Fabrication of Bismuth- and Aluminum-Substituted Dysprosium Iron Garnet Films for Magneto-Optic Recording by Pyrolysis and Their Magnetic and Magneto-Optic Properties

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Polycrystalline bismuth- and aluminum- substituted dysprosium and yttrium iron garnet ($Bi_xR_{3-x}Al_yFe_{5-y}O_{12}$, R=Dy or Y, $0 \leq x \leq 3$, $0 \leq y \leq 3$) films have been prepared by pyrolysis The crystallization temperatures, the solubility limit of bismuth ions into the garnet phase, and magnetic and magneto-optic properties of the films have been investigated as a function of bismuth and aluminum concentration. It was found that the crystallization temperatures of these films rapidly decreasd as bismuth concentration (x) increased up to x=1.5 and then remained unchanged at x > 1.5, whereas, showed no changes as aluminum concentration (y) increased up to y=1.0 and then gradually increased at y > 1.0. The solubility limit of bismuth ions was x=1.8 when y=0 but increased to x=2.3 when y= 1.0. It was demonstrated that the magnetic and magneto-optic properties of the dysprosium iron garnet films could be tailored by bismuth and aluminum substitution suitable for magneto-optic recording as follows. The saturation magnetization and coercivity data obtained for the films indicated that the film composition at which the magnetic compensation temperature became room temperature was y=1.2 when x=1.0. Near this composition the coercivity and the squareness of the magnetic hysteresis loop of the films were several kOe and unit, respectively. The Curie temperatures of the films increased with the increase of x but decreased with the increase of y, and was 150-250°C when x=1.0 and y=0.6-1.4. The Faraday rotation at 633 nm of the films increased as x increased but decreased as y increased, and was 1 deg/μm when x=1.0 and y=1.0. Based on the data obtained, the appropriate film composition for magneto-optic recording was estimated as near x=1 0 and y=1.0 or $BiDy_2AlFe_4O_{12}$.

Key words : Iron garnet. Bismuth, Aluminum, Dysprosium, Thin film, Magnetic property, Magneto-optic property, Magneto-optic recording.

I. Introduction

B i-substituted iron garnet films exihibit a strong Faraday rotation in the visible wavelengthes,[1] and hence are promising candidates for high density magneto-optic recording media. To use this film as a magneto-optic recording medium, magnetization of the film needs to be directed perpendicular to the film plane. Perpendicular magnetization is obtained when $K_u > 2\pi M_s^2$, where K_u is the uniaxial magnetic anisotropy constant and M_s is the saturation magnetization of the film.[2] Thus to obtain perpendicular magnetization, large K_u but small M_s are desirable.

Previous studies have shown that the M_s of the films can be reduced by doping Al ions.[3] And the K_u of the films prepared by pyrolysis techniques adopted in this work can be given by $K_u = -(3/2) \sigma \lambda_s$, where σ is the thermal stress between the film and substrate and λ_s is the magnetostriction coefficient of the film.[4] Thus to obtain large K_u, σ needs to be large and λ_s negative with a large $|\lambda_s|$. With a given substrate it is known that σ does not change much depending on film composition, since the thermal expansion coefficients of iron garnets are not much different even though film composition changes.[5]

Thus λ_s is the main factor to determine the K_u value. Previous studies have also shown that among various iron garnets, DyIG ($Dy_3Fe_5O_{12}$) provides the largest negative λ_s.[6]

Therefore, DyIG was slected as a host film compositon in this work and Bi- and Al-substituted DyIG films were prepared to tailor magnetic and magneto-optic properties of the films suitable for magneto-optic recording. The film composition investigated was $Bi_xDy_{3-x}Al_yFe_{5-y}O_{12}$ with $0 \leq x \leq 3$ and $0 \leq y \leq 3$. Films based on YIG ($Y_3Fe_5O_{12}$) compositon with Bi and Al substitution were also investigated for comparison. The films were prepared on a glass substrate by a simple chemical process spin coating followed by themal decompositon and crystallization or pyrolysis, since pyrolysis allows a fine adjustment of the complex compositions as those of the films.[7]

II. Experimental

Films of about 0.3 μm in thickness were prepared on a glass (Corning 7059) substrate (50×50×1 mm³) by spinning in metal nitric solutions followed by thermal decomposition up to 400°C. The amorphous films obtained were then crystallized by annealing for 3 hours at elevated

temperatures ranging from 580°C to 700°C. The details of the film preparation were reported elsewhere.[8]

The crystal phases in the films were analyzed by x-ray diffractometry. The saturation magnetization and coercivity of the films were measured using a vibrating sample magnetometor (VSM). The Curie temperatures of the films were determined from the temperature dependence of the Faraday rotation. The Faraday rotation of the films were measured using polarization modulation techniques by the helium-neon laser with the wavelength of 633 nm.

