

## Crystallographic and Magnetic Properties of $Mn_xFe_{3-x}O_4$ Powders

Woo Hyun Kwon, Jae-Gwang Lee\*, Won Ok Choi, and Kwang Pyo Chae

*Department of Applied Physics, Konkuk University, Chungbuk 380-701, Korea*

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$Mn_xFe_{3-x}O_4$  powders have been fabricated by using sol-gel methods; their crystallographic and magnetic properties were investigated by using X-ray diffraction, scanning electron microscopy, Mössbauer spectroscopy, and vibrating sample magnetometer. The  $Mn_xFe_{3-x}O_4$  ferrite powders annealed at 500 °C had a single spinel structure regardless of the  $Mn^{2+}$ -doping amount and their lattice constants became larger as the  $Mn^{2+}$  concentration was increased. Their Mössbauer spectra measured at room temperature were fitted with 2 Zeeman sextets due to the tetrahedral and octahedral sites of Fe ions, which made them ferrimagnetic. The magnetic behavior of  $Mn_xFe_{3-x}O_4$  powders showed that the  $Mn^{2+}$ -doping amount made their saturation magnetization increase, but there were no severe effects on their coercivities. The saturation magnetization of the  $Mn_xFe_{3-x}O_4$  powder varied from 38 emu/g to 70.0 emu/g and their minimum coercivity was 111.1 Oe.

**Keywords :** Mn-Fe ferrite, sol-gel method, Mössbauer spectroscopy, soft magnetic material

### 1. Introduction

Recently, many researchers have focused on magnetic oxide particles due to their potential applications for microwave devices, magnetic semiconductors, and magnetic sensors [1-3]. Various methods, such as a sol-gel method, a microwave-assisted method, and a conventional ceramic method using oxide powders have been developed to apply their magnetic properties for practical devices for a few decades and their products have been used implemented widely into daily life [1, 2, 4]. Magnetite and Mn-contained ferrite powders have been studied intensively for the possibility of using them as magnetic semiconductors; however,  $Mn^{+2}$  and  $Fe^{+2}$  in the ferrite powders were oxidized easily and the formation of  $Fe_2O_3$  and  $Mn_2O_3$  during the heat treatment made their electric and magnetic properties degraded. It is very important to make pure magnetite and  $Mn^{2+}$ -doping ferrite powders for their good electro-magnetic properties. In our lab, we have worked on these subjects for a long time: The fabrication of pure magnetite and Mn-contained ferrite powders was strongly dependent on their surrounding environment, thus it was not easy to fix their process [5, 6]. In particular, when nano-sized particles were annealed,

a small amount of exposed oxygen changed their ion states, which made their structure and magnetic properties change drastically.

In this paper,  $Mn_xFe_{3-x}O_4$  ( $x = 0.0, 0.2, 0.4, 0.6, 0.8,$  and  $x = 1.0$ ) powders were fabricated by using a sol-gel method and their structural and magnetic properties would be measured and discussed as a function of the  $Mn^{2+}$ -doping amount. We used the following techniques for measurements: X-ray diffractometer (XRD), scanning electron microscopy (SEM), Mössbauer spectroscopy, and vibrating sample magnetometer (VSM) at room temperature.

### 2. Experiments

A sol-gel method has been used for preparing  $Mn_xFe_{3-x}O_4$  ( $x = 0.0, 0.2, 0.4, 0.6, 0.8,$  and  $x = 1.0$ ) powders. First, the measured amount of  $Mn(NO_3)_2 \cdot H_2O$  was dissolved in 2-methoxyethanol (2-MOE) using an ultra-sonic cleaner for 30-40 min; then, the proper amounts of  $(C_2H_5O_2)_2Fe$  and  $Fe(NO_3)_3 \cdot 9H_2O$  were added and refluxed at 80 °C for 12 h. The purity of all used chemicals was 98% and their total amount was 7 g in 200 cc of 2-MOE. The refluxed solutions were completely dried at 90 °C in a dry oven. The samples were grounded briefly and fired at 500 °C in a  $N_2$  atmosphere for 12 h: Heat-treatment in a  $N_2$  atmosphere could prevent the oxidation of  $Fe^{2+}$  and  $Mn^{2+}$ . Judging from the previous experimental results [5, 6], 500 °C was high enough to form single-phased ferrite powders and

