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Nonstoichiometric Properties of Bi-Substituted Yttrium Iron Garnet Sputtered Films

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Structural, magnetic and magnetooptical properties of nonstoichiometric Bi-substituted yttrium iron garnet (Bi-YIG) films have been studied in terms of Fe concentration. The garnet films were prepared by rf sputtering using targets which had various Fe contents. In the wide range of Fe content from about 3.9 to 5.4, garnet phases were obtained at an annealing temperature of 650°C. For the Fe contents ranging from 1.9 to 5.1, saturation magnetization increased linearly, and beyond the Fe content of 5.1, it dropped sharply. By considering the magnitude of Faraday rotation of the garnet phase formed in the films (θ_F/M_s) and Curie temperature, it is expected that the Bi concentration in the garnet-phase crystallites in the prepared films increases as Fe content increases. It was observed, in energy dispersive X-ray spectrometry (EDX) and secondary ion mass spectrometry (SIMS) analyses, that the excess Bi ions in low-Fe-content films concentrated at the surface, near the film-substrate interface, at the edge of the films and at grain boundaries.

KEYWORDS: nonstoichiometric properties, Bi-YIG, sputtered films, saturation magnetization, Faraday rotation, Curie temperature, TEM image, SEM image, SIMS analyses, Bi distribution

1. Introduction

Bismuth-substituted iron garnet films are a very attractive material for magnetooptical applications. The sputtering method has been applied to the preparation of garnet films because some remarkable progress has been made by substitution of, for example, Bi^{3+} and Ce^{3+} to the garnet structure. It was reported that in spite of the considerable deviation from the stoichiometric composition of garnet, a single phase of garnet structure could be obtained by the sputtering method.[1,2] It is worthwhile to determine the composition range in which the garnet structure can be obtained, and to clarify the film structure in order to obtain high-quality films for use as magnetooptical media.

In this paper, we prepare Bi-YIG sputtered films using targets which have various Fe contents, and analyze the structural, magnetic and magnetooptical properties of the films.

2. Experimental

The films were prepared on vitreous SiO_2 and Corning 0317 glass substrates by rf sputtering under the conditions given in Table I. The targets were prepared first by mixing oxide powders, then were fired at 800°C for 4 h and ground with a mill. Then they were pressed at 200 kg/cm^2 to form disks. The disk diameter of the target was 100 mm and the spacing between the target and the substrate was 40 mm. The as-deposited amorphous films were annealed in air at 650°C for 4 h to crystallize the films. Annealed films were examined by X-ray diffraction with a Cu–Kα source. The film thickness was measured using a surface step analyzer (Dektak). The chemical composition of the prepared films was determined by inductively coupled plasma spectroscopy. Saturation magnetization (M_s) was measured using a vibrating sample magnetometer (VSM). The magnetic field was applied up to 2 kOe. The Faraday rotations were measured by the polarization modulation method. These optical measurements were carried out in the visible-wavelength region.

Table I. Sputtering conditions.

Target	$Bi_2YFe_zO_{4.5+1.5z}$ (x=1, 2, 3, 4, 5, 6)
Sputter gas	Ar, 6.7 Pa
Substrate	Corning 0317, SiO_2 (Vitreous)
Substrate temperature	400°C
rf Power density	2.5 W/cm^2
Deposition rate	4.3 nm/min

3. Results and Discussion

3.1 *Film composition*

Film compositions of as-deposited films are given in Table II. We show two kinds of film composition in Table II. One is that in which the sum of cations in films is assumed to equal the sum of cations in targets (a). Comparing the film composition (a) with target composition, the content of Y in the films is more than that in the targets, while the Bi content is less than that in the targets. However, the contents of Bi and Y in the films are almost constant, and the Fe content in the films is slightly more than the Fe content in tar-

Table II. Film compositions.