III. Results and Discussion

1. Crystallization temperature

The minimum temperatures required to obtain fully crystallized single-phase-YIG films by annealing the amorphous films prepared are plotted as a function of Bi and Al concentration in Fig. 1. The temperatures were estimated from the fact that the x-ray diffration intensity of the garnet lines and the saturation magnetization of the films did not increase further over the temperatures. For an Al concentration of y=1.0 (solid line) it is seen that as the Bi concentration (x) increases the crystallization temperature rapidly decreases until x reaches 1.5. The crystallization temperature then becomes less sensitive to further substitution. While for a Bi concentration of x=1.5 (dotted line), as the Al concentration (y) increases, the crystallization temperature remains unchanged until y is greater than 1.0, then it gradually increases for further substitution. While not shown similar trend was obtained for the DyIG films.

The rapid reduction of the crystallization temperature at x < 1.5 with the increase of x is probably due to the high mobility of the Bi ions in the amorphous oxide film.
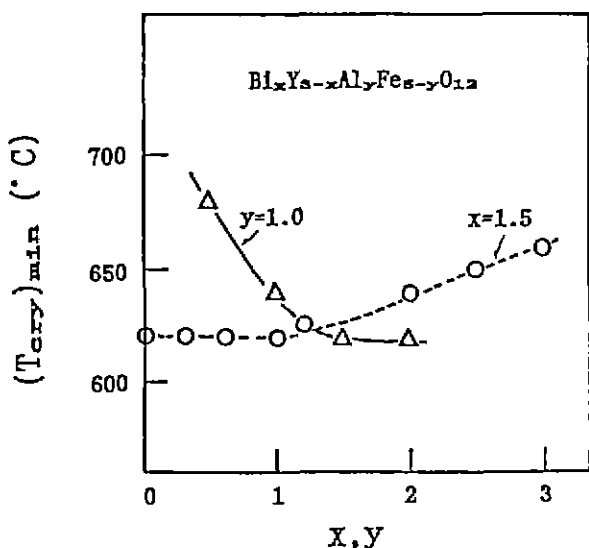
Previous studies have shown that the crystal grain size of the garnet phase in the films after being annealed at a temperature increases as x increases,[9] indicating the high mobility of the ions. The high mobility of the Bi ions is probably caused by the weak chemical bond with the oxygene ions. It is known that when the films are prepared by sputter-deposition, Bi ions are selectively resputtered. For sputtered film this leads the need to compensate the Bi lost using a Bi-overdosed target.[1,10,11]

As x increases further and x > 1.5, the garnet phase seems to become difficult to be nucleated due to the distortion caused by the large Bi ions. Previous studies have also shown that the garnet grain size in the films rapidly increases as x increases higher than 1.5,[8] indicating the reduced number of nuclei. This may explain the fact observed that the crystallization temperature remains unchange at x > 1.5.

It appears that the Al substitution stabilizes the garnet phase by reducing the lattice distortion due to the large Bi ions and as a result the crystallization temperature remains unchanged when y < 1.0 even though y increases. The followed gradual increase of the crystallization temperature at y > 1.0 may be attributed to the low mobility of the Al ions due to the strong bond with the oxygen ions.

