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Synthesis and Mössabuer Spectroscopy Studies of $Nd_{1-x}Bi_xY_2Fe_5O_{12}$ Nano-Particles

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The garnets $Nd_{1-x}Bi_xY_2Fe_5O_{12}$ (x=0.0, 0.25, 0.5, 0.75 and 1.0) have been studied by x-rays, electron microscopy, ferromagnetic resonance, vibrating sample magnetometer and Mössbauer spectroscopy. Ultra-fine polycrystalline cubic samples have been prepared by a melt-salt routed sol-gel method. The Mössbauer spectra consist of two sets of six-line patterns corresponding to Fe^{3+} at the tetrahedral 24(d) and octahedral 16(a) sites. Magnetic hyperfine fields of $Nd_{0.5}Bi_{0.5}Y_2Fe_5O_{12}$ at 12 K are found to be 548 kOe (octahedral site) and 475 kOe (tetrahedral site), respectively. It is found that Debye temperatures for the tetrahedral and octahedral sites of $Nd_{0.75}Bi_{0.25}$-$Y_2Fe_5O_{12}$ are θ_{tet}=436 K and θ_{oct}=285 K, respectively. The iron ions at both sites are highly covalent ferric. The Néel temperature decreases linearly with Bi concentration, from 630 K for x=0.0 to 600 K for x=1.0, suggesting that the superexchange interaction for the Nd-O-Fe link is stronger than that for the Bi-O-Fe link. As a consequence, the coercivity of $Nd_{1-x}Bi_xY_2Fe_5O_{12}$ drastically decreases and the magnetization remains almost constant as x increases.

1. Introduction

Fine-grained rare-earth iron garnet (RIG) is of interest for microwave devices and magneto-optic media because the threshold magnetic field H_c is enhanced for the nonlinear excitation of spinwave modes [1]. Previous studies have shown that YIG powders, which replace Y-ions with Bi-ions, have a lower coercivity than pure YIG powder [2]. Nd-ions in a ferrite powder have high magnetization and can be easily replaced by Y or Bi. The conventional ceramic method for the preparation of garnet involves high temperatures, resulting in the loss of fine particle nature. A number of wet chemical methods have been developed to prepare fine particles [3-4]; one of them is a sol-gel pyrolysis method, which is used to fabricate ultra-fine ferrite powders in our laboratory [5-6]. In this study, $Nd_{1-x}Bi_xY_2Fe_5O_{12}$ powders are grown by a sol-gel method and their magnetic and physical properties are characterized using X-ray diffraction patterns (XRD), a vibrating sample magnetometer (VSM), scanning electron microscopy (SEM) and Mössbauer spectroscopy.

2. Experiment

Polycrystalline $Nd_{1-x}Bi_xY_2Fe_5O_{12}$ powders were prepared by the sol-gel pyrolysis method. Appropriate portions of $Nd(NO_3)_3 \cdot 5H_2O$, $Bi(NO_3)_3 \cdot 6H_2O$, $Y(NO_3)_3 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved into ethylene glycol. Crystalline garnet powders were obtained after heat treatment at 800-1000 in an O_2 flow for 8 hours. X-ray diffraction patterns of samples were obtained using Cu-K_α radiation. Crystal shapes and grain sizes were also examined by SEM, XRD and Mössbauer spectroscopy. Magnetization of garnet powders was measured with a VSM at room temperature in fields up to 10 kOe. Mössbauer spectroscopy of the electromechanical type was used to identify detailed magnetic properties of garnet powders.

