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Temperature Dependent Cation Distribution in $Tb_2Bi_1Ga_1Fe_4O_{12}$

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In this study, heavy rare earth garnet $Tb_2Bi_1Ga_1Fe_4O_{12}$ powders were fabricated by a sol-gel and vacuum annealing process. The crystal structure was found to be single-phase garnet with a space group of *Ia3d*. The lattice constant a_0 was determined to be 12.465 Å. From the analysis of the vibrating sample magnetometer (VSM) hysteresis loop at room temperature, the saturation magnetization and coercivity of the sample are 7.64 emu/g and 229 Oe, respectively. The Néel temperature (T_N) was determined to be 525 K. The Mössbauer spectrum of $Tb_2Bi_1Ga_1Fe_4O_{12}$ at room temperature consists of 2 sets of 6 Lorentzians, which is the pattern of single-phase garnet. From the results of the Mössbauer spectrum at room temperature, the absorption area ratios of Fe ions on 24*d* and 16*a* sites are 74.7 % and 25.3 % (approximately 3:1), respectively. These results show that all of the non-magnetic Ga atoms occupy the 16*a* site by a vacuum annealing process. Absorption area ratios of Fe ions are dependent not only on a sintering condition but also on the temperature of the sample. It can then be interpreted that the Ga ion distribution is dependent on the temperature of the sample. The Mössbauer measurement was carried out in order to investigate the atomic migration in $Tb_2Bi_1Ga_1Fe_4O_{12}$.

Keywords : vacuum annealing process, $Tb_{3-x}Bi_xFe_5O_{12}$, cation distribution, Mössbauer spectroscopy

1. Introduction

Heavy rare earth (RE) iron garnet has a canted magnetic structure at low temperature which is described as a "double umbrella structure". The heavy RE ion spins form a double cone around the [111] axis, and this spinning affects the iron set of the 16*a* site [1]. It is well known that Bi^{3+} ions and RE ions enhance magneto-optical activity in RE iron garnets [2]. The large increase of the Faraday rotation (FR) in RE garnets is attributed to the *a-d* super-exchange coupling and spin-orbit (SO) interaction [3]. In the RE iron garnet the bismuth raises the T_N, which indicates that this behavior is attributed to the influence of the Bi ions on the super-exchange interaction between *a-d* sub-lattices [4]. It has been reported that, for these materials that are related to the negative magnetization, the net magnetization has a negative value at a low temperature under a field cooled condition for $Tb_2Bi_1Fe_5O_{12}$ [5], and for $Ho(Fe_{0.6}Mn_{0.4})_{12}$ systems [6]. Terbium Bismuth Gallium Iron Garnet (TbBiGaIG) is the candidate material for the Faraday rotator for wide band and temperature-stabilized optical isolators [7]. It is well known that heavy RE iron garnet exhibits the compensation phenomenon. The compensation phenomenon attracted attention for new concepts of integrated optical isolators based on non reciprocal optical mode interference [8]. In an RE iron garnet system, both octahedral (16*a*) and tetrahedral (24*d*) sites are occupied by Fe^{3+} ions. When the gallium ion is substituted in a garnet system, the cation distribution of gallium and iron ions between 16*a* and 24*d* sites depends on the temperature. The heat treatment changes the sign of the Faraday effect by moving some of the Ga ions from the 24*d* to the 16*a* site [8, 9].

In this work, we report on the structural and magnetic properties of $Tb_2Bi_1Ga_1Fe_4O_{12}$ powders, which are prepared by sol-gel and vacuum annealing processes. The distribution of gallium and iron in $Tb_2Bi_1Ga_1Fe_4O_{12}$ is explained by the analysis of the local structure of iron sub-lattices using Mössbauer spectroscopy.

2. Experiment

$Tb_2Bi_1Ga_1Fe_4O_{12}$ compounds were prepared by a sol-gel and vacuum annealing process. High purity Terbium, Bismuth, Gallium and Iron nitrate were dissolved in 2-

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methoxyethanol (2-MOE) and acetic acid. The solution was refluxed at 80 °C for 24 h and dried at 120 °C for 48 h in an oven. The powder obtained from this process was sealed in evacuated quartz tubes. The annealing process initially occurred at room temperature, which was slowly raised to 1000 °C over a period of seven days.