2. Solubility limit of Bi ions into the garnet phase

It was found that the solubility limit of Bi ions into the garnet phase could be increased by substituting Al ions together with Bi ions. As an example, Fig. 2 shows the phase diagram obtained for YIG films when Bi content (x) was fixed to x=2.0 but Al content (y) was varied.
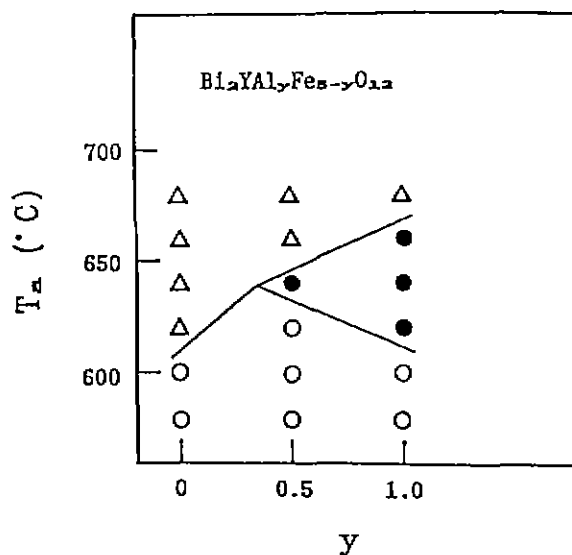

Fig. 1. The minimum crytallization temperature $(T_{cry(min)})$ versus Bi(x) and Al(y) concentrations.

Fig. 2. The crystal phases detected for the films with a Bi concentration (x) of x=2.0 and with various Al concentration (y) after being annealed at T_a for 3 hours. The closed circles denote the single phase garnet, the open circles the amorphous phase, and the triangles the mixed phase of the garnet and impurity.

The triangles denote the mixed phase of impurity and the garnet, the closed circles the single phase garnet, and the open circles the amorphous phase which was not crystallized. As shown, when y=0, the impurity phase was detected. This indicates that the solubility limit of Bi ions is x < 2.0 when y=0. When y=0.5 and 1.0, however, there was a garnet-single-phase region at a certain temperature range, which becomes wider as Al substitution increases from y=0.5 to y=1.0. To investigate if the Bi ions were incoporated into the garnet phase in the film with the latter composition, the lattice constant of the garnet phase in the film was calculated from the x-ray diffraction lines obtained. The results were shown in Fig. 3 together with the lattice constant of the films with lower x. Since the lattice constant linearly increases as Bi content x increases up to 2 and the slope agreed with the value reported in literatures,[12] it appeared that the Bi ions in the film were fully incoporated into the ganet phase.

While not shown the solubility limit of the Bi ions at 640°C estimated in this work was x≈1.8 when y=0 and x= 2.3 when y=1.0. This is an another evidence which indicates that the Al substitution stabilize the garnet phase with high Bi concentration. Similar results were obtained for DyIG films.

3. Magnetic properties

The saturation magnetization and coercivity of DyIG and YIG films with Bi concentration of x=0.5, 1.0, and 1.5 are shown in Figs. 4 and 5, respectively, as a function of Al concentration (y). For a y the saturation magnetization increases (Fig. 4), as x increases. While for an x, as y increases, the saturation magnetization generally decreases (Fig. 4). Since the dysprosium is a magenetic ion, the DyIG films have the magnetic compensation temperature. As shown in Figs 4 and 5, the compensation temperatures of the films with x=0.5 and 1.0 become

room temperature when y=0.7 and 1.2, respectively. The coercivity of the films becomes several kiloOersteds near these compositions (Fig. 4). While not shown, near these compositions the squareness of the magnetic hysteresis loops of the films were unit. Thus, for magneto-optic recording, film composition needs to be adjusted near these compositions.

The Curie temperatures of DyIG and YIG films with x= 1.0 and 1.5 are plotted as a function of y in Fig. 6. For both films, the Curie temperature linearly decreases as y
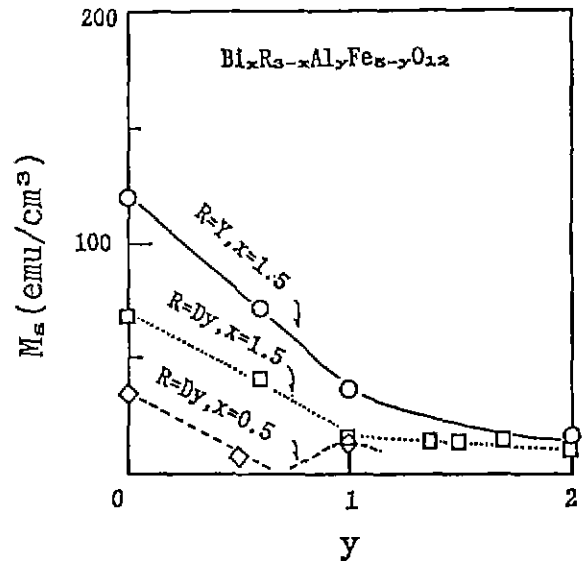

