The Effect of Manganese Substituted M-type Hexagonal Ba-ferrite

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The Mn-substituted M-type Ba-ferrite (BaFe$_{12-x}$Mn$_x$O$_{19}$; x = 0, 2, 4, 6) powders were prepared by the HTTD (High Temperature Thermal Decomposition) method. The effect of Mn^{3+} Jahn-Teller ions on the magnetic properties has been studied by x-ray diffraction, vibrating sample magnetometry, and Mössbauer spectroscopy. With increasing Mn substitution, the lattice parameter a_0 increases while c_0 decreases. The magnetocrystalline anisotropy constants (K_1) were determined as 2.9, 2.2, 1.8, and, 1.3×10^6 erg/cm^3 for x = 0, 2, 4, and 6, respectively, by the LAS method. We have studied the change of cation distribution by Mössbauer spectroscopy which is closely related to K_1.

Keywords : Ba-ferrite, Mössbauer spectra, magnetocrystalline anisotropy, cation distribution

1. Introduction

M-type hexaferrite MFe$_{12}$O$_{19}$ (M = Ba, Sr, Pb, La) has been intensively investigated for use as a high density perpendicular magnetic recording media, as a permanent magnet, and as a microwave absorption device [1, 2] because of its suitable coercivity, high magnetocrystalline anisotropy, and high chemical stability. Cation such as Al^{3+}, Cr^{3+}, Co^{2+}-Ti^{4+}, Co^{2+}-Sn^{4+}, and Zn^{2+}-Zr^{4+} were substituted for Fe^{3+} to control its coercivity and magnetic properties [3-7]. The structure of the barium ferrite is symbolically described as $RSR*S*$, where R is a three-layer block (two O$_4$ containing one BaO$_3$) with the composition Ba^{2+}Fe$^{3+}_6$O$^{2-}_{11}$, and S is a two O$^{2-}_4$-layer block with the composition Fe$^{3+}_6$O$^{2-}_8$, where the asterisk means that the corresponding block has been turned 180° around the hexagonal c axis. The Fe^{3+} ions are arranged in five different kinds of interstitial sites, of which three are octahedral sites ($12k$, $4f_2$, and $2a$), one is a tetrahedral site ($4f_1$), and one is a site in which the ferric ion is surrounded by five oxygen atoms forming a trigonal bi-pyramid ($2b$).

In this paper, we report on the site occupation, as determined by Mössbauer spectroscopy, and the magneto-crystalline anisotropy of a Mn^{3+} Jahn-Teller ion substitut-ed BaFe$_{12-x}$Mn$_x$O$_{19}$ ($0.0 \leq x \leq 6.0$).

2. Experiments

Manganese substituted Ba-ferrite polycrystalline powders were prepared by the HTTD (High Temperature Thermal Decomposition) method [8]. Ba(acac)$_2$ [(C$_5$H$_8$O$_2$)$_2$Ba·xH$_2$O], Fe(acac)$_3$ [(C$_5$H$_8$O$_2$)$_3$Fe], and Mn(acac)$_3$ [(C$_5$H$_8$O$_2$)$_3$Mn] were used as starting materials. These were dissolved in oleylamine, with the stoichiometric ratio of Ba/(Fe, Mn) = 1/12. The solution was refluxed at 330 °C for 1 h under Ar, and was subsequently dried at 60 °C. Finally, the precursor powders were sintered at 950, and 1050 °C for 6 h in air.

The crystal structure of the samples was examined by x-ray diffraction with Cu $K\alpha$ radiation (λ = 1.5406 Å). The temperature dependence of magnetization was measured by VSM with a maximum field of up to 10 kOe in a 50-780 K temperature range and the hysteresis loops under 15 kOe were also measured. In order to observe the magnetic hyperfine interactions of iron ions in five sublattices of Ba-ferrite, Mössbauer spectra were recorded with a 40 mCi ^{57}Co source in an Rh matrix.

