# Structural, Magnetic, and Magneto-Optic Properties of Nonstoichiometric Bismuth-Substituted Yttrium Iron Garnet Films Prepared by Pyrolysis

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Polycrystalline nonstoichiometric bismuth-substituted yttrium iron garnet films with cation ratios of Bi : Y : Fe = 1.5 + $u$ : 1.5 : 5 and Bi : Y : Fe = 1.5 : 1.5 + $v$ : 5, where $-0.7 \leq u \leq 1.0$ and $-0.7 \leq v \leq 1.3$, have been prepared by pyrolysis. The crystal phases formed in these films at various temperatures have been analyzed by high power x-ray diffractometry (XRD). The saturation magnetization, the Curie temperatures, and the Faraday rotation at the wavelength of 633 nm have been measured as a function of $u$ and $v$. The XRD studies indicated that the bismuth and yttrium depleted ($u < 0$ and $v < 0$) films consisted of the mixed phases of garnet and impurity. While in the bismuth and yttrium overdosed films, no impurity lines were observed over a wide composition range of $0 \leq u \leq 0.5$ and $0 \leq v \leq 0.7$. The observed magnetic and magneto-optic data of these overdosed films, however, could only be reasonably explained by assuming the presence of samll amount of spurious phases, not detectable by the XRD.

## Ⅰ. Introduction

Bismuth-substituted iron garnet films have been used for magneto-optic and microwave devices[1], [2]. The iron garnet has a cubic symmetry with a space group of $I_{a\bar{3}d}$[3]. In a unit cell of the garnet structure, there are three types of cation sites ; three dodecahedral, two octahedral and three tetrahedral sites[3]. The dodecahedral sites are occupied by large ions such as bismuth and yttrium. Both the octahedral and tetrahedral sites are normally occupied by iron ions. In the stoichiometric bismuth-substituted yttrium iron garnet $Bi_xY_{3-x}Fe_5O_{12}$, the ratio of the sum of bismuth and yttrium concentraton to iron concentration, therefore, should be 3/5. However, it has been reported that in sputtered films the ratio is often significantly less than 3/5 or greater than 3/5[4], [5].

This work is the first systematic attempt to clarify the structural, magnetic, and magneto-optic properties of these films. The films with intentionally depleted and overdosed bismuth and yttrium were prepared by spin coating followed by thermal decomposition and crystallization or by pyrolysis. Pyrolysis was used because it allows to precisely control the chemical composition of multi-component systems such as Bi-Y-Fe-O studied[6].

This paper describes the phase diagrams, the saturation magnetization, the Curie temperatures, and the Faraday rotation of the nonstoichiometric films, and discusses the structures of these films.

## Ⅱ. Experiments

Bismuth-substituted yttrium iron garnet films with cation ratios of Bi : Y : 1.5 + $u$ : 1.5 : 5 and Bi : Y : Fe = 1.5 : 1.5 + $v$ : 5, where $-0.7 \leq u \leq 1.0$ and $-0.7 \leq v \leq 1.3$, were prepared on glass substrates (Corning 7059) by spin-coating the metal nitric solutions followed by thermal decomposition. The amorphous films obtained were then annealed for 3 hours at elevated temperatures ranging from 550 ℃ to 770 ℃. The details of the film preparation are reported elsewhere[7].

The crystal phases in the films were analyzed by the high power (40 kV, 150 mA) x-ray diffractometry(XRD). The film structures were observed by the backscattered scanning electron microscopy(BSSEM). The chemical uniformity of the

films were examined by the electron probe micro-analysis(EPMA). The saturation magnetization of the films were measured by the vibrating sample magnetometry(VSM). The Curie temperatures were determined from the temperature dependence of the Faraday rotation. The Faraday rotation at the wavelength of 633 nm of the films were measured by polarization modulation techniques using a helium-neon laser.

## Ⅲ. Results

The crystal phases in the films analyzed by the high power XRD and the BSSEM are shown in Figure 1. The closed circles denote garnet phases

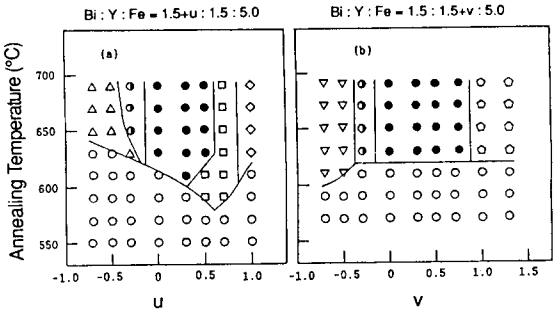


Fig. 1. Phase diagrams for the bismuth and yttrium depleted and overdosed films. The closed circles denote the garnet phases with no impurity lines, the open circles denote the amorphous phases which were not crystallized, and others denote the mixed phases of the garnet and impurity.