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\*Corresponding author: Tel: +82-43-840-3624

Fax: +82-43-851-4169, e-mail: [jglee01@kku.ac.kr](mailto:jglee01@kku.ac.kr)

their particle sizes would be approximately 30-40 nm. A  $N_2$  gas flowed rapidly during the early annealing process to remove all oxygen and gases emitting from powders inside a quartz tube; the flow rate was fixed at 5-10 cc/min. as the temperature was 500°C. X-ray diffractometer (XRD) with a  $Cu-K\alpha$  radiation was used to check their crystal structures and to verify the variation of lattice distance as a function of the substituted amount of  $Mn^{2+}$ . Field-emitting scanning electron microscopy was used to observe the shape and sizes of  $Fe_3O_4$  and  $MnFe_2O_4$  powders. Mössbauer spectra were recorded using a 30 mCi  $^{57}Co$  source in a Rh matrix with the spectrometer working at constant acceleration at room temperature. The parameters were obtained by a least-square fitting program assuming Lorentzian line shapes. All parameters were given with respect to ones of an Fe-foil. Saturation magnetization and coercivities of annealed powders were measured by using a vibration sample magnetometer (VSM) at room temperature and the maximum field; 6 KOe was large enough to study the magnetic behavior of soft magnetic powders even though the field was not strong enough to saturate all ferrite particles.

### 3. Results and Discussion

The result of XRD measurements for  $Mn_xFe_{3-x}O_4$  powders annealed at 500°C was shown in Fig. 1: All samples had a characteristic spinel structure regardless of  $Mn^{2+}$  amounts. From the previous results [5, 6], it was known that the  $Mn_xFe_{3-x}O_4$  powders started to be formed at above 250°C and that the heat treatment in a  $N_2$  atmosphere successfully prevented the oxidation of  $Fe^{2+}$  and  $Mn^{2+}$ , which meant their ion states were unchanged and  $Fe^{2+}$  ions were successfully replaced with  $Mn^{2+}$ . As the  $Mn^{2+}$  concentration increased, the major peak (311) moved toward a lower angle due to their different ion sizes. However, there was no major variation in peak widths regardless of the  $Mn^{2+}$  amount, which meant their particle sizes not to be changed significantly. There was a small peak in Fig. 1a) at near 20.9°, which was observed irregularly; however, it would not have an effect on the magnetic properties of the  $Mn_xFe_{3-x}O_4$  powders.

Figure 2 showed that the relation between the lattice distance and the substituted  $Mn^{2+}$  amount. The lattice distance was calculated using Bragg's diffraction law. As the substituted  $Mn^{2+}$  amount increased, the lattice distance of  $Mn_xFe_{3-x}O_4$  powders changed linearly from 8.336 Å to 8.470 Å: The radius of  $Mn^{2+}$  (0.91 Å) is larger than the one of  $Fe^{2+}$  (0.80 Å). As  $Mn^{2+}$  was introduced, it was substituted with  $Fe^{2+}$  and the increase in  $Mn^{2+}$  concentration made their lattice distances larger. There was a