3. Results and Discussion

Fig. 1 shows the x-ray diffraction patterns of the Mn-substituted BaFe$_{12-x}$Mn$_x$O$_{19}$ ($0.0 \leq x \leq 6.0$) at room temper-

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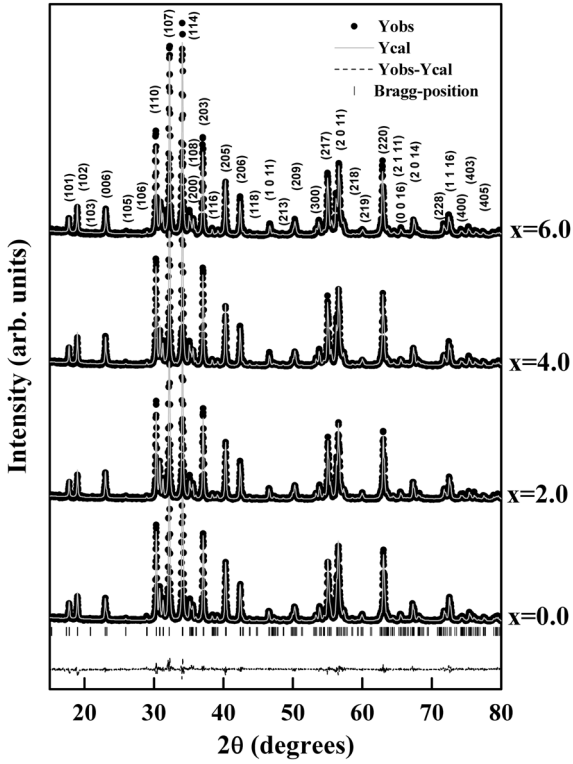Fax: +82-2-910-5170, e-mail: cskim@phys.kookmin.ac.kr

Fig. 1. Refined x-ray diffraction data of $BaFe_{12-x}Mn_xO_{19}$ at room temperature. The solid circles, continuous lines, and the dotted line represent the observed, the calculated, and the difference (obs-cal) profiles, respectively. Tick marks represent the Bragg position of the reflections.

Table 1. Refined x-ray diffraction parameters of $BaFe_{12-x}Mn_x$-O_{19}. Here, a_o and c_o are lattice parameters, V is the volume of the unit cell, and ρ_x is the x-ray density

x	a_o (Å)	c_o (Å)	c_o/a_o	V (Å^3)	ρ_x (g/cm^3)
0.0	5.894	23.214	3.949	698.378	5.285
2.0	5.896	23.191	3.934	698.116	5.278
4.0	5.9	23.169	3.927	698.502	5.267
6.0	5.905	23.137	3.918	698.736	5.257

Table 2. The saturation magnetization M_s, H_c is the coercivities, K_1 is the magnetocrystalline anisotropy constants, and H_A is the anisotropy field of $BaFe_{12-x}Mn_xO_{19}$

x	M_s (emu/g)	H_c (Oe)	K_1 ($\times 10^6$erg/cm^3)	H_A (kOe)
0.0	61.7	5,944	2.9	16.2
2.0	47.4	5,758	2.2	16.3
4.0	30.4	6,277	1.8	19.0
6.0	15.0	8,207	1.3	27.2

ature. An analysis of x-ray diffraction patterns by the Rietveld refinement method using the FULLPROF program showed that all samples of $BaFe_{12-x}Mn_xO_{19}$ had a magnetoplumbite hexagonal structure with the space group $P6_3/mmc$ as shown in Fig. 1. The refined x-ray diffraction parameters, lattice constant, volume of unit cell (V), and x-ray density (ρ_x) at room temperature for $BaFe_{12-x}Mn_xO_{19}$ are presented in Table 1. As the Mn substitution increases, the lattice constant a_o and V increases, while c_o and the x-ray density ρ_x decreases. This can be expected when considering that the ionic radius of 0.66 Å for the Mn^{3+} ions is larger than that of the 0.64 Å for Fe^{3+} ions. Also, the hexagonal crystal structure is distorted, as though it were expanded along the a-axis by the effect of Mn^{3+} ions distribution.

With an increasing x, the saturation magnetization, M_s is obviously decreased with 47.4, 30.4, and 15.0 emu/g for $x = 2.0$, 4.0, and 6.0. However, the coercivity, H_c is slightly decreased at $x = 2.0$, and then greatly increased over $x = 2.0$ as shown in Table 2. The $BaFe_6Mn_6O_{19}$ shows a very high H_c of 8,207 Oe. Fig. 2 shows the temperature dependence of the zero field cooled (ZFC)

magnetization curves with a 10 kOe applied field in the temperature range of 50-780 K. In the ZFC curve, the magnetization decreases steadily with an increase in temperature up to the Curie temperature. The Curie temperature is obtained by the dM/dT curves of the ZFC. As the Mn^{3+} substitution increased, the Curie temperature decreased. The decrease of the Curie temperature means that the Mn^{3+}-O^{2-}-Fe^{3+} super-exchange interaction is weaker than the Fe^{3+}-O^{2-}-Fe^{3+} super-exchange interaction.