3. Results and Discussion

The powders have only the single phase garnet structure regardless of the amount of Bi substitution, according to the X-ray diffraction patterns. As shown in Fig. 1 and Table 1, the lattice parameter (a_0) is independent of Bi content. The crystallite sizes were calculated from the XRD line broadening of the (420) peak, using the classical Scherrer relationship [3], $D_{hkl}=k\lambda/B\cos\theta$, where D_{hkl} is the particle diameter in Å, k is a constant (shape factor) with a value of 0.9, B is the half-maximum line width, and λ is the X-ray wavelength. The particle sizes of $Nd_{1-x}Bi_xY_2Fe_5O_{12}$ (x= 0.25, 0.5, 0.75, and 1.0) were 131 nm,125 nm,120 nm, and 110 nm, respectively. Scanning electron microscopy images of the powders indicate that the powders are composed of grains with an average size of 200-300 nm. The grain sizes decrease as the amount of Bi increases. Powders heated at and below 800°C contain a small amount of α-Fe_2O_3. Typi-

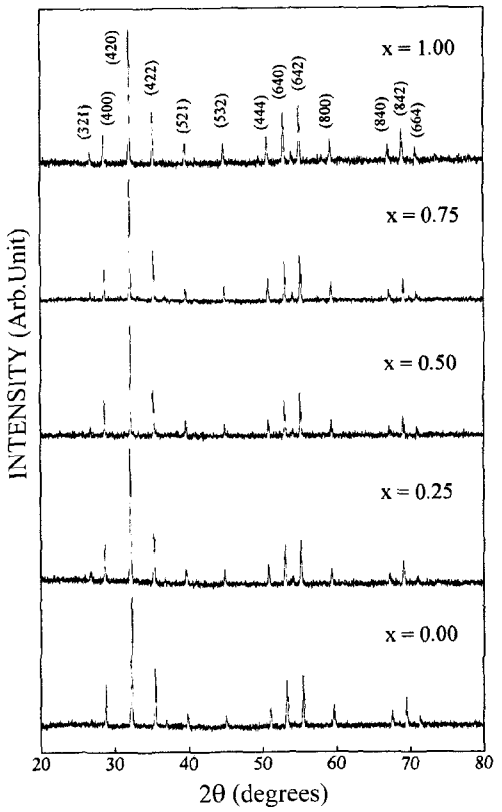

Fig. 1. X-ray diffraction patterns for $Nd_{1-x}Bi_xY_2Fe_5O_{12}$.

cal SEM images of the $Bi_1Y_2Fe_5O_{12}$ and $Nd_{0.75}Bi_{0.25}Y_2Fe_5O_{12}$ powders annealed at 950°C are shown in Fig. 2(a) and (b).

Table 1 and Figure 3 display the saturation magnetization (M_s) and coercivity (H_c) of the $Nd_{1-x}Bi_xY_2Fe_5O_{12}$ powder at

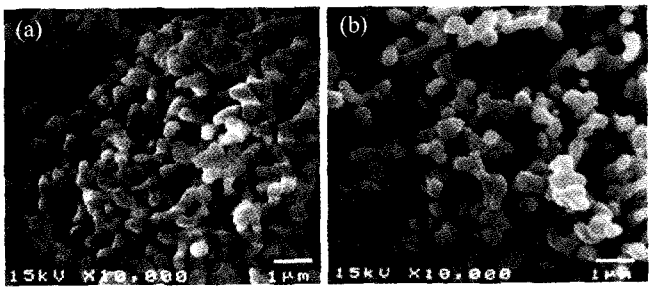

Fig. 2. Scanning electron microscopy image of (a) $Bi_1Y_2Fe_5O_{12}$ and (b) $Nd_{0.75}Bi_{0.25}Y_2Fe_5O_{12}$.

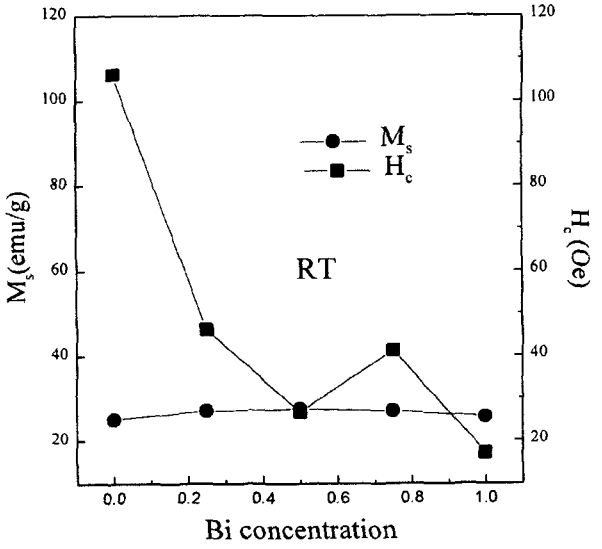

Fig. 3. Saturation magnetization (M_s) and coercivity as a function of Bi concentration.

