reported that the saturation magnetization reduced by a factor of 2 due to the spin canting configuration in the surface layers of the Bi-DyAlIG fine particles [3][11]. Thus the spin structure characteristic of the particles also should be taken into account as we determine the magnetic compensation composition, although we cannot demonstrate the spin structure of the present Bi-DyAlIG particles.

Fig. 5. AFM images of $\text{BiDy}_2\text{Al}_y\text{Fe}_{5-y}\text{O}_{12}$ fine particles in the coating films.

3.2 Properties of the coating films

Figures 5 (a), (b), (c) and (d) show AFM images of the Bi-DyAlIG fine particles in the coating films which were milled for 30h. The primary size of the fine particles is about 10 nm. The size is almost the same as that of the coprecipitated fine particles. From the SEM images of the coating films, no aggregate of the fine particles was observed. It is confirmed that the fine particles are uniformly dispersed. The size is much smaller than the wavelengths of the read and write lasers for visible light and near future magneto-optical storage system.

Fig. 6. SEM images of $\text{BiDy}_2\text{Al}_y\text{Fe}_{5-y}\text{O}_{12}$ fine particles in the coating films.

Fig. 7. Absorption coefficient α of $\text{BiDy}_2\text{Al}_y\text{Fe}_{5-y}\text{O}_{12}$ coating films at 520 nm.

3.3 Magneto-optical properties of the coating films

Figure 7 shows the absorption coefficient α of the Bi-DyAlIG coating films at wavelength 520 nm. The absorption coefficient at the coating films was decreased with increasing y .

Figure 8 shows the Faraday rotation θ_F of the Bi-DyAlIG coating films at the 520 nm, where anticlockwise rotation of the polarization was defined to be positive of θ_F when viewed along the light propagation. The θ_F decreases with increasing y . In the region from $y = 0.8$ to 0.9 , direction of the Faraday rotation was reversed. This result leads to a compensation of the magnetic moments.

The relation between the figure of merit θ_F/α at 520 nm of the coating films and y are shown in figure 9. The θ_F/α for the coating films shows the maximum value at $y = 0.4$. The value of θ_F/α at from $y = 0.0$ to 0.6 is about 1.0 degree.

Fig. 8. Faraday rotation θ_F of $\text{BiDy}_2\text{Al}_y\text{Fe}_{5-y}\text{O}_{12}$ coating films at 520 nm.

4. Conclusions

We successfully synthesized nano-size Al-substituted Bi-DyIG ($\text{BiDy}_2\text{Al}_y\text{Fe}_{5-y}\text{O}_{12}$; $0 \leq y \leq 1.1$) fine particles by a coprecipitation and heat treatment. Thin films were prepared by coating an ink which was made through a planetary process milling. The magnetic and magneto-optical properties of the fine particles and coating films were investigated.

The fine particles of $\text{BiDy}_2\text{Al}_y\text{Fe}_{5-y}\text{O}_{12}$ exhibited a magnetic compensation at room temperature with the composition of $y = 0.9$. Fine particles of $y = 0.9$ have a high coercive force of 450 Oe. The Faraday rotation θ_F decreased with increasing y . In the region from $y = 0.8$ to 0.9 , the rotating direction of the θ_F was reversed. The figure of merit θ_F/α of the coating films from $y = 0.0$ to 0.6 is about 1.0 degree at 520 nm. These results indicate that the coating films are promising candidate for a new large scale magneto-optical storage media.

Fig. 9. Figure of merit of $\text{BiDy}_2\text{Al}_y\text{Fe}_{5-y}\text{O}_{12}$ coating films at 520 nm.

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