The magnetocrystalline anisotropy constant K_1 and anisotropy field H_a of $BaFe_{12-x}Mn_xO_{19}$ were determined by the law of approach to saturations (LAS) method. The LAS method can be described as [9].

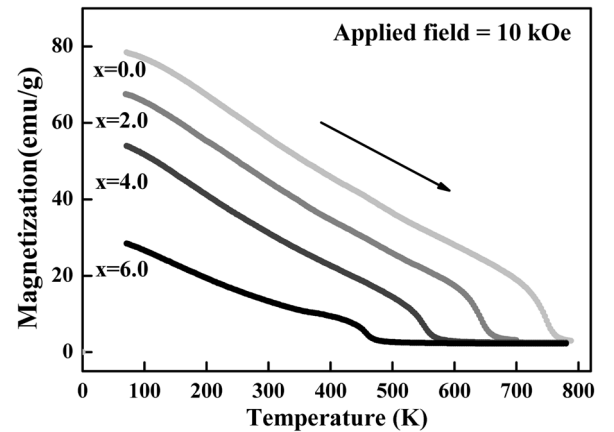$$M = M_s\left(1 - \frac{A}{H} - \frac{B}{H^2} - \frac{C}{H^3} - \cdots\right) + \chi_P H \qquad (1)$$

Fig. 2. Temperature dependence of zero field cooled magnetization curves of $BaFe_{12-x}Mn_xO_{19}$.

Here, A is the inhomogeneity parameter, B is the aniso-tropy parameter, and χ_p is the paramagnetic susceptibility at high fields, where the saturation magnetization M_s and B is the magnetization dependent process parameter such as

$$B = \frac{H_A^2}{15} = \frac{4K_1^2}{15M_s^2} \qquad (2)$$

The anisotropy constant K_1 and the anisotropy field H_a can be obtained by fitting the magnetization curve using Eqs. (1) and (2). Table 2 shows the magnetocrystalline anisotropy constants (K_1) and the anisotropy field (H_a) of $BaFe_{12-x}Mn_xO_{19}$ with various Mn concentrations. With an increase of the Mn concentration x, K_1 is linearly reduced, and H_a is simultaneously increased. In Ba-ferrite, the $12k$ and $2b$ sublattices Fe^{3+} ions could contribute to the over-all uniaxial anisotropy [4]. Therefore, a reduced occupancy of spin-up ($12k$) and spin-down ($4f_2$) sites could explain the relative reduction of magnetocrystalline anisotropy. This is due to the decrease of the number of $N_{Fe}(i)$ in the $12k$ site with an increase of x.

Fig. 3 shows the Mössbauer spectra of $BaFe_{12-x}Mn_xO_{19}$ ($0.0 \leq x \leq 6.0$) at 200 K. All spectra were fitted with five six-line sub patterns corresponding to the $4f_2$, $2a$, $4f_1$, $12k$, and $2b$ sites of the M-type hexagonal structure for the site occupancy and hyperfine interaction of Fe ions. From the relative areas, $S(i)$ $i = 1$-5, the site occupation numbers of Fe^{3+} ($N_{Fe}(i)$) and Mn ions ($N_{Mn}(i)$) on the ith site can be determined based on Eqs. (3) and (4) [7].
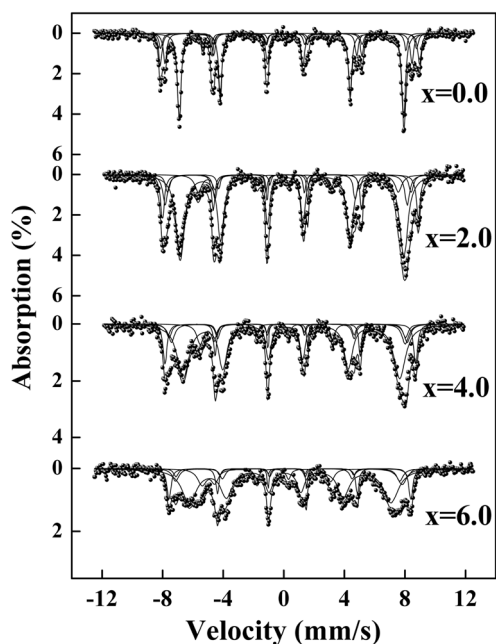