The crystal structure of the sample was examined by using an X-ray diffractometer with Cu-Kα radiation and was analyzed by Rietveld refinement. The magnetization measurements in the temperature range of 40 to 650 K were performed using a VSM in zero-field cooling (ZFC) conditions under a 100 Oe applied field. Mössbauer spectra were recorded using a constant acceleration Mössbauer spectrometer with a ^{57}Co source in an Rh matrix [10].

3. Results and Disscussion

The x-ray diffraction pattern of the compounds shows a single phase crystal structure of the space group (*Ia*3*d*) {Tb(24*c*); Bi(24*c*); Fe(16*a*); Ga(16*a*); Fe(24*d*); O(96*h*) (u,v,w)} with a lattice constant a_0 = 12.465 Å. The x-ray diffraction pattern of the samples was refined by Rietveld profile analysis using the FULLPROF program, with the peak shapes approximated by a Pseudo-Voigt function. The Bragg factor R_B and the structure factor R_F for the sample were 5.66 % and 5.18 %, respectively. The cation distribution for $Tb_2Bi_1Ga_1Fe_4O_{12}$ was verified, and was determined to be $[Tb_2^{+3}Bi_1^{+3}]^{24c}[Fe_3^{+3}]^{24d}[Ga_1^{+3}Fe_1^{+3}]^{16a}O_{12}^{-2}$ by using Rietveld refinement. The refined x-ray diffraction pattern of the sample is shown in Fig. 1.

In order to study the change in the detailed local structure, we obtained Mössbauer spectra at various temperatures. The Mössbauer spectra of $Tb_2Bi_1Ga_1Fe_4O_{12}$ are shown in Fig. 2.

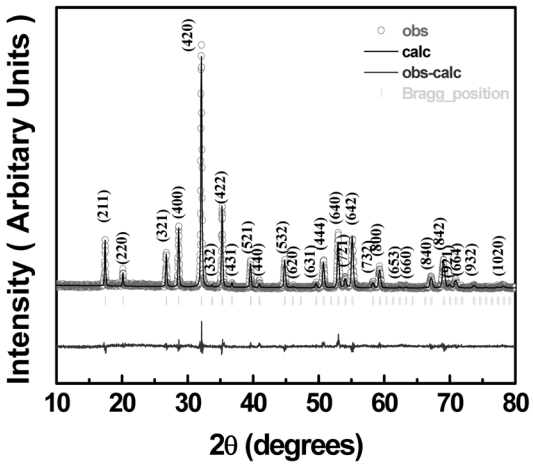

Fig. 1. Rietveld refinement of x-ray diffraction patterns for $Tb_2Bi_1Ga_1Fe_4O_{12}$. Solid circle and continuous lines represent the observed, calculated, and difference profiles, respectively. Thick marks show the Bragg position.

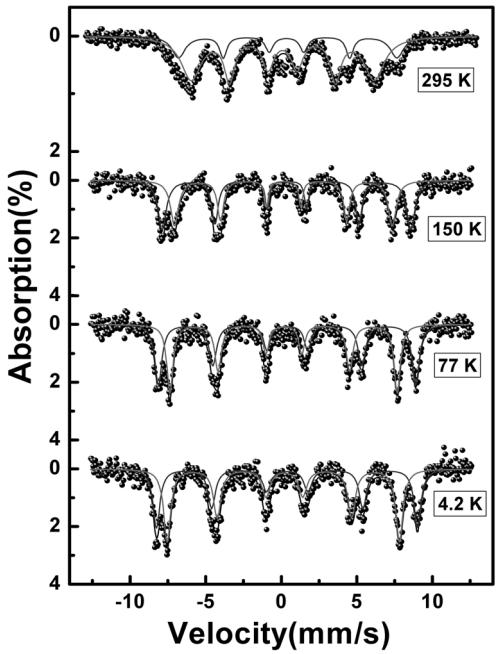

Fig. 2. Mössbauer specta of $Tb_2Bi_1Ga_1Fe_4O_{12}$ at various temperatures.

