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MAGNETIC AND MAGNETO-OPTICAL PROPERTIES OF Ca-DOPED Bi-YIG SPUTTERED FILMS

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Abstract- Ca-doped Bi-YIG films were prepared by rf-sputtering, and their magnetic and magneto-optical properties in the visible wavelength region have been investigated. The films were deposited on vitreous SiO_2 and Corning #7059 glass substrates at 400°C. The sputtering was conducted with an Ar pressure of 6.7 Pa, deposition rate was 3.3 nm/min, and a rf-power density of 2.5 W/cm^2. The deposited films were annealed in air at 500~1000°C for 4h to convert to polycrystalline films. The films annealed at 600~700°C were determined to be the garnet phase and they showed large saturation magnetizations more than 100 emu/cm^3. The magnetization of Ca doped films was constant in the range of Ca ratio x = 0.0~1.0, however, the θ_F decreased with x in the same composition range. It was found that the θ_F of $Bi_2YCaFe_yO_{12}$ films increased, while the M_s of the films decreased, in the composition range of y = 3.5~5.0.

I. Introduction

Bismuth substituted iron garnet(Bi-YIG) is a very promising material for magneto-optical media and has been applied in magneto-optical devices working in the infrared wavelength region. However, in the visible wavelength region, Bi-YIG films have a large absorption caused by Fe^{3+} ions, and their figure of merit is considerably smaller than that in the infrared wavelength region. We have previously investigated Ca-doped Bi-YIG films to decrease the optical absorption[1]. In this paper, we discuss the effects of Ca^{2+} substitution in highly Ca-doped Bi-YIG sputter films.

II. Experimental

A. Target preparation

Targets for the sputtering were prepared by first mixing the oxide powders of Bi_2O_3, Y_2O_3, Fe_2O_3 and CaO, then firing at 800°C for 4h and grinding with a mill. The obtained powder was pressed at 200 kg/cm^2 to form a target disk. The diameter of the target was 100 mm, and the thickness was 3 mm. Figure 1 shows the target preparation procedure.

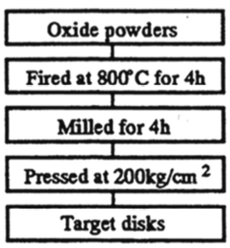

Figure 1. Target disk preparation procedure.

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B. Film preparation

Ca-doped Bi-YIG films were prepared on vitreous SiO_2, Corning #7059 glass and sapphire substrates by rf-sputtering. The sputtering conditions are given in Table I. The sapphire substrates, which have higher melting point than vitreous SiO_2 and #7059, were used for exact measurements of film thicknesses. The film thickness was about 600nm.

TABLE I
Sputtering Condition

Target composition	$Bi_2YCa_xFe_{5-x}O_{12}$ (x=0.0, 0.3, 0.5, 1.0, 1.5)
	$Bi_2YCaFe_yO_{12}$ (y=3.0, 3.5, 4.0, 4.5, 5.0, 6.7)
Sputter gas	Ar, 6.7 Pa
Substrate	Corning #7059, SiO_2(Vitreous), Sapphire
Substrate temperature	400 °C
rf-power density	2.5 W/cm^2
Deposition rate	5.0 nm/min
Target-substrate distance	40 mm

As the deposited films were amorphous, they were annealed in air at 500~1000°C for 4h. The annealed films were examined by x-ray diffraction analysis with Cu Kα. Film thickness was measured with a DEKTAK thickness meter. The film composition was determined with an EDX analyzer. Saturation magnetization (M_s) and coercive force (H_c) were measured with a VSM. The magnetic field applied was up to 2 kOe. The Faraday rotation angle (θ_F) was measured by the polarization modulation method.

III. Results and Discussion

A. Magnetic and magneto-optical properties of $Bi_2YCa_xFe_{5-x}O_{12}$ films

Figure 2 shows the x-ray diffraction patterns of the sputtered and annealed films prepared with the targets of $Bi_2YCa_xFe_{5-x}O_{12}$. The films were annealed at 650°C for 4h. All peaks of the films with x = 0.0, 0.3, 0.5, 1.0 were assigned to garnet. Garnet peaks were not observed with the films of x = 1.5. The variations of M_s and θ_F against the Ca content x are shown in Fig.3. The films showed constant M_s values for x = 0.0~1.0, however θ_F decreased monotonically with Ca content. Geller *et al.* reported that Ca^{2+} substitutes for cations on 24*c* sites in the garnet structure[2],[3].