with no impurity lines, the open circles denote amorphous phases which were not crystallized, and others denote mixed phases with the garnet and impurity lines. Note that garnet phases with no impurities were observed over a wide overdosed composition range, $0 < u \leq 0.5$ and $0 < v \leq 0.7$ at the temperatures higher than 630 ℃. The EPMA studies indicated that the chemical compositions of these films agreed well with the starting compositions. No evidences of compositional inhomogeneity were observed. When u and v were much greater than 0.5 and 0.7, both impurity lines in the XRD diagrams and impurity segregation at the garnet grain boundaries in BSSEM micrographs were observed.

When $u = -0.3$ and $v = -0.3$, no impurity lines were observed in the XRD diagrams but amorphous phases which were not crystallized were observed aorund the garnet grains in the BSSEM micrographs. These phases were denoted as the half-closed circles in Figure 1. When $u < -0.3$ and $v < -0.3$, both impurity lines and amorphous phases were observed.

The following magnetic and magneto-optic data were confined to the films with $0 < u \leq 0.5$ and $0 < v \leq 0.7$ in which no impurity phases were observed. the data were collected for the films annealed at 670 ℃. In Figure 2 through 4 the experimental data are shown as the closed circles. Also

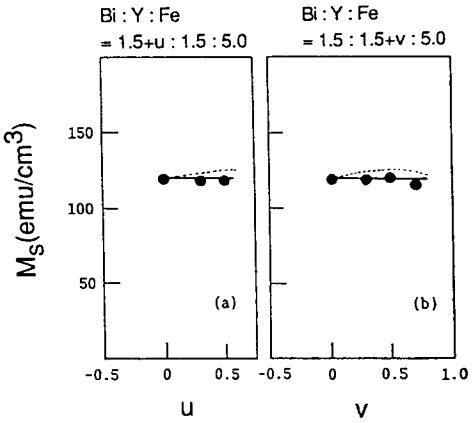


Fig. 2. Comparison of the measured(closed circles) to the calculated(solid and dotted lines) saturation magnetization($M_s$) for the bismuth and yttrium overdosed films.

shown are the calculated values, the dotted and solid lines, which will be discussed in the next section.

The saturation magnetization of the films are shown as a function of $u$ and $v$ in Figure 2. No considerable changes are observed with the increase of $u$ and $v$, compared to the film with $u = v = 0$.

The Curie temperatures of the films are shown as a function of $u$ and $v$ in Figure 3. The Curie

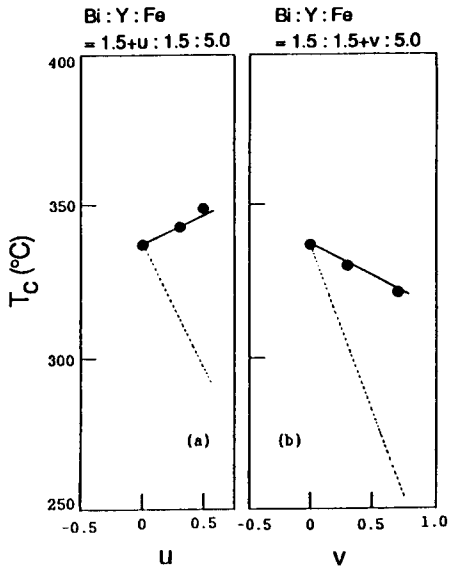


Fig. 3. Comparison of the measured(closed circles) to the calculated(solid and dotted lines) Curie temperatures($T_c$) for the bismuth and yttrium overdosed films.

temperatures are increased as $u$ increases but decreased as $v$ increases.

The Faraday rotation at 633 nm of the films are plotted as a function of $u$ and $v$ in Figure 4. The absolute values of the Faraday rotation are increased with $u$ but decreased with $v$.

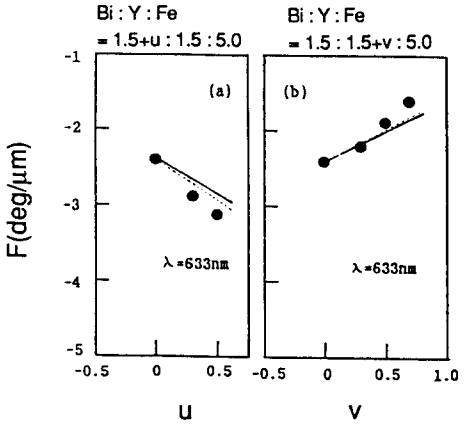


Fig. 4. Comparison of the measured(closed circles) to the calculated(solid and dotted lines) Faraday rotation($F$) at the wavelength of 633 nm for the bismuth and yttrium overdosed films.