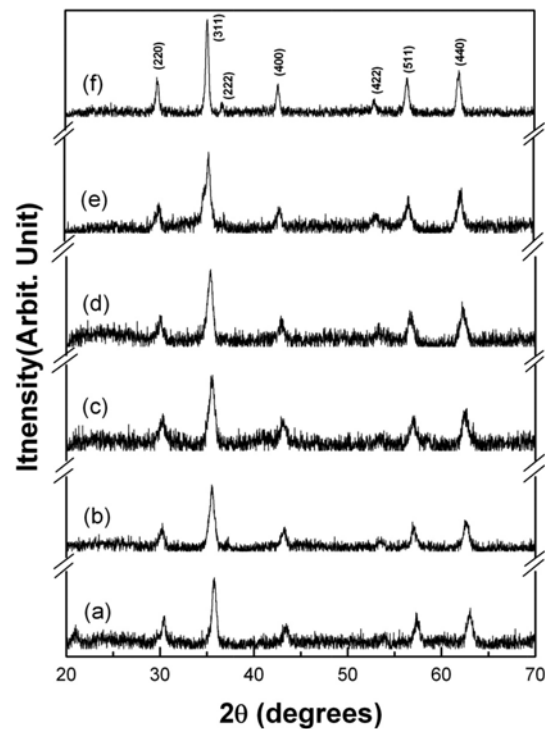


Fig. 1. X-ray diffraction patterns of  $Mn_xFe_{3-x}O_4$  powders: (a)  $x = 0.0$ , (b)  $x = 0.2$ , (c)  $x = 0.4$ , (d)  $x = 0.6$ , (e)  $x = 0.8$ , (f)  $x = 1.0$ .

large error bar for the pure  $Fe_3O_4$  powder in Fig. 2 due to their small particles. The intensity and peak width for the pure magnetite in Fig. 1a) indicates that its particle size was much finer than the one made by a conventional ceramic method.

Figure 3 showed images of  $MnFe_2O_4$  and  $Fe_3O_4$  powders annealed at 500°C were taken on field-emitting scanning electron microscopy. Their images were typical for spinel ferrite powders fabricated by a sol-gel method. The mark-

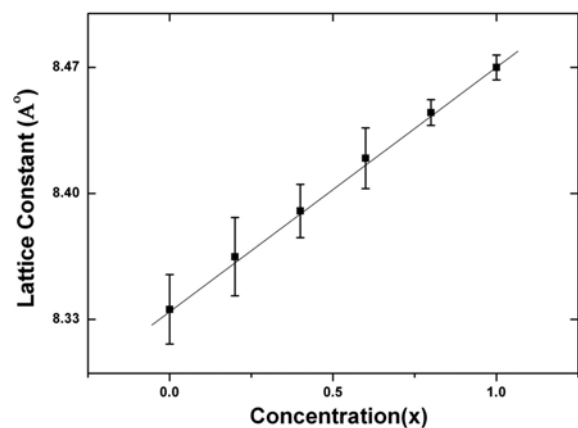
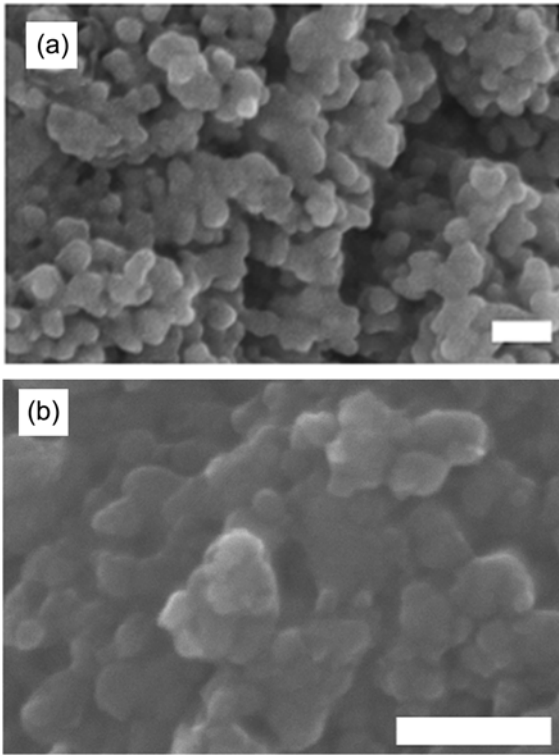
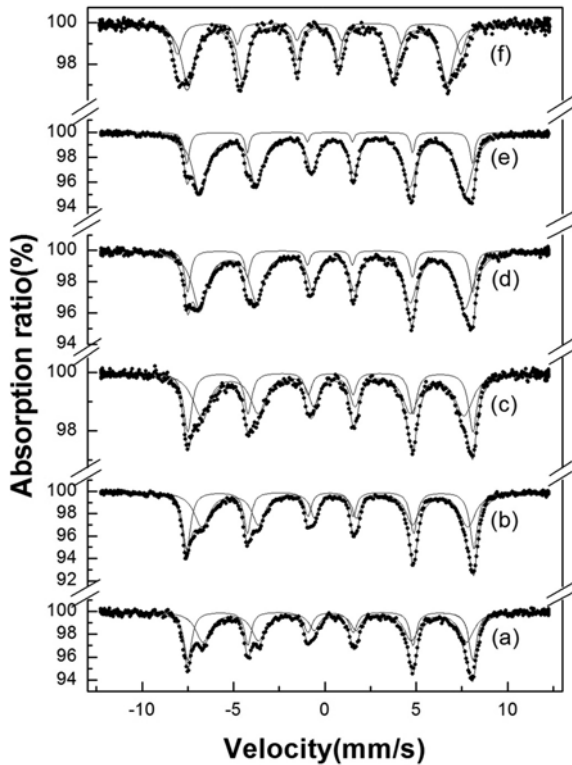