room temperature. The saturation magnetization (M_s) is independent of Bi concentration, however, the coercivity (H_c) rapidly decreases as Bi increases in Nd-Bi substituted garnet. This result shows that H_c can be controlled in Bi-substituted garnet, and that M_s is nearly constant in Nd-substituted garnet.

Figure 4 shows Mössbauer absorption spectra as a function of Bi concentration at room temperature. The spectra are composed of two sets of six-line hyperfine patterns corresponding to the 16(a) and 24(d) sites, which is a typical pattern for a garnet powder. The magnetic hyperfine field in 24(d) site decreases as Bi increases; however, that of the 16(a) site is independent of Bi concentration. The isomer shifts indicate that the valence state of Fe ions in the 16(a) and 24(d) sites has a ferric character. Figure 5 shows Mössbauer spectra for $Nd_{0.75}Bi_{0.25}Y_2FeO_{12}$ powder measured from 12 K to the Néel temperature. The Néel temperature measurements show a linear increase as the Bi concentration in Nd-YIG decreases, as shown in Table 1. This implies that the Nd-O-Fe link strengthening of the superexchange interaction is stronger than the Bi-O-Fe link strengthening in $Nd_{1-x}Bi_xY_2Fe_5O_{12}$.

The Debye temperatures of 16(a) and 24(d) decrease as the amount of Bi increases in Nd-YIG. The Debye tempera-

Table 1. Lattice parameter (a_0), hyperfine field (H_{hf}), quadrupole splitting (ΔE_Q), isomer shifts (δ), saturation magnetization (M_s), coercivity (H_c) at room temperature, and Néel temperature (T_N)

x	a_0 (Å)	H_{hf} (kOe)		ΔE_Q (mm/s)		δ (mm/s)		M_s	H_c	T_N
		16(a)	24(d)	16(a)	24(d)	16(a)	24(d)	(emu/g)	(Oe)	(K)
1.00	12.439	491	397	-0.03	0.00	0.25	0.04	26	17	600
0.75	12.435	492	401	-0.03	0.01	0.22	0.01	27	41	603
0.50	12.450	493	404	-0.01	0.01	0.24	0.03	28	27	605
0.25	12.437	494	406	-0.01	0.00	0.26	0.04	27	46	610
0.00	12.472	494	407	-0.03	0.01	0.25	0.04	25	106	630

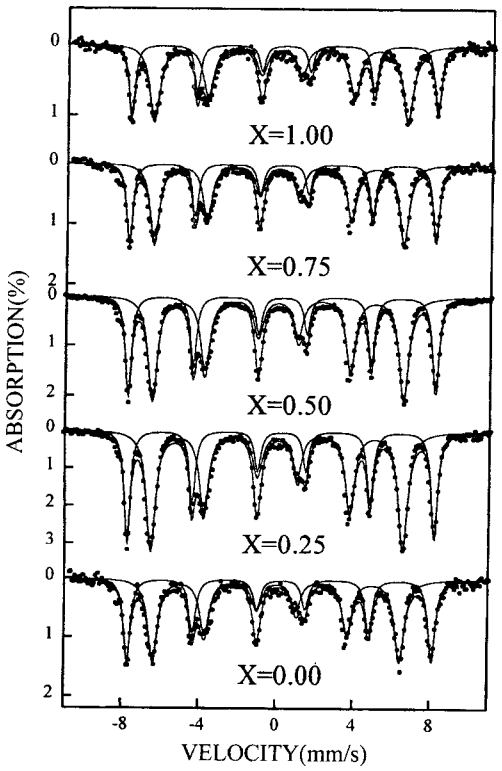

Fig. 4. Mössbauer spectra for $Nd_{1-x}Bi_xY_2Fe_5O_{12}$ at room temperature.