## Ⅳ. Discussion

The fact that the films with only the garnet phase were not obtained in the bismuth and yttrium depleted region ($u < 0$ and $v < 0$) indicated that the garnet phase is unstable if there are vacancies in the dodecahedral sites. Since, the smallest examined $u$ and $v$ were 0.3, it appears that the garnet phase is unstable if more than 0.3 per formular unit of dodecahedral sites are vacant.

In the bismuth and yttrium overdosed ($u > 0$ and $v > 0$) films, no impurity lines were detected by the XRD over the wide range of $0 < u \leq 0.5$ and $0 < v \leq 0.7$. One explanation of the magnetic and magneto-optic data of these films may be given by assuming

i) for all starting compositions, a garnet phase forms, having both octahedral and tetrahedral sites filled by Fe ions, and the dodecahedral sites filled by Bi and Y ions, in a ratio equal to the nominal one,
ii) the rest of the starting material forms small amount of spurious phases, not detectable by the XRD, whose effect on the saturation magnetization, the Curie temperature, and the Faraday rotation is, in first approximation, negligible.

In this assumption, the actual formulae of the garnet phases in these films having nominally $u = 0.5$ and $v = 0.7$ are $\{Bi_{1.71}Y_{1.29}\}[Fe_2](Fe_3)O_{12}$ and $\{Bi_{1.22}Y_{1.78}\}[Fe_2](Fe_3)O_{12}$, respectively. (For $u = 0.5$, Bi : Y : Fe = 2.0 : 1.5 : 5. Thus Bi, Y and Fe concentrations per formula unit would be $3(2.0/3.5) = 1.71$, $3(1.5/3.5) = 1.29$, and 5. And in the spurious phases Bi : Y = (2.0 − 1.71 = 0.19) : (1.5 − 1.29 = 0.21). From this it follows that

a) the saturation magnetization ($M_s$) of all the films is almost the same, in excellent agreement with the data, see the solid lines in Figure 2.
b) On the basis of Hansen et al. [3], Bi substi-

tution in yttrium iron garnet yields a Faraday rotation ($F$) (at 633 nm) variation of $-2.06$ deg/$\mu$m per Bi per formula unit. The expected $F$ variations with respect to the sample with $u = v = 0$ (having formula $\{Bi_{1.5}Y_{1.5}\}[Fe_2](Fe_3)O_{12}$) are therefore :

$\Delta F = -2.06 \times 0.21 = -0.43$ deg/$\mu$m for $u = 0.5$, and

$\Delta F = +2.06 \times 0.28 = +0.58$ deg/$\mu$m for $v = 0.7$,

in reasonable agreement with the data, see the solid lines in Figure 3.

c) On the basis of Hansen et al. [3], Bi substitution in yttrium iron garnet yields a Curie temperature ($T_c$) variation of +38 K per Bi per formula unit. The expected $T_c$ variations with respect to the sample with $u = v = 0$ are therefore:

$\Delta T_c = +38 \times 0.21 = +8$ K for $u = 0.5$, and

$\Delta T_c = -38 \times 0.28 = -11$ K for $v = 0.7$,

also in reasonable agreement with the data, see the solid lines in Figure 4.

Another possibility that should be considered is that the yttrium ions enter both the dodecahedral and octahedral sites. In this assumption, the actual formulae of the garnet phases in the films having $u = 0.5$ and $v = 0.7$ are $\{Bi_{1.88}Y_{1.12}\}[Y_{0.29}Fe_{1.71}](Fe_3)O_{12}$ and $\{Bi_{1.38}Y_{1.62}\}[Y_{0.40}Fe_{1.60}](Fe_3)O_{12}$, respectively. (For $u = 0.5$, Bi : Y : Fe = 2.0 : 1.5 : 5. Then Bi, Y, and Fe concentrations per formula unit would be $2.0(8/8.5) = 1.88$, $1.5(8/8.5) = 1.41$, and $5(8/8.5) = 4.71$. Thus Y concentration in the octahedral site would be $(1.88 + 1.41) - 3 = 0.29$). It should be noted that there has been no consensus between reseachers whether the yttrium ions could enter the octahedral sites or not. On the basis of Nielsen[8] or Gualtieri et al. [9], in iron garnets, $Y^{3+}$ does not enter the octahedral sites or enters the sites, to a very limited extent, 0.05 ions per garnet formula unit. Belt et al. [10], however, reported that $Y^{3+}$ enters the octahedral site to a relevant amounts, 0.3 ions per garnet formula unit.

