研　究

Effects of the Substitution of Nonmagnetic Ions in Bi-YIG Coating Films on the Magneto-Optical Properties

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SYNOPSIS

Fine particles of bismuth-substituted yttrium iron garnet doped with aluminum, gallium and indium ions are prepared by coprecipitation method. The films with these particles are obtained by dispersing particles on glass substrates with an appropriate epoxy binder. The magnetic and magneto-optical properties of the particles and the films are examined. The lattice sites occupied by aluminum, gallium and indium ions are determined by the relationship between the saturation magnetization and substitution content. The canting of the magnetic moments from the average magnetization axis of the iron ions is deduced in the indium substituted particles. The figure of merit of indium substituted samples remains constant up to the substitution content of 0.5.

KEY WORDS

Bi-YIG, garnet, particles, magnetic properties, magneto-optical properties, coprecipitation method, coating technique, Faraday effect

1 Introduction

Since bismuth yttrium iron garnet (Bi-YIG) film has a large Faraday rotation in visible wavelength, it has been believed that the Bi-YIG could be the most promising material for magneto-optical devices. The films of Bi-YIG can be prepared by various techniques, i.e., sputtering and liquid phase epitaxy[1]. Recently, another subtle technique was also developed by Hirano *et al.*[2], where the Bi-YIG particles were dispersed in epoxy binder and coated on glass substrates. The method was further optimized, and magneto-optical properties comparable to the film prepared by sputtering method were attained[3]. However, better performances of magneto-optical properties of the film are necessary for development of magneto-optical devices.

There are two approaches to improve the magneto-optical performance of the Bi-YIG particles dispersed films, i.e., to reduce the absorption and/or to enhance the Faraday rotation. It is known that the Bi-YIG garnet structure has three crystallografically different sites, where the 24*c* dodecahedral sites are occupied by bismuth and yttrium ions and 16*a* octahedral and 24*d* tetrahedral sites are occupied by iron ions. The effective Faraday rotation is determined by the difference in the opposite contributions due to the iron ions on 16*a* and 24*d* sites[1]. This implies that the substitution of nonmagnetic ions on the iron sites can change the Faraday rotation. Moreover, the absorption in the visible wavelength also should be changed by such substitution[1,4]. Therefore, the substitution of nonmagnetic ions possibly give a key information to improve the magneto-optical performance of Bi-YIG particles coated films.

In this paper, we investigate the effects of substitution of non-magnetic ions on the magnetic and magneto-optical properties of Bi-YIG films. Magnetic measurements are performed for the samples substituted by aluminum, gallium, and indium. A detailed magneto-optical properties are presented for the films obtained by substitution of indium ions.

2 Experimental

Aluminum, gallium and indium substituted Bi-YIG (Bi-YMIG, where M = aluminum, gallium and Indium) particles were prepared by coprecipitation process described elsewhere[2,5]. In this process, aqueous solutions of bismuth (Bismuth (III) Nitrate Pentahydrate), yttrium (Yttrium (III) Nitrate Hexahydrate), iron (Iron (III) Nitrate Enneahydrate) and M (Aluminum (III) Nitrate Enneahydrate, Gallium (III) Nitrate-99,99 % and Indium (III) Nitrate-99,9 %) nitrates corresponding to the composition of $Bi_{1.5}Y_{1.5}M_xFe_{5-x}O_{12}$ ($0 \leqq x \leqq 1.0$) were prepared. When the solutions were mixed with NH_4OH (25 %), the various species coprecipitated out of solution, upon completion of the coprecipitation at pH of ~ 10. The coprecipitates were then filtered and thoroughly washed to remove any remaining alkaline ions. The coprecipitates were then dried at 100 °C for 2 hours and then annealed at 700 °C or 650 °C for 4 hours to form garnet particles. These particles were then characterized.

The crystal structure of the particles was examined by X-ray diffraction (XRD) (RINT2100V, Rigaku) analysis with a Cu-Kα source. The lattice constant was obtained using the Nelson-Riley function. The cations composition was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES SPS4000, Seiko Instruments). The saturation magnetization (M_s) and the Curie temperature (T_C) were measured by a superconducting quantum interference device (SQUID) magnetometer (MPMS, Quantum Design) and vibrating sample magnetometer (VSM-BHV-55, Riken Denshi), respectively.