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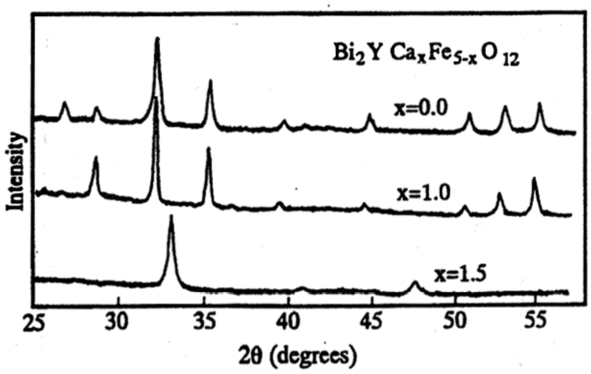

Figure 2. X-ray diffraction patterns of Ca-doped Bi-YIG films.

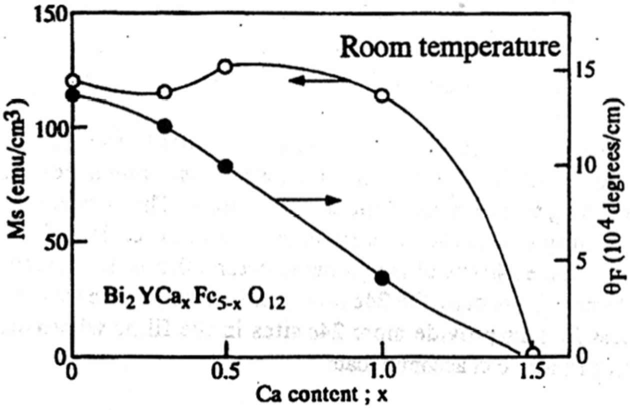

Figure 3. Magnetization and Faraday rotation of Ca-doped Bi-YIG films at 520nm as a funtion of Ca content.

It is expected that θ_F and M_s increases with the fraction of garnet phase in the films. Therefore in Fig.4, we plot θ_F/M_s as a function of x for the $Bi_2YCa_xFe_{5-x}O_{12}$ system, and investigate the magneto-optical properties of the garnet phase which formed in the films. The θ_F/M_s decreases with Ca content. This result implies that the Bi^{3+} ions in the 24*c* sites are replaced by the Ca^{2+} ions. The result also implies that the affinity of Ca for the 24*c* sites are larger than that of Bi. In these films, the garnet crystals are dispersed in non magnetic phases composed of Bi, Y, Ca, Fe oxides.

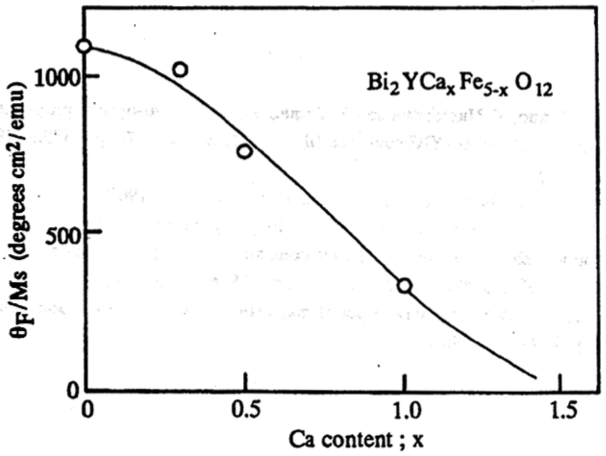

Figure 4. θ_F/M_s vs. Ca content.