The Mössbauer spectrum for the sample consisted of two six-line hyperfine patterns 24*d* (inner sextet) and 16*a* (outer sextet). The spectrum of $Tb_2Bi_1Ga_1Fe_4O_{12}$ at room temperature consists of 2 sets of 6 Lorentzians, which is the pattern of a single-phase garnet. From the analyzed results of the Mössbauer spectrum at room temperature, the absorption area ratios of Fe ions on 24*d* and 16*a* sites are 74.7 % and 25.3 % (approximately 3:1), respectively. In the case of our previous results for $Tb_2Bi_1Fe_5O_{12}$ [5], the area absorption ratios of Fe ions on 24*d* and 16*a* sites are 60.8 % and 39.2 % (approximately 3:2), respectively. This proportion is the conventional absorption area ratios of Fe ions of iron garnet. It is noticeable that the Mössbauer absorption area ratio of the 16*a* site increases steadily with an increasing temperature up to 150 K from 4.2 K, and then it rapidly decreases over 150 K and reaches a value of 25.3 %, while it shows an opposite tendency in the 24*d* site. The detailed Mössbauer absorption ratios are listed in Table 1. This opposite tendency can be explained by the migration of Fe ions from the 16*a* site to the 24*d* site, and the simultaneous migration of gallium ions from the 24*d* site to the 16*a* site. Now, the cation distribution of $Tb_2Bi_1Ga_1Fe_4O_{12}$ is $Tb_2Bi_1(Ga_{1-x}Fe_{2+x})^{24d}(Ga_xFe_{2-x})^{16a}O_{12}$, indicating the x Fe ions have migrated from the 24*d* sites to the 16*a* sites (the same number of Ga ions have moved from the 16*a* sites to the 24*d* sites). The absorption area ratio of the 16*a* and 24*d* subspectra for the above distri-

Table 1. The Mössbauer parameters for $Tb_2Bi_1Ga_1Fe_4O_{12}$

Temp. (K)	H_{hf} (KOe)		ΔE_Q (mm/s)		δ (mm/s)		AR (%)	
	16*a*	24*d*	16*a*	24*d*	16*a*	24*d*	16*a*	24*d*
4.2	537	477	–0.01	–0.03	0.38	0.17	44.6	55.4
77	529	467	–0.01	–0.01	0.39	0.16	50.1	49.9
150	511	448	–0.01	–0.01	0.36	0.15	53.2	46.8
295	449	377	0.04	0.01	0.38	0.09	25.3	74.7

H_{hf} : magnetic hyperfine field, ΔE_Q: electric quadrupole spilittings, δ: isomer shifts, and AR: absorption area ratios

bution is [11-13],

$$\frac{I_{16a}}{I_{24d}} = \frac{(2-x)\, f_{16a}}{(3-x)\, f_{24d}} \quad (1)$$

where f_{16a} and f_{24d} represent the recoil-free fractions of 16*a* and 24*d* site Fe ions, respectively. It can be analogized to the Ga ion distribution obtained from this result. It is noticeable that all of the nonmagnetic Ga atoms occupy the 16*a* site from the vacuum annealing process. This is also in accord with the x-ray diffraction refinement results.

From the results of the Mössbauer spectra at various temperatures, the absorption area ratios of Fe ions are dependent not only on the sintering condition but also on the temperature of the sample. The Mössbauer parameters, magnetic hyperfine field, quadrupole splitting, isomer shifts, and absorption area ratios at various temperatures for $Tb_2Bi_1Ga_1Fe_4O_{12}$ are presented in Table 1. The area absorption ratios at 4.2 K, 77 K, 150 K, and 295 K of Fe ions on 24*d* and 16*a* sites are (55.4 %, 44.6 %), (49.9 %, 50.1 %), (46.8 %, 53.2 %), and (74.7 %, 25.3 %), respectively. The Ga ions showed random distribution at both sites (16*a*, 24*d* sites) at 4.2 K due to the absorption area ratios of Fe ions on 24*d* and 16*a* sites are approximately 3:2. However, at temperatures ranging from 4.2 K to 150 K, Ga ions migrate from the 16*a* site to the 24*d* site. At temperatures ranging above 150 K, in contrast to the previous expectation, Ga ions migrate from the 24*d* site to the 16*a* site. Finally, at room temperature all of the nonmagnetic Ga atoms occupy the 16*a* site. It can be interpreted that the Ga ion distribution is affected by the temperature of the sample at all temperature ranges.