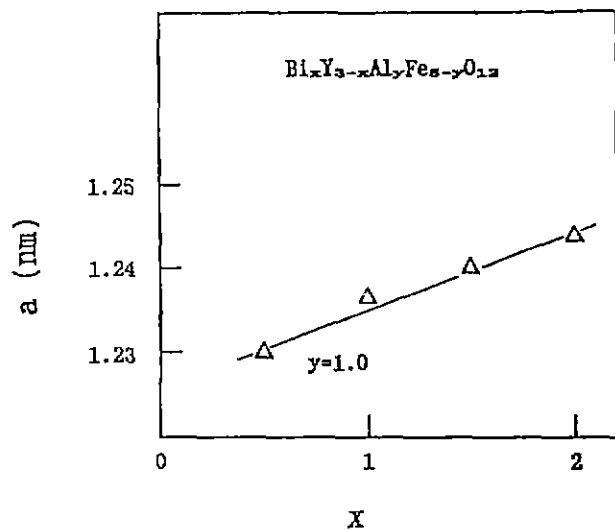**Fig. 4.** The saturation magnetization (M_s) versus Al concentration (y).

Fig. 3. The lattice constant (a) versus Bi concentration(x).
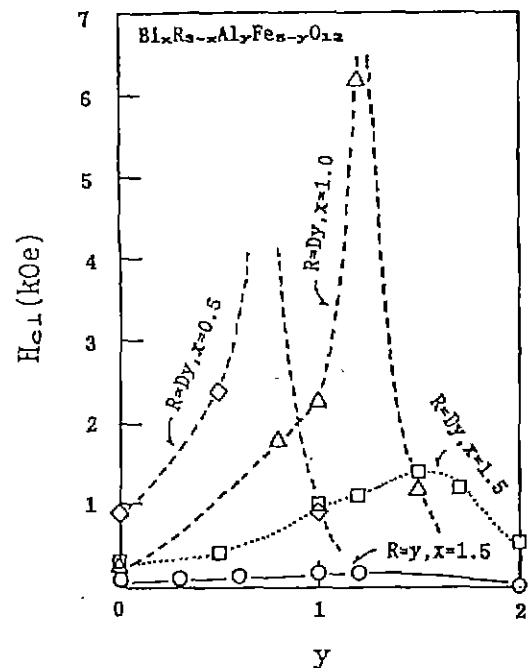

Fig. 5. The coercivity (H_c) measured perpendicular to the film plane versus Al concentration (y).
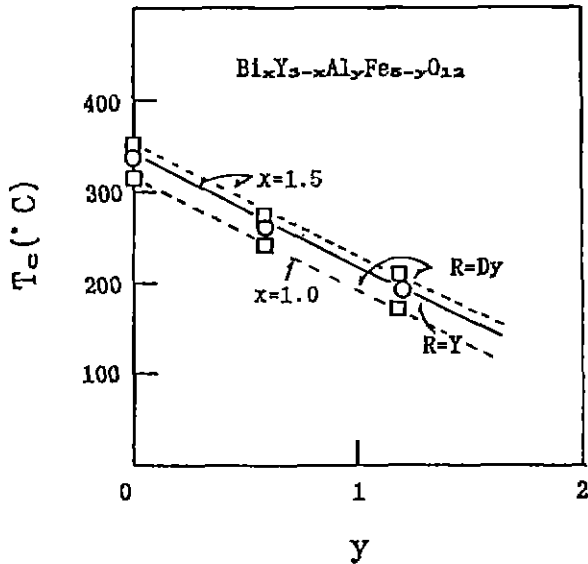
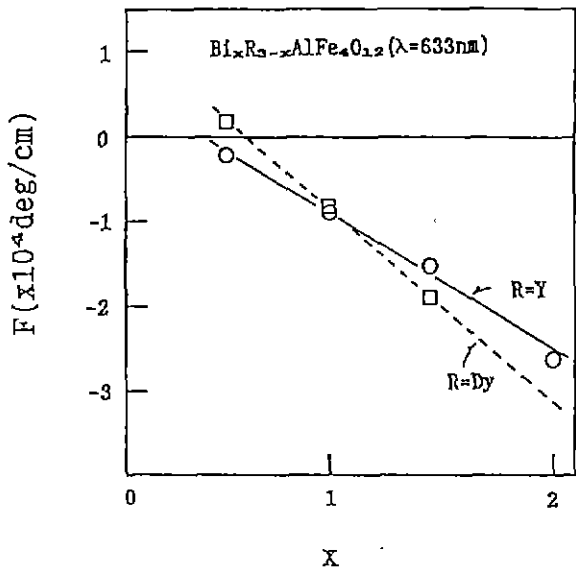**Fig. 6.** The Curie temperature (T_c) versus Al concentration (y).