Figure 5 shows the saturation magnetizations of the YIG, Bi-YIG and (Ca, Bi)-YIG films as a function of the annealing temperature. It is noted that at about 700°C or above, the M_s of Bi- and (Ca, Bi)-YIG films decrease rapidly with increasing annealing temperature. The drop of M_s around 800°C implies that the garnet structure of Bi- and (Ca, Bi)-YIG decomposes at this temperature. Neither magnetization nor garnet phase were detected with YIG films below 800°C, but garnet phase was observed when the films were annealed over 900°C.

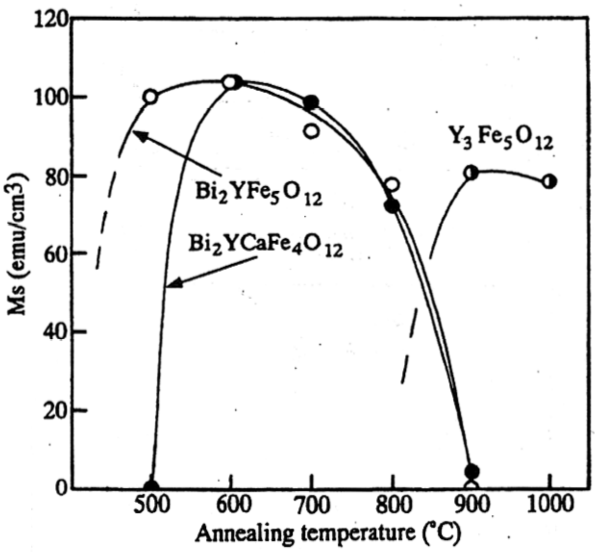

Figure 5. Magnetization of Ca-doped Bi-YIG films as a function of annealing temperature.

B. Magnetic and magneto-optical properties of $Bi_2YCaFe_yO_{12}$ films

Through the measurements of magnetic properties of $Bi_2YCa_xFe_{5-x}O_{12}$ films, we showed that Ca-containing films exhibited constant values of M_s, even though the films contained less Fe ions at $x = 1.0$. In this section, we investigate the effect of Fe concentration in the films on the magneto-optical properties at the Ca content of $x = 1.0$. Films were prepared for $Bi_2YCaFe_yO_{12}$ system with y = 3.0, 3.5, 4.0, 4.5, 5.0, 6.7.

The x-ray diffraction patterns of the films are shown in Fig.6. All films showed garnet peaks, and in the films of y = 3.0, 3.5, 6.7, non-garnet peaks were also observed. This result indicates formation of a garnet phase in a wide range of Fe concentration in the films.

Figure 7 shows the relation between M_s and Fe content measured on the films in this system. The M_s decreases with Fe content in the range between $y = 3.5$ and 5.0. It should be noted that the large M_s value of 130 emu/cm^3 was obtained with such Fe deficient films at $y = 3.5$.

The relation between θ_F and Fe content is shown in Fig.8. The correlation between θ_F and y in this system differ from that between M_s and y, that is, the θ_F increases with y in the range of $y = 3.5$~5.0.

The θ_F/M_s for $Bi_2YCaFe_yO_{12}$ system is shown in Fig.9 as a function of y. It is expected that higher values of θ_F/M_s indicate the formation of garnet phase which exhibits larger θ_F.

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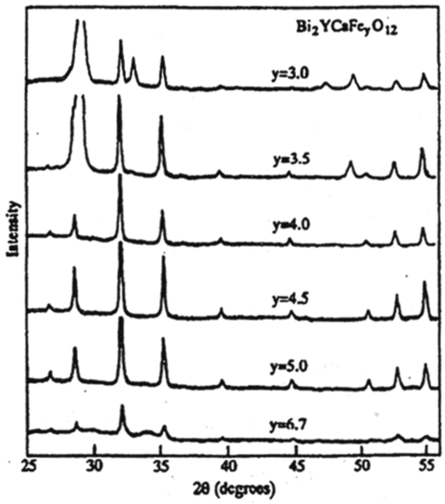

Figure 6. X-ray diffraction patterns of large amount Ca doped Bi-YIG films.