To disperse the particles on glass substrates, the garnet particles were mixed with an epoxy binder (Epo-tek 396, Epoxytechnology) dissolved in cyclohexanone and milled with a planetary milling machine (Pulveritte 7, Fritsch Co.) for ~ 30 hours. Using a rod coater, a 1.2 μm thick coated film was obtained on a Corning # 7059 glass substrate. These coated films were then dried at 80 °C for 2 hours or 70 °C for 4 hours. The film thickness was determined using a surface step profiler (Dektak 3030, Sloan).

The absorption coefficient was measured with an ultra violet-visible spectrophotometer (U-2000A, Hitachi) at wavelengths between 520 nm and 700 nm. The Faraday rotation was also measured by the polarization modulation method at 520 nm (MOE-7, Jasco). The relative magneto-optical performance of the various films was evaluated using the figure of merit (θ_F/α ratio).

3 Results and Discussion

3.1 Structural characterization

The XRD profiles of gallium substituted particles show only the garnet phase over the entire range of substitution content. On the other hand, other phases appear above the content of $x=0.46$ and 0.7 in the aluminum and indium substituted samples, respectively. The peak intensities are also decreased accompanied with the existence of the impurity phases.

To visualize this behavior, we show the content dependence of the lattice constant calculated from the XRD data using the Nelson-Riley function (Fig. 1). The lattice constant of the gallium substituted samples decreases linearly with increasing x. However, in the case of aluminum ones, the decrease in the lattice constant deviates from the linearity with respect to the content above $x=0.46$. The lattice constant of indium substituted samples also exhibit the deviation above $x=0.7$, although the lattice conversely expands with increasing the content. The increase in the lattice constant of the indium substituted samples is due to the substitution of indium ions onto the 16*a* sites. These behavior are consistent with the XRD profiles. The decrement in the lattice constant of gallium substituted samples is smaller than that of aluminum ones, which is associated with the size of the nonmagnetic ion relative to that of iron ions in the 24*d* sites. Gilleo *et al.* also reported the similar tendency in YIG particles[6].

3.2 Magnetic characterization

The substitution site of nonmagnetic ions in the garnet crystal was also determined by the saturation magnetization (M_s) of these particles at 5 K. Fig. 2 shows the content dependence of the M_s of aluminum, gallium and indium substituted samples measured in a field of 10 kOe. The magnetization curve of Bi-YIG particles shown in the inset of Fig. 2 guarantees the magnetic saturation in 10 kOe. The dash line represents the values based on the Néel model for the substitution onto the tetrahedral and octahedral sites. The M_s of the indium substituted samples increases with increasing x, whereas the aluminum and gallium ones decrease with x. This result suggests that aluminum and gallium ions are substituted preferentially on the 24*d* tetrahedral sites and indium ions are substituted on the 16*a* octahedral sites. The same behaviors of M_s with x were also obtained in YIG system[7,8,9] and in Bi-YIG system[10]. The M_s of the indium substituted samples considerably deviates from the Néel model at high content x. The

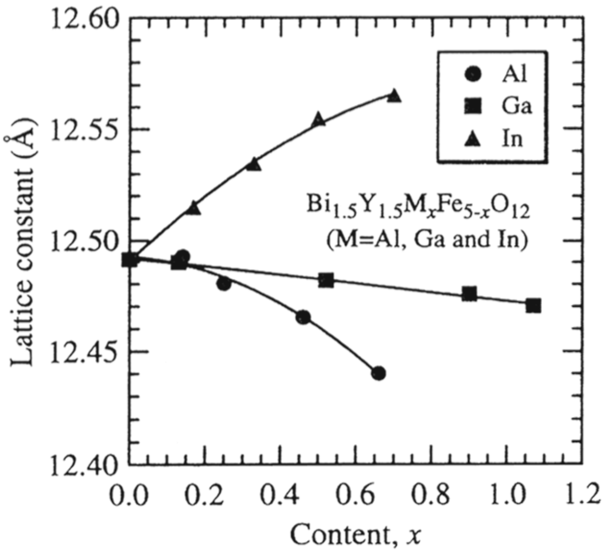

Fig.1 Lattice constant of nonmagnetic ions (Al, Ga and In) substituted Bi-YIG particles annealed at 700 °C as a function of content.

deviation may be caused by the canting[11] of iron moments on 24*d* sites owing to the substitution of non-magnetic ion. Geller *et al.*[9] reported that in the case of the indium substituted YIG system, the M_s shows a maximum due to the canting effect at $x=0.7$, which corresponds to the same region in the present case. We should also note that the deviation may be associated with the decrease in the XRD intensity, namely, the existence of other phases observed around this content.