Sample No.	Target			Film						(Bi+Y)/Fe
				(a)			(b)			
	Bi	Y	Fe	Bi	Y	Fe	Bi	Y	Fe	
1	2	1	1	1.7	1.3	1.0	3.4	2.7	1.9	3.21
2	2	1	2	1.4	1.2	2.4	2.2	1.9	3.9	1.05
3	2	1	3	1.7	1.0	3.3	2.2	1.4	4.4	0.82
4	2	1	4	1.5	1.1	4.4	1.7	1.2	5.1	0.57
5	2	1	5	1.5	1.1	5.4	1.6	1.0	5.4	0.48
6	2	1	6	1.5	1.0	6.5	1.3	0.9	5.8	0.38

gets. The other is that in which we assume the ratio of cations to anions to be 8/12 (b), because this ratio is for a garnet structure. We will use composition (b) as the film composition in this paper. The values of 0.38–3.21 for (Bi+Y)/Fe listed in Table II indicate considerable deviation from the stoichiometric garnet value of 0.6.

3.2 *Film structure*

The X-ray diffraction patterns of the samples are shown in Fig. 1, where 2θ is scanned from 15° to 45°. The sample number in Fig. 1 is consistent with that in Table II. For Sample 1, garnet peaks are nominally observed. For Sample 2, while a slight impurity phase appears, almost all peaks are assigned to garnet. All peaks of Samples 3, 4 and 5 are assigned to garnet. Then, for Sample 6, the intensity of garnet peaks becomes weak and an impurity phase appears. The garnet structure can be obtained in the wide range of Fe content from about 3.9 to 5.4 at the annealing temperature of 650°C.

Figures 2 and 3 show transmission electron microscope (TEM) images and transmission high-energy electron diffraction (THEED) patterns of Samples 4 and 2. Films are prepared on NaCl substrates in order to obtain the samples for TEM analysis. For Sample 4 ($Bi_{1.7}Y_{1.2}Fe_{5.1}O_{12}$ film) in Fig. 2, there are two areas shown as A and B. In Area A, grains of about 100 nm in diameter are clearly confirmed. The THEED pattern of Area A is assigned to garnet. On the other hand, the grain boundaries are not clear in Area B. In the THEED pattern of Area B, sizes of grains seem to be smaller than those in Area A, and there are unknown phases besides the garnet phase. In Fig. 3, grains of

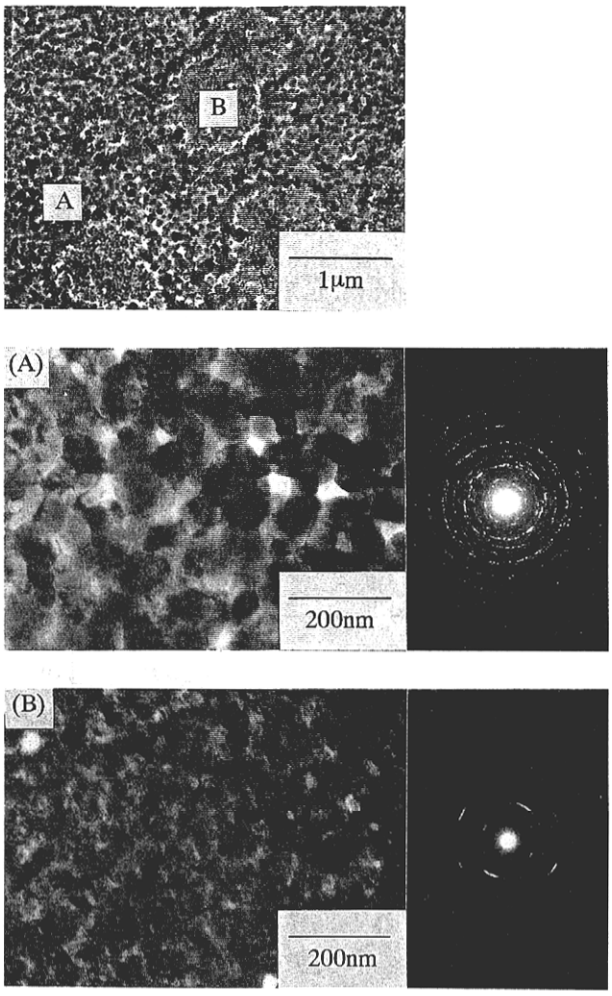

Fig. 2. TEM images and THEED patterns of $Bi_{1.7}Y_{1.2}Fe_{5.1}O_{12}$ film annealed at 650°C.