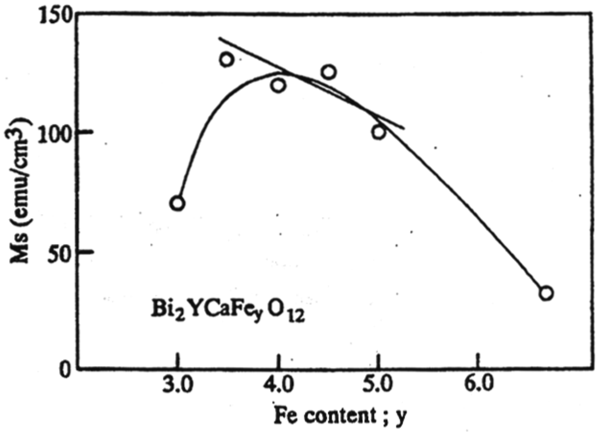

Figure 7. Magnetization as a function of Fe content.

Therefore, the correlation between θ_F/M_s and y demonstrate that the garnet crystals formed through the annealing process in the films show larger Faraday rotation when they contain more Fe ions, in the region of $y = 3.0\sim5.0$. The magneto-optic effect in Bi-YIG crystals is generally attributed to the Bi^{3+}ions in 24*c*

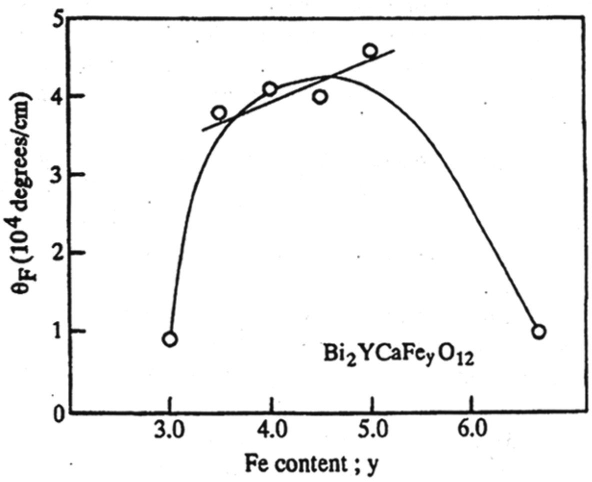

Figure 8. Faraday rotation at 520nm as a function of Fe content.

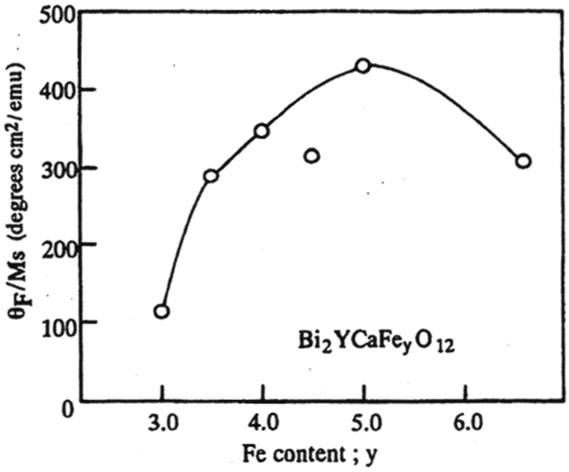

Figure 9. θ_F/M_s vs. Fe content.

site[4]. From the data in Fig.9, it is probable that the Bi content in the garnet crystals in the films increases with increasing Fe content, when Ca concentration is constant. This dependence is possibly due to the affinity difference between Bi and Ca regarding the 24*c* site of the garnet structure, that is, the Ca ions preferentially occupy the 24*c* sites, and when *y* increases, the excess Fe ions provide more 24*c* sites in the films where the excess Bi ions can accommodate.

IV. Conclusions

Bi-YIG polycrystalline films containing large amount of calcium ions were prepared by rf-sputtering, and the Faraday rotation in the visible wavelength region was investigated. In wide ranges of Ca and Fe concentrations, the garnet, *magnetic*, phase was formed, however, the phase decomposed at higher temperature above 800°C. It is concluded that Ca containing Bi-YIG films exhibit a constant M_s in a composition range where the Fe content is lower than the stoichiometric amount in the garnet structure, and that the θ_F of the films is decreased by Ca ions contained in the garnet phase in the films. It is suggested that Ca has a larger affinity for the 24*c* site of garnet than Bi has.

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