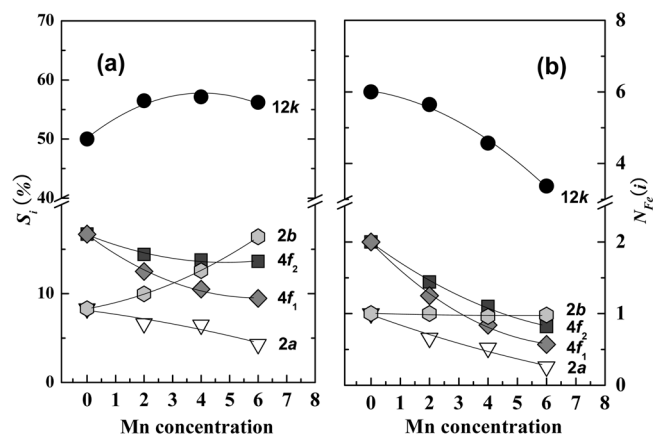**Fig. 3.** Mössbauer spectra of $BaFe_{12-x}Mn_xO_{19}$ ($0.0 \leq x \leq 6.0$) at 200 K.

Fig. 4. (a) The relative areas S_i in each site by Mössbauer spectra and (b) the occupation number of Fe ions in the five sublattices for $BaFe_{12-x}Mn_xO_{19}$ ($0.0 \leq x \leq 6.0$).

$$N_{Fe}(i) = C_{Fe}\frac{S(i)}{\displaystyle\sum_{i=1}^{5} S(i)}, \qquad (3)$$

Here, C_{Fe} is the composition of the Fe ions in a chemical formula and $N(i)$ is the occupation number of the atom in each site.

$$N_{Mn}(i) = N(i) - N_{Fe}(i), \qquad (4)$$

The occupation fraction of Mn ions, $N_{Mn}(i)$, in the sub-lattices can be described as

$$F_{Mn}(i) = \frac{N_{Mn}(i)}{N(i)} \times 100\%. \qquad (5)$$

The results are shown in Fig. 5. The number of Fe ions does not change for the $2b$ site, but decreases for the $4f_1$, $2a$, and, $4f_2$, sites with an increasing x. This indicates that Mn^{3+} ions preferentially occupy the $4f_1$, $2a$, and $4f_2$ sites.
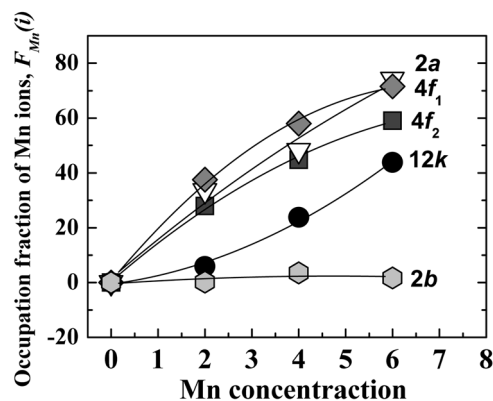

Fig. 5. The occupation fraction of Mn ions in the five sublattices for $BaFe_{12-x}Mn_xO_{19}$ ($0.0 \leq x \leq 6.0$) by the relative area of subspectra.

The relative areas of $BaFe_8Mn_4O_{19}$ at various temperatures were 13.8%, 6.48%, 10.5%, 57.15%, and 12.06% for $4f_2$, $2a$, $4f_1$, $12k$, and $2b$ subspectra, respectively. The isomer shifts, δ_i indicated that the valence state of all Fe ions were ferric (Fe^{3+}).

In summary, Mn-substituted Ba-ferrite powders have been synthesized by the HTTD method. The site occupancies [10], as determined with the Mössbauer spectra, show that the Mn^{3+} ions preferentially occupy the $4f_1$, $2a$, and $4f_2$ sites. The results show that the coercivity, magnetization and magnetocrystalline anisotropies are closely related to the distributions of Mn^{3+} on the five sublattices. This result demonstrates that the substitution of Mn ion on barium hexaferrite can be controlled for the magnetic properties induction of coercivities and the decrease of magnetization.

Acknowledgment

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