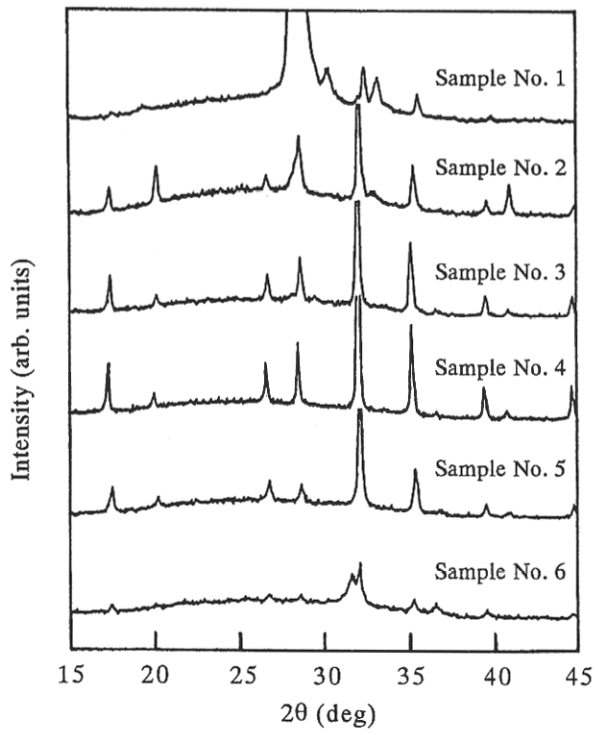

Fig. 1. X-ray diffraction patterns of the films with various Fe contents.

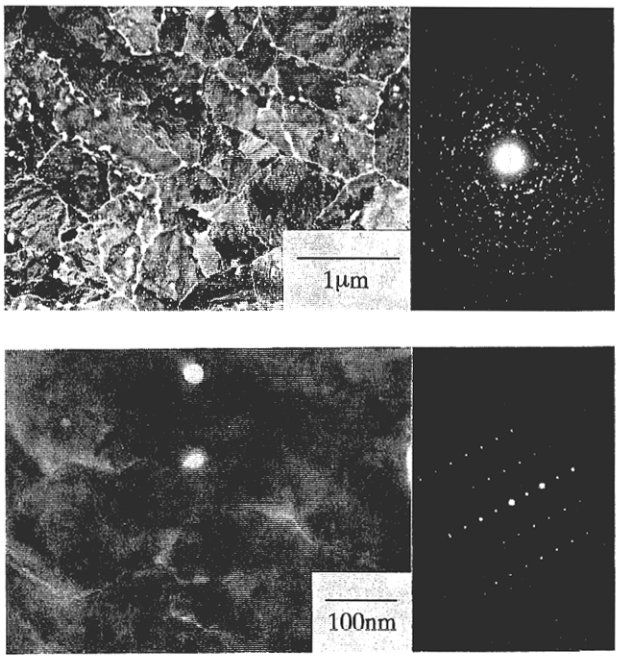

Fig. 3. TEM images and THEED patterns of $Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ film annealed at 650°C.

about 1 μm in diameter are observed in Sample 2 ($Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ film) and they are well-crystallized. Since Sample 2 has composition considerably deviating from that of stoichiometric garnet, it can be considered that the grains grow largely due to little nucleation and fast diffusion rate of Bi. According to the THEED pattern, this film also contains some unknown phases. However, some parts of the film are confirmed to be single crystals of garnet from the diffraction pattern of the magnified images shown in Fig. 3.

3.3 *Magnetic and magnetooptical properties*

M_s and Faraday rotations (θ_F) of the films are shown in Fig. 4 as functions of Fe content. M_s increases linearly for Fe content less than 5 and drops sharply for Fe content over 5. It is presumed that M_s increases in proportion to the volume of crystallites having the garnet structure up to Fe content of 5, after which the garnet structure decomposes suddenly. The Faraday rotation of the films was measured at 520 nm. The curve of the Faraday rotation as a function of Fe content is similar to that of M_s. Upon comparing the film with Fe content 3.9 and the film with Fe content 5.4, M_s is found to be almost the same; however, the value of Faraday rotation for 5.4 Fe film is about twice that for 3.9 Fe film.