Fig. 3 shows the temperature dependence of magnetization curves after zero-field cooling (ZFC) and field cooling (FC) with a 100 Oe applied field for $Tb_2Bi_1Ga_1Fe_4O_{12}$. The T_N was determined to be 525 K by magnetization curves. By comparing this with the T_N of RE iron garnets (560 K), it can be seen that the T_N of $Tb_2Bi_1Ga_1Fe_4O_{12}$ is slightly lower than that of the RE iron garnets. The lower T_N of $Tb_2Bi_1Ga_1Fe_4O_{12}$ can be explained by the influence of the weakened super-exchange interaction between the *a-d* sub-lattices by doping nonmagnetic Ga ions. In addition, the saturation magnetization is lower than that of $Tb_2Bi_1Fe_5O_{12}$ [5], which is attributed to the weakened super-exchange interaction between the *a-d* sub-lattices. In general, the heavy RE iron garnets exhibit the compensation phenomenon in temperature dependence of magnetization curves. However, in this case of $Tb_2Bi_1Ga_1Fe_4O_{12}$, we could not detect the compensation phenomenon in magnetization curves. The abnormal magnetic transition at 450 K, which appears to be similar to the compensation phenomena, seemed to be the spin reorientation phenomena. These abnormal magnetic transitions are attributed to the distribution of nonmagnetic Ga ions which is affected by the temperature of the sample at all temperature ranges. The negative magnetization which is detected in the FC magnetization of $Tb_2Bi_1Fe_5O_{12}$ [5] was not detected in this case. This phenomenon can be explained by the influence of the weakened covalent interaction between bismuth and iron by doping nonmagnetic Ga ions. The negative magnetization is related to the strong local anisotropy induced by the strong covalent interaction between bismuth and iron [5].

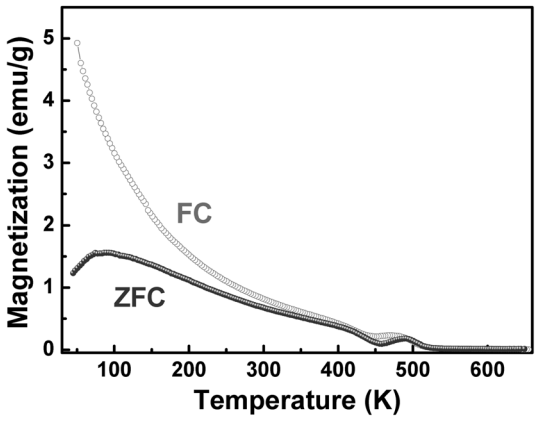

Fig. 3. Temperature dependence of magnetization of $Tb_2Bi_1Ga_1Fe_4O_{12}$ with 100 Oe applied field.

4. Summary

We have studied the cation distribution in $Tb_2Bi_1Ga_1$-

Fe_4O_{12} powders which were prepared by sol-gel and the vacuum annealing process. From the result of nonmagnetic Ga ion distribution, $Tb_2Bi_1Ga_1Fe_4O_{12}$ showed weakened super-exchange interaction, and a covalent interaction. These phenomena affect T_N and the net magnetization of sample. A Mössbauer measurement was carried out in order to investigate the atomic migration in $Tb_2Bi_1Ga_1Fe_4O_{12}$. We suggest that the control of site preference of the Ga cation from the 24*d* site to the 16*a* site was accomplished by the high temperature vacuum annealing process.

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