In order to clarify the cause of the deviation, we further optimized the condition of sample preparation for indium substituted samples. Fig. 3 shows the M_s of the indium substituted samples as a function of annealing temperature. The M_s increases abruptly above 630 °C and reaches the saturation at 650 °C, indicating the complete of the crystallization. Therefore we prepared the indium substituted samples with various indium content under the annealing condition of 650 °C. Fig. 4 demonstrates the content dependence of the lattice constant of indium substituted samples annealed at 650 °C. The lattice constant increases linearly with increasing the content over the entire region, suggestive of the successful optimization of annealing condition. The M_s of the indium substituted samples were also measured for various substitution contents (Fig. 5). In spite of the successful crystallization, the M_s shows a visible deviation from the Néel model above $x=0.6$. Thus the deviation should be due to the canting of the magnetic moments of iron ions on 24*d* sites.

3.3 Optical and magneto-optical properties

We turn to the optical and magneto-optical properties of indium substituted samples annealed at 650 °C. Fig. 6 shows the absorption coefficient α measured at three different wavelengths. The reduction in the α is observed with increasing the content for all the wavelengths, although the decrement measured at 633 nm and 700 nm is not

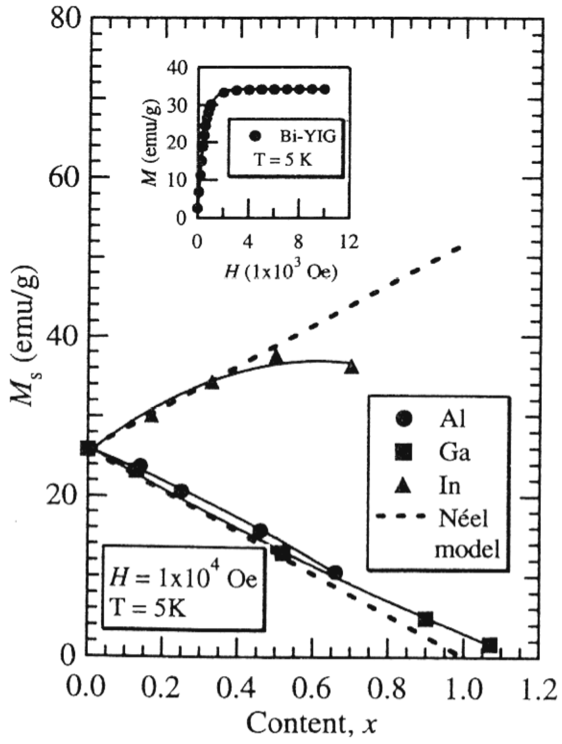

Fig.2 Saturation magnetization of nonmagnetic ions (Al, Ga and In) substituted Bi-YIG particles (annealed at 700 °C) measured at 5K in $H=10$ kOe as a function of content. The inset is the magnetization of the Bi-YIG particles as a function of applied field measured at 5 K. The dashed line represents the values based on the Néel model.

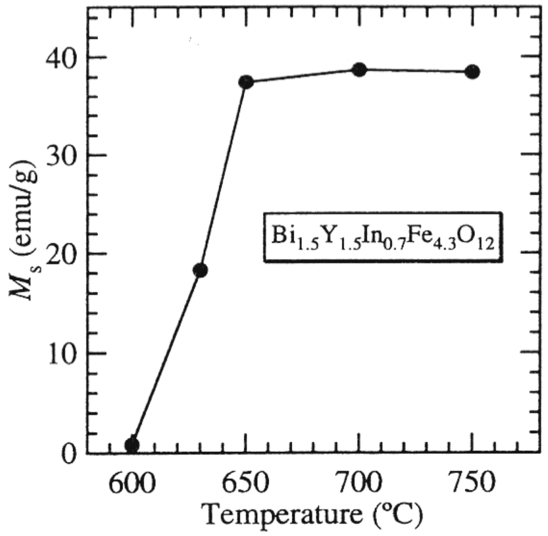

Fig.3 Saturation magnetization of indium substituted sample ($x=0.7$) as a function of heat treatment temperature.