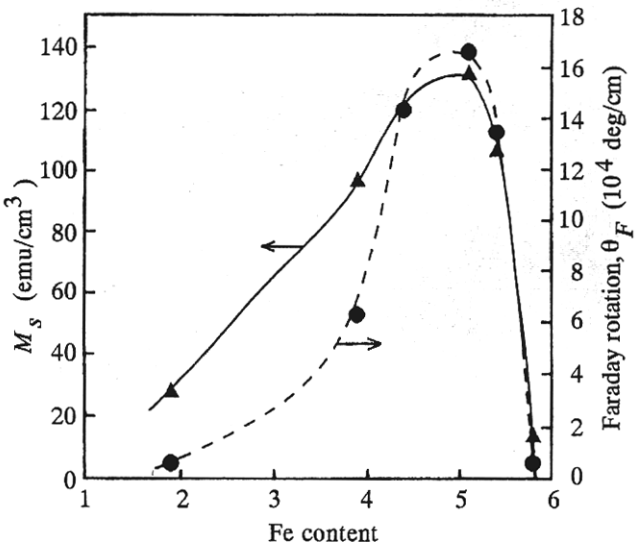

Fig. 4. Saturation magnetization and Faraday rotation (at 520 nm) of the films with various Fe contents.

Figure 5 shows θ_F/M_s as a function of Fe content. It could be assumed that there were no other magnetic phases except the garnet phase in the films. Therefore, the value of θ_F/M_s represents the magnitude of Faraday rotation of the garnet phase formed in the films. In the region of Fe content ranging from 4.4 to 5.4, although the value of θ_F/M_s increases gradually, it is almost constant. For the film with Fe content of 3.9, θ_F/M_s is half the value of the films with Fe content ranging from 4.4 to 5.4. It is considered that in the film with Fe content of 3.9, Bi and Y are contained in the amorphous phase. Y is incorporated more stably in the garnet structure than Bi because a special technique must be used to prepare highly Bi-substituted YIG.[3] Considering that Faraday rotation is much enhanced by Bi,[4,5] this result suggests that the garnet phase formed in the films with Fe content of 3.9 contains fewer Bi ions than the garnet phase formed in the films with Fe content around 5.

Figure 6 shows the Curie temperature of the films with various Fe contents. It is reported that the Curie temperature increases linearly with Bi content in the system of $Bi_xY_{3-x}Fe_5O_{12}$.[6] In this case, since the Curie temperature increases as Fe content increases, it is considered the Bi content of the garnet structure increases with Fe content. This result is consistent with the consideration of Fig. 5.

3.4 *Distribution of Bi*

Although Sample 2 ($Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ film) contains more Bi ions in the film than Sample 4 ($Bi_{1.7}Y_{1.2}Fe_{5.1}O_{12}$

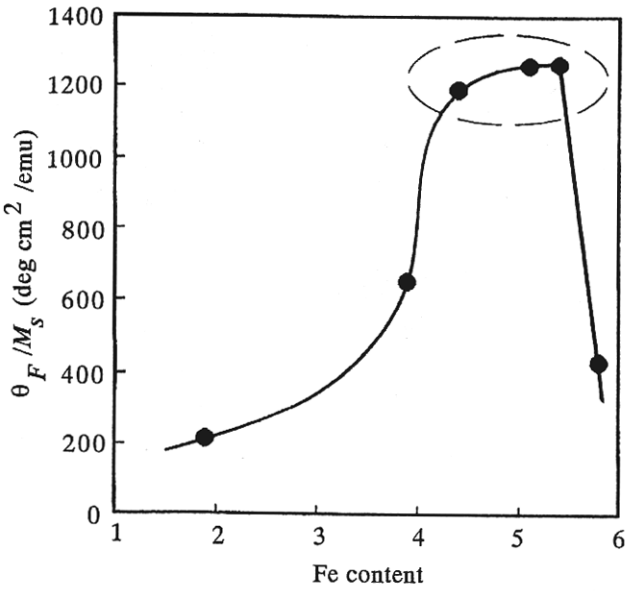

Fig. 5. θ_F/M_s vs Fe content for the films annealed at 650°C.