Since the systematic magnetic and magneto-optic data of the garnets with both Bi and octahedral substitution, $\{Bi_xY_{3-x}\}[M_yFe_{2-y}](Fe_3)O_{12}$, where M denotes the diamagnetic ion, are lacking, for comparison, the individual data of garnets with Bi substitution [3], $\{Bi_xY_{3-x}\}[Fe_2](Fe_3)O_{12}$, and of garnets with In substitution [2], $\{Y_3\}[In_yFe_{2-y}](Fe_3)O_{12}$, were used to calculate the $M_s$, the $F$, and the $T_c$ of the garnets. The individual contributions of the Bi and the In ions were linearly added to produce the combined contribution from both ions. The $T_c$ were also calculated using the Neel's molecular field theory[11] and the method of Gilleo[11]. For the molecular field calculation, the Hansen's fitting parameter[3] for the Bi substitution and the Dionne's semiempirical equations[12] for the octahedral substitution were linearly combined. To modify the Gilleo's equation, the experimentally obtained increase rate[3] of the $T_c$ by the Bi substitution was linearly combined. The calculated $T_c$ by the three different methods agreed well within 2 %. The calculated values are shown as dotted lines in Figure 2 through 4.

As shown the calculated $M_s$ and $F$reasonably fit the data. The calculated $T_c$, however, are significantly smaller than the data, and even the sign of the expected trend is opposite to the one observed for the samples with $u > 0$.

Third possibility would be that the sum of the Bi and Y concentration per formula unit in the samples is 3 and the Fe concentration per formula unit is less than 5. This woulld result vacancies in the octahedral and/or tetrahedral sites. (For $u = 0.5$, Bi : Y : Fe = 2.0 : 1.5 : 5. Thus Bi, Y, and Fe concentrations per formula unit would be $2.0(3/3.5) = 1.71$, $1.5(3/3.5) = 1.29$, and $5(3/3.5) = 4.28$. Then Fe vacancy concentration would be $5 - 4.28 = 0.72$). In this assumption, the calculated vacancy concentrations were about a factor of 2.5 times higher than the Y concentrations in the octahedral sites on the basis of the second assumption. Since the high vacancy concentration would significantly decrease the number of the strong superexchange interactions per formula unit, the expected $M_s$, $T_c$, and $F$ would deviate much more from the data.

## V. Conclusions

It was found that the Bi and Y depleted films consist of mutiphases. In the Bi and Y overdosed films, no impurity lines are observed in the high power XRD diagrams over a wide composition range. The observed magnetic and magneto-optic data of these films, however, could only be reasonably explained by assuming that, for all starting compositions, a garnet phase forms, having both octahedral and tetrahedral sites filled by Fe ions, and the dodecahedral sites filled by Bi and Y ions, in a ratio equal to the nominal one, and the rest of the starting material forms small amount of spurious phases, not detectable by the XRD.

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# 열분해법에 의해 제조한 비화학양론조성을 갖는 비스머스 치환 이트리움-철-가네트 박막의 구조적, 자기적 및 자기광학적 특성

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열분해법을 이용하여, 양이온 비가 Bi : Y : Fe = 1.5 + $u$ : 1.5 : 5 및 Bi : Y : Fe = 1.5 : 1.5 + $v$ :5 ($-0.7 \leq u \leq 1.0$, $-0.7 \leq v \leq 1.3$)인, 비화학양론조성을 갖는 비스머스 치환 이트리움 철 가네트 다결정 박막을 제조했다. 각 열처리 온도에서 생성된 이 박막들내의 결정상들을 고출력 X-선 회절 분석기를 이용하여 분석했다. 또한, $u$, $v$에 따른 이 박막들의 포화자화, 큐리온도 및 파장 633 nm에서의 훼러데이 회전각을 측정했다. 비스머스 및 이트리움을 화학양론조성보다 소량 투여한 박막들에서는, 가네트상과 함께 불순물상이 관찰되었다. 한편, 비스머스 및 이트리움을 과량 투여한 박막들에서는 불순물상에 의한 회절 라인은 검출되지 않고, 가네트상에 의한 회절 라인만이 넓은 조성 영역 ($0 \leq u \leq 0.5$, $0 \leq v \leq 0.7$)에서 관찰되었다. 그러나, 이 과량 투여한 박막들의 자기적 및 자기광학적 특성은, X-선 분석으로는 검출되지 않는 미량의 불순물상이 존재한다고 가정하는 것에 의해서만 설명할 수 있었다.