Fig. 2. Variation of lattice parameters as a function of Mn concentration in  $Mn_xFe_{3-x}O_4$ .



**Fig. 3.** Scanning electron microscopy images of a)  $Fe_{3-x}O_4$  and b)  $MnFe_2O_4$  powders. The marked length is 20 nm.



**Fig. 4.** Mössbauer spectra measured at room temperature of  $Mn_xFe_{3-x}O_4$  powders: (a)  $x = 0.0$ , (b)  $x = 0.2$ , (c)  $x = 0.4$ , (d)  $x = 0.6$ , (e)  $x = 0.8$ , and (f)  $x = 1.0$ .

ed lengths in these micrographs were 20 nm and their particle sizes were about 30-40 nm. The particle sizes were large enough to be ferrimagnetic, but they were too small to have typical magnetic properties of a bulk ferrite powder. These results were not very different from the mean particle sizes estimated by using Scherrer analysis with the (311) reflection plane.

Mössbauer absorption spectra measured at room temperature for  $Mn_xFe_{3-x}O_4$  powders were shown in Fig. 4. All of spectra were fitted with 2 sextet subspectra, which meant the powders to have spinel structures and their particle sizes large enough to be ferrimagnetic. The typical Mössbauer absorption spectrum for the pure magnetite powder was shown in Fig. 4a) and as the amount of the doped Mn ions increased, absorption spectra changed their shapes into those of typical Mn ferrite powders. The increasing  $Mn^{2+}$ -doping amount made the hyperfine field for one of the subspectra decreased rapidly while the one for the other was unchanged. The area ratio of the 2 sites strongly depended on the doping concentration. Detailed analysis results as a function of the  $Mn^{2+}$ -doping amount were shown in Table 1. It was well-known that  $Fe_3O_4$  had an inverse-spinel iron distribution such as  $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$  and that  $MnFe_2O_4$  had the mixed iron distribution, i.e.,  $Mn_{0.8}^{2+}Fe_{0.2}^{3+}[Mn_{0.2}^{2+}Fe_{0.1.8}^{3+}]O_4$  [7, 8]. These data were obtained with samples made by a conventional ceramic method, so their grain sizes might be very large and they had bulk-like magnetic properties. Our powders fired at 500°C, as shown in Fig. 3, consisted of 30-40 nm grains. There

**Table 1.** Mössbauer parameters of  $Mn_xFe_{3-x}O_4$  measured at room temperature.  $H_{hf}$  is the magnetic hyperfine field, QS is the quadrupole splitting, IS is the isomer shift relative to metallic iron, and area ratio (oct./tet.) represents the Mössbauer spectrum area ratio of A and B sites.