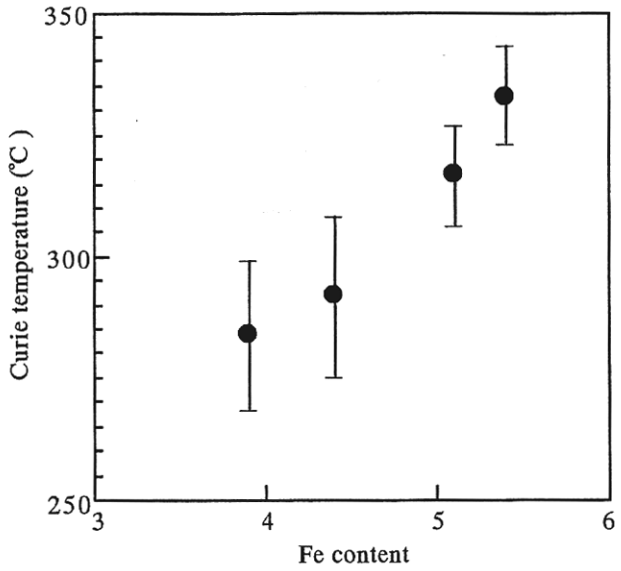

Fig. 6. Curie temperature of the films with various Fe contents.

film), θ_F/M_s of Sample 2 is much smaller than that of Sample 4. Considering that a large amount of Bi remains outside of the garnet structure in the film, the area where Bi ions are concentrated in the films must be clarified.

Figure 7 shows a scanning electron microscope (SEM) image near the edge of a $Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ film annealed at 650°C. Compositions are measured with EDX at points A, B and C. The results are indicated in Table III. The proportion of Bi increases the toward the edge of the film. This result is also confirmed in the as-deposited Sample 2 film, but in Sample 4, this tendency is not observed.

The depth profile of as-deposited $Bi_{1.7}Y_{1.2}Fe_{5.1}O_{12}$ film is shown in Fig. 8. This profile was obtained by SIMS. The primary ion is Ar^+ and four mass numbers of 29 for Si, 54 for Fe, 89 for Y and 209 for Bi, are detected as + polarity. It is found that a certain amount of Bi concentrates at the surface of the film and near the film-substrate interface. The inner part of the film is homogeneous. This tendency is also confirmed in Sample 2.

The backscattered electron SEM image of Sample 2 is shown in Fig. 9. This specimen is prepared by removing segregated Bi at the surface by Ar ion sputtering in SIMS. Grains of about 1 μm in diameter are observed. It is considered that heavy atoms are concentrated at grain boundaries since heavy atoms are strongly detected because of their high reflection efficiency. Compositions are measured by EDX in grains and at grain boundaries. The results, in which we assume the ratio of cations to anions as 8/12, are shown in Table IV. The composition in a grain is close to that of stoichiometric garnet. On the other hand, the amount of Fe at grain boundaries is much lower than that in a grain. Excess heavy ions seem to be concentrated at grain boundaries.

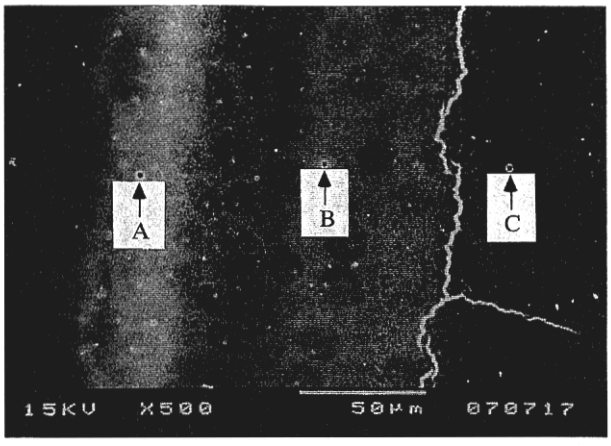

Fig. 7. SEM image of $Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ film annealed at 650°C.