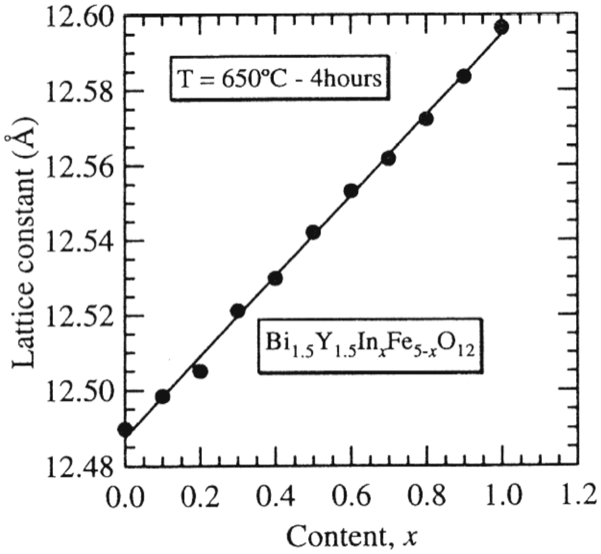

Fig.4 Lattice constant calculated from XRD data of indium substituted particles annealed at 650 °C as a function of content.

pronounced because of the considerable reduction of the α. It should be noted that the dip of the α is also observed at around $x=0.5$ for all the wavelengths. It is plausible that the dip originates from the scattering of the light at surface roughness of the film and/or at micro-bubbles in the epoxy binder of the film. In fact, the surface morphology is quite sensitive to the temperature to harden the binder, which changes the reflection rate of light at the surface.

Fig. 7 shows the Faraday rotation (θ_F) of indium substituted samples as a function of the content. The θ_F decreases monotonically with increasing the content, which also indicates that the dip of the α is unlikely to be affected by the change in the electronic structure induced by the substitution. The magneto-optical performance factor, i.e., figure of merit, can be derived using the θ_F as shown in Fig. 8. It is obvious that the large value of the figure of merit at $x=0.5$ is reflected by the dip in the α. Thus it is likely that the figure of merit remains constant below $x=0.5$ and decrease monotonically above this content. Reexamination is required to clarify the behavior of the figure of merit in addition to the characterization of the micro-morphology of the binder.

Finally, we should comment on the magneto-optical properties of aluminum and gallium substituted samples.

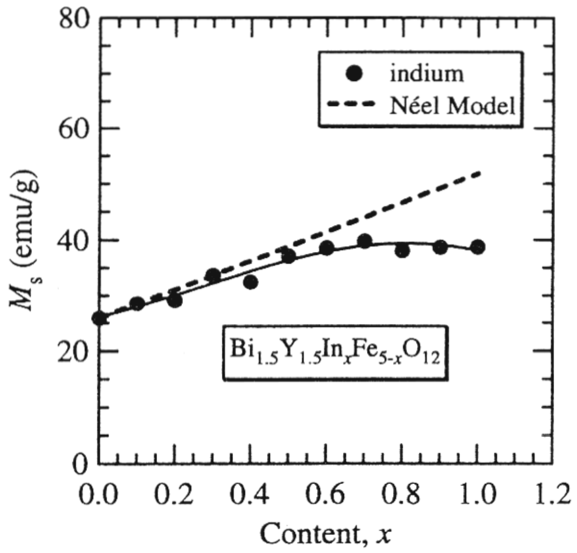

Fig.5 Saturation magnetization of indium substituted particles annealed at 650 °C as a function of content.