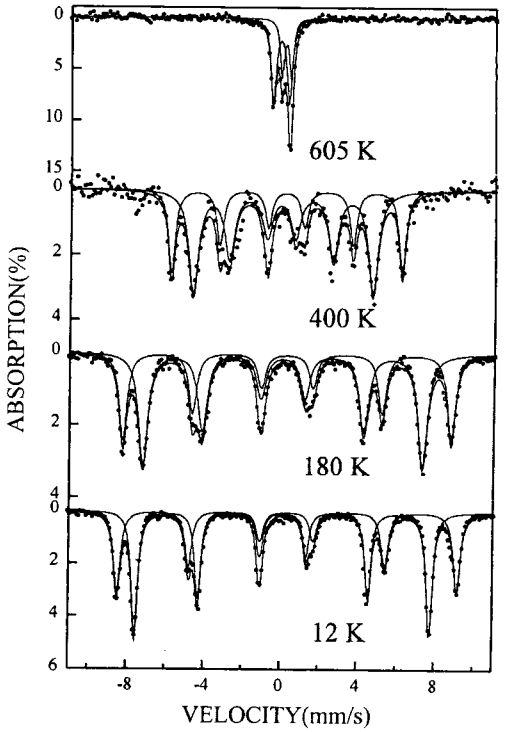

Fig. 5. Mössbauer spectra for $Nd_{0.75}Bi_{0.25}Y_2Fe_5O_{12}$ at various temperature.

tures for the tetrahedral (θ_{tet}) and octahedral (θ_{oct}) sites of $Nd_{1-x}Bi_xY_2Fe_5O_{12}$ are 427 K and 306 K at x=0.75; 316 K and 282 K at x=0.5; and 315 K and 280 K at x=1.0.

The fractional change of the average magnetic hyperfine field, $[H_{hf}(T)-H_{hf}(0)]/H_{hf}(0)$ decreases as temperature increases, according to Eq. (1) [7].

$$\frac{H_{hf}(T)-H_{hf}(0)}{H_{hf}(0)}=-B_{3/2}\left(\frac{T}{T_N}\right)^{3/2}-C_{5/2}\left(\frac{T}{T_N}\right)^{5/2} \quad (1)$$

T_N is the Néel temperature, $H_{hf}(T)$ is the magnetic hyperfine field at temperature T K, and $H_{hf}(0)$ is the magnetic hyperfine field at 0 K. The spinwave constants ($B_{3/2}$) of $Nd_{1-x}Bi_xY_2Fe_5O_{12}$ (x=0.25, 0.5, 0.75, and 1.0) were 0.17, 0.19, 0.2, and 0.21, respectively. These results indicate that the spin-waves have long wavelengths and they are excited in Bi-substituted Nd-YIG.

Acknowledgements

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References

[1] N. Adachi, T. Hibi and T. Okuda, J. Mag. Magn. Mater., **177-181**, 233 (1998).
[2] Y. Y. Song, S. C. Yu, W. T. Kim, J. R. Park and T. H. Kim, J. Mag. Magn. Mater., **177-181**, 257 (1998).
[3] P. Vaqueiro, M. P. Crosner-Lopez and M. A. Lopez-Quintela, J. Solid State Chem., **126**, 161 (1996).
[4] M. Gomi, T. Okazaki and M. Abe, IEEE Tans. Magn., **MAG-23**, 2967 (1987).
[5] C. S. Kim, Y. R. Uhm and J. G. Lee, J. Magn. Soc., Japan **23**, 534 (1999).
[6] C. S. Kim, Y. R. Uhm and J. G. Lee, (to be published).
[7] R. L. Mössbauer and W. H. Wiedermann: Z. Phys., **159**, 33 (1960).