		IS	QS	$H_{hf}$	Area ratio
		(mm/s)	(mm/s)	(kOe)	(oct./tet.)
$Fe_3O_4$	oct.	0.549	0.002	447.7	1.331
	tet.	0.303	0.006	484.2	
$Mn_{0.2}Fe_{2.8}O_4$	oct.	0.563	0.016	451.6	1.315
	tet.	0.305	0.009	487.5	
$Mn_{0.4}Fe_{2.6}O_4$	oct.	0.471	0.046	446.7	1.786
	tet.	0.305	0.008	484.2	
$Mn_{0.6}Fe_{2.4}O_4$	oct.	0.438	0.026	450.8	4.236
	tet.	0.280	0.0004	483.8	
$Mn_{0.8}Fe_{2.2}O_4$	oct.	0.431	0.016	449.8	7.197
	tet.	0.272	0.006	484.8	
$MnFe_2O_4$	oct.	0.404	0.001	440.5	3.312
	tet.	0.302	0.004	481.4	

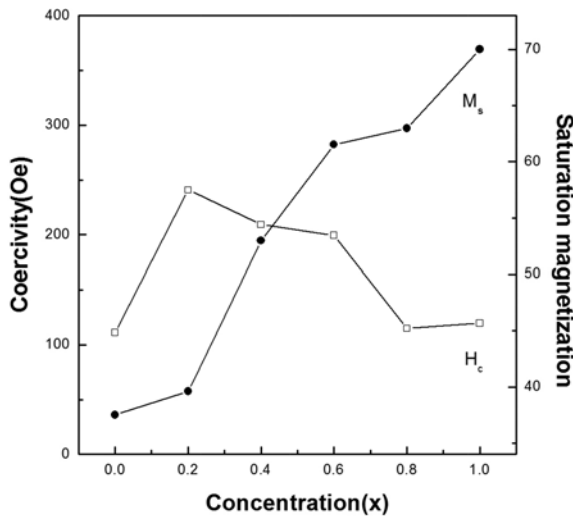


Fig. 5. Variation of the saturation magnetization ( $M_s$ ) and the coercivities ( $H_c$ ) of  $Mn_xFe_{3-x}O_4$  powders.

were a number of iron ions that were not involved in the formation of ferrite powders and the uneven ion distribution made the widths of subspectra wide.

The saturation magnetization and coercivities of  $Mn_xFe_{3-x}O_4$  powders as a function of the  $Mn^{2+}$ -doping amount investigated at room temperature were shown in Fig. 5. As shown in Fig. 5, pure Mn ferrite and magnetite powders had a soft magnetic property and their mixed  $Mn_xFe_{3-x}O_4$  powders were soft-magnetic, as well. Their saturation magnetization varied from 38 emu/g to 70.0 emu/g, as the substituted Mn amount increased; the  $Mn^{2+}$ -doping amount made their saturation magnetization increase rapidly, but there was no significant effect in their coercivities. In the case of making the nano-sized particles, their magnetic properties strongly depended on the annealing process, i.e., the saturation magnetization of the pure  $Fe_3O_4$  powder annealed at 500°C varied from 30 emu/g to 50 emu/g. The measured saturation magnetization could not be explained easily with the  $Fe^{2+}$  and  $Mn^{2+}$  distribution obtained by Mössbauer spectroscopy measurement. However, it was clear that the replacement of  $Fe^{2+}$  with  $Mn^{2+}$  made the saturation magnetization increase slowly, but their coercivities varied from 100 Oe to 240 Oe without preference.

## 4. Conclusion

Magnetic and structural properties of  $Mn_xFe_{3-x}O_4$  powders using a sol-gel method were investigated as a function of the amount of  $Mn^{2+}$ -incorporated; The results of XRD measurements showed that the heat treatment in a  $N_2$  atmosphere prevented the oxidation of  $Mn^{2+}$  and  $Fe^{2+}$  and that the formation of a spinel ferrite powder fired at 500°C was identified. In addition, the large ion radius of  $Mn^{2+}$  made their lattice distance of the ferrite powders increase slowly. Mössbauer spectroscopy measurements showed that ferrite powders had a spinel structure and that they were ferromagnetic. As the  $Mn^{2+}$ -doping amount increased, the patterns of Mössbauer absorption spectra were changed rapidly and their widths of subspectra increased. Ferrite powders annealed at 500°C had soft magnetic properties regardless of the  $Mn^{2+}$ -doping amount;  $Mn^{2+}$  increased their saturation magnetization.

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