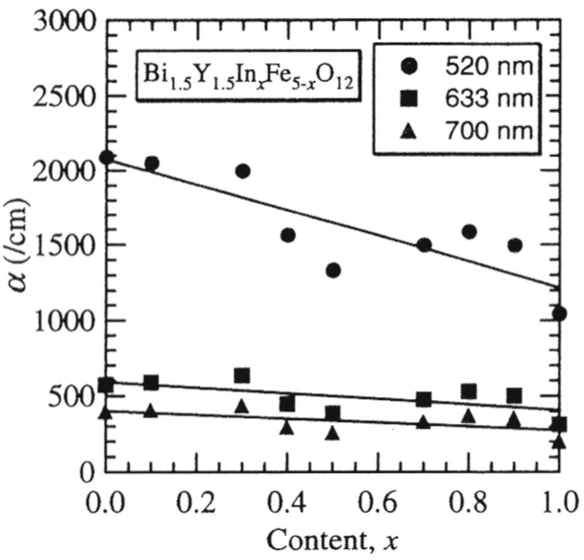

Fig.6 Absorption coefficient of indium substituted film (annealed at 650 °C) measured at 520, 633 and 700 nm as a function of content.

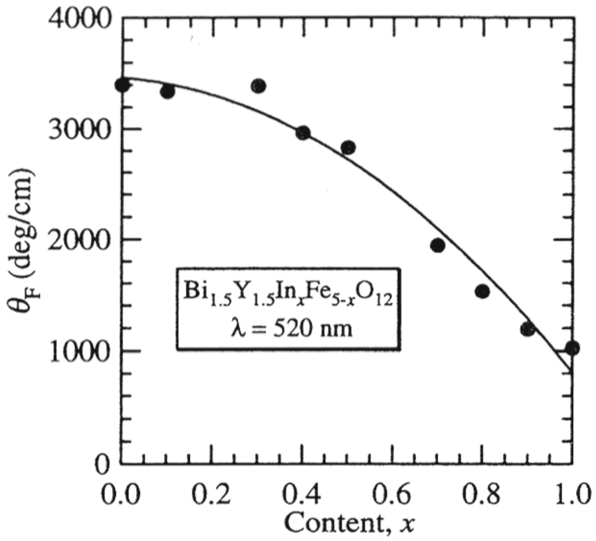

Fig.7 Faraday rotation of indium substituted film (annealed at 650 °C) measured at 520 nm as a function of content.

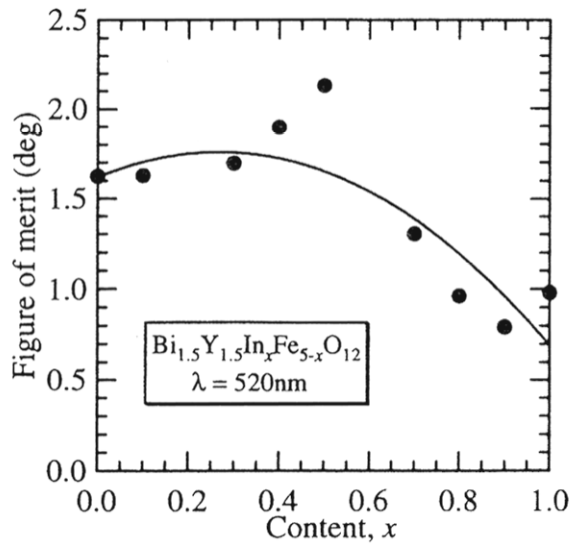

Fig.8 Figure of merit calculated by θ_F and α of indium substituted films (annealed at 650 °C) as a function of content.

Although the detailed feature was not measured for these samples, our preliminary experiments on the samples annealed at 700 °C indicates that the Faraday rotation and the figure of merits monotonically decrease with the content for both the samples.

4 Summary

Nonmagnetic ions (aluminum, gallium and indium) substituted Bi-YIG fine particles were prepared by coprecipitation and heat treatment. The film with magneto-optical particles were prepared by mixing with epoxy binder, milling and coating on glass substrates. The indium substituted particles were successfully prepared by optimizing the annealing temperature. The deviation of the magnetic characteristics from the Néel model can be interpreted by the canting effects of the magnetic moments of iron ions at 24*d* sites. The figure of merit persists up to $x=0.5$ and shows a gradual decrease above this content. The optimization of drying condition of the film should be performed to clarify the detailed profile of the figure of merit as a function of the substitution content.

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