Table III. Compositions at points A, B and C in Fig. 7.

Point	Bi	Y	Fe (at.%)
A	55	13	32
B	36	20	44
C	23	24	53

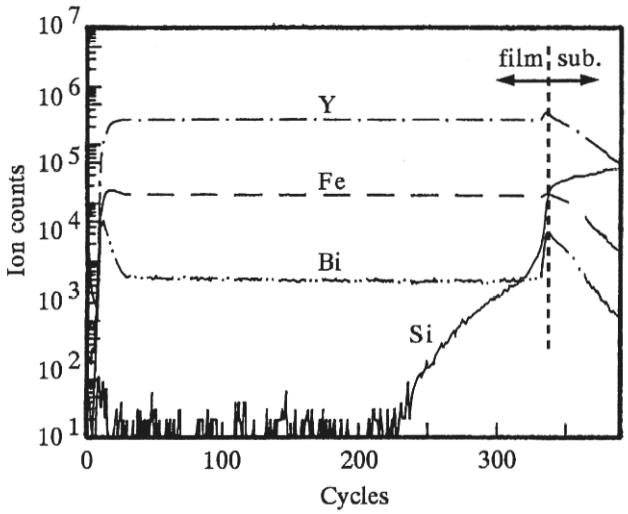

Fig. 8. Depth profile of as-deposited $Bi_{1.7}Y_{1.2}Fe_{5.1}O_{12}$ film, where 500 Å of Au was coated on the surface of the film.

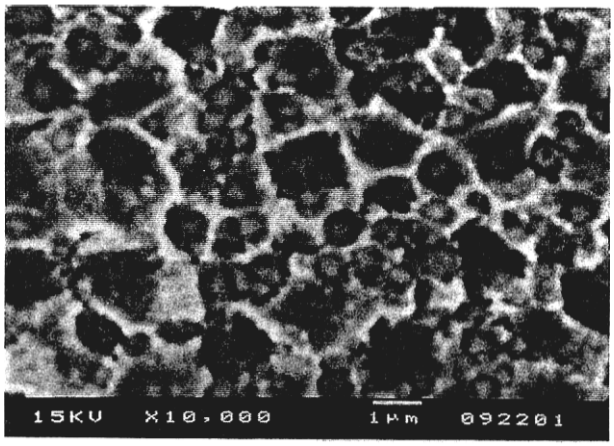

Fig. 9. Backscattered electron SEM image of $Bi_{2.2}Y_{1.9}Fe_{3.9}O_{12}$ film annealed at 650°C.

Table IV. Compositions in a grain and at grain boundaries in Fig. 9.

	Bi	Y	Fe
Grain	1.3	2.0	4.7
Boundary	2.1	2.3	3.6

From these results, it is considered that excess Bi ions concentrate at the surface, near the film-substrate interface, at the edge of the film and at grain boundaries.

4. Conclusions

Aiming at the determination of the composition range in which the garnet structure is obtained, we prepared films by rf-sputtering using $Bi_2YFe_xO_{4.5+1.5x}$ targets. Through the magnetic and magnetooptical measurements on various Bi-YIG sputtered films, the following results were obtained. In the wide range of Fe

content from about 3.9 to 5.4, the garnet structure could be obtained at the annealing temperature of 650°C. It is presumed that M_s increases in proportion to the volume of crystallites having garnet structure up to Fe content of 5, and garnet structure decomposes with Fe content over 5. Not all Bi ions were incorporated in the garnet phase of the film with Fe content of 3.9; therefore, the film showed a small value of θ_F/M_s. This result was supported by Curie temperature data of the films.

From the results of EDX and SIMS analyses, it is considered that excess Bi ions concentrate at the surface, near the film-substrate interface, at the edge of the film and at grain boundaries.

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