Fig. 7. The Faraday rotation (F) at the wavelength of 633 nm versus Bi concentration (x).

Fig. 8. The Faraday rotation (F) at the wavelenth of 633 nm versus Al concentration (y).

tation generally decreases as y increases for both films and changes its sign at the compensation composition for the DyIG films.

IV. Conclusions

It was found that the crystallization temperatures of DyIG and YIG films rapidly decreased as bismuth concentration (x) increased up to x=1.5 and then remained unchanged at x > 1.5, whereas, showed no changes as aluminum concentration (y) increased up to y=1.0 and then gradually increased at y > 1.0. The solubility limit of bismuth ions was x=1.8 when y=0 but increased to x= 2.3 when y=1.0.

It was demonstrated that the magnetic and magneto-optic properties of the DyIG films could be tailored by bismuth and aluminum substitution suitable for magneto-optic recording. The appropriate film composition for magneto-optic recording was estimated as near x=1.0 and y=1.0 or $BiDy_2AlFe_4O_{12}$. The film with this composition showed the coercivity of 2.3 kOe, the squareness of the magnetic hysteresis loop of unit, the Curie temperature of 190°C, and the Faraday rotation at 633 nm of 1 deg/μm.

increases. The Curie temperature of the DyIG films increases as x increases. Modest Curie temperatures (150 - 250°C) suitable for magneto-optic recording are obtained when x=1.0 and y=0.6-1.4, and when x=1.5 and y=0.8-1.7.

4. Magneto-optic properties

The Faraday rotation at the wavelengh of 633 nm of the DyIG and YIG films with an Al concentration of y=1.0 are plotted as a function of Bi concentration (x) in Fig. 7. The absolute value of the Faraday rotation linearly inceases as x increases. For the dysprosium iron garnet films the Faraday rotation changes its sign at the compensation composition. The Faraday rotation of the DyIG and YIG films with x=1.0 and 1.5 are plotted as a function y in Fig. 8. The absolute value of the Faraday ro-
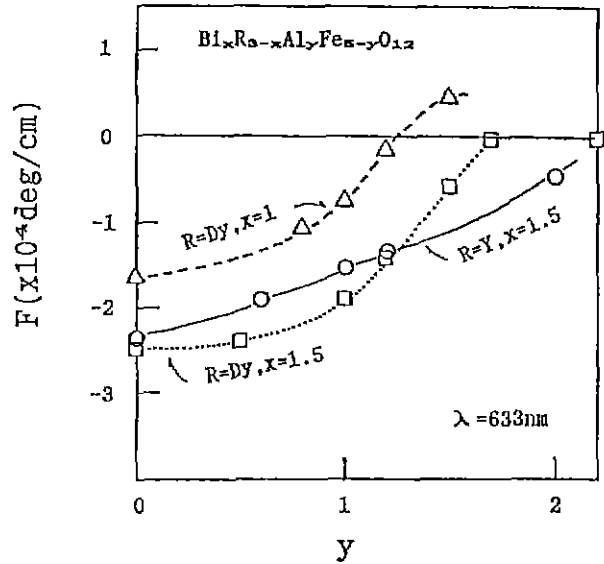
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