Magnetic Properties of MgFe_2O_4 Nanoparticles and Zn Doping Effect

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$\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) nanoparticles encapsulated in amorphous SiO_2 were prepared using a wet chemical method, and their magnetic properties were studied. The diameters of these particles were estimated from X-ray diffraction (XRD) patterns as ranging near 4.5 nm. Magnetization measurements were carried out for all samples under a ± 50 kOe field. The blocking temperature T_B was determined to be approximately 20–60 K from the temperature dependence of the field-cooled (FC) and the zero-field-cooled (ZFC) magnetizations. The M - H curve indicated ferromagnetic behavior at 5 K and superparamagnetic ($x = 0 - 0.6$) and paramagnetic ($x = 0.8$) behavior at 300 K. The sample with $x = 0.4$ had the largest maximum magnetization M_S under an applied field of 50 kOe at 5 K, and the sample with $x = 0.2$ has the largest M_S at 300 K among all the samples.

Key words: ferrite, magnetization, relaxation

1. INTRODUCTION

Magnetic nanoparticles have been attracting much attention because they show unique features such as quantum size effects and magnetic tunneling. They are also important for technological applications, not only in high-density magnetic recording systems but also as a material in the medical field. We have reported the characteristics of ferrite nanoparticles with various compositions such as CoFe_2O_4 , NiFe_2O_4 , MgFe_2O_4 , MnFe_2O_4 , CuFe_2O_4 , and DyFeO_3 [1-11]. On the other hand the physical properties of MgFe_2O_4 have also been reported separately [12, 13], because MgFe_2O_4 is known as good catalytic material [14] and is noted for other various applications [15-17]. In this paper, we introduce the synthesis of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) nanoparticles of approximately 4.5 nm in size and discuss the dependence of their magnetic characteristics on the Zn^{2+} ion contents.

Bulk MgFe_2O_4 crystal has an incomplete inverse spinel structure, where the A sites contain some of the Mg^{2+} ions and the B sites contain most of the Mg^{2+} ions [3, 4]. Here, the A sites are tetrahedral sites, and the B sites are octahedral sites. The magnitude of the magnetization depends on the distribution of the magnetic ions in the A and B sites. In this system, the Mg^{2+} and Zn^{2+} ions are nonmagnetic, so the magnetization would be dependent on the distribution of Fe^{3+} ions. It is known that Zn^{2+} ions prefer to be distributed in the A sites. In some reports on bulk MgFe_2O_4 crystal, the site distribution was observed to change according to the Zn^{2+} ion doping. As a result, the magnetization increased upon doping, even though Zn^{2+} ions are nonmagnetic [1, 2, 8, 16-20]. It is very curious and interesting that when Zn^{2+} ions are added to spinel ferrites, their magnetization increases with the content nonmagnetic Zn ions. This can be observed up to a Zn content value (x) of approximately 0.4 in the formula

unit of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, and then at higher Zn^{2+} ion contents the magnetization begins to decrease [18]. In this article, the dependence of the magnetic properties of Mg-Zn ferrite particles with diameters of approximately 4.5 nm on the Zn^{2+} ion contents is reported.

2. EXPERIMENT

$\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) nanoparticles were prepared using a wet chemical method. Aqueous solutions of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were mixed with a solution of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$. The mole ratio of the prepared reagent was $\text{Mg}:\text{Zn}:\text{Fe}:\text{Si} = (1-x):x:2:3$. The obtained precipitates were washed several times with distilled water and dried at approximately 350 K in a thermostat. The as-prepared samples were subjected to heat treatment in a furnace in air at annealing temperatures between 1023 and 1073 K. All samples were examined by performing $\text{Cu K}\alpha$ X-ray ($\lambda = 0.154$ nm) powder diffraction, after which magnetization measurements were carried out with a SQUID magnetometer in external fields between -50 and 50 kOe within the temperature range from 5 to 300 K.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction

Fig. 1 shows the XRD patterns for the $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) samples. The XRD patterns have broad peaks approximately $2\theta = 20^\circ$ because of the amorphous SiO_2 , and a single-phase spinel structure was observed. The samples prepared using this method consisted of magnetic clusters encapsulated by amorphous SiO_2 , which was confirmed by TEM images in previous studies [8, 10]. The particle size can be controlled using the annealing temperature, and the average particle sizes of all samples were estimated to be approximately 4.5 nm.

Fig. 1 X-ray diffraction patterns of the $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) nanoparticle samples. Particle sizes were estimated to be between 4.3 and 4.7 nm depending on the annealing temperature.

Table I. Dependence of blocking temperature T_B on the Zn content x

Zn content / x	0	0.2	0.4	0.6	0.8
T_B / K	60	55	45	30	20

Fig. 2 Temperature dependence of the FC and ZFC magnetization for $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) nanoparticle samples under a 100 Oe field.

3.2 Magnetization measurements

Fig. 2 shows the temperature dependence of both the FC and ZFC magnetizations for all samples under an external field of 100 Oe. We define the FC-ZFC bifurcation temperature as the blocking temperature (T_B), above which the magnetic spins in the particle are supposed to fluctuate with thermal energy and behave superparamagnetically. The T_B was observed to be between 20 and 60 K, and it shifted to lower temperature as the Zn^{2+} ion contents increased. This phenomenon reflects the reduction in the anisotropy energy in the particles. It is expected that ferromagnetic behavior would be exhibited below T_B , while superparamagnetic or paramagnetic behavior would be observed above T_B . The dependence of the blocking temperature on the Zn^{2+} ion contents x is summarized in Table I.

Figs. 3(a) and (b) show the magnetization curves for different Zn^{2+} ion contents observed at 5 K and 300 K,

respectively. The curves indicate ferromagnetic behavior when measured at 5 K, below T_B , as shown in Fig. 3 (a). In Fig. 3 (b), the magnetic curves of the samples with $x = 0 - 0.6$ indicate superparamagnetic behavior and the sample with $x = 0.8$ exhibits paramagnetic behavior at 300 K, above T_B . The M_S values of all samples at 5 K and 300 K are summarized in Table II and Fig. 4. The M_S value increased with the Zn^{2+} ion contents up to $x = 0.4$, and then it decreased for larger amounts of Zn^{2+} ions at 5 K. This behavior at 5 K is similar to that of the bulk crystal [18]. On the other hand, at 300 K, the M_S value increased up to $x = 0.2$, then decreased for larger amounts of Zn^{2+} ions. The M_S values of all samples are much smaller at 300 K than at 5 K. This phenomenon is characteristic of small particles according to the relation between the anisotropy energy Kv and thermal energy kT , where K is the anisotropy constant, v is the volume of

Fig. 3 Magnetization curves for $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) nanoparticles at (a) 5 K and (b) 300 K.

Table II. M_S of $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) nanoparticles at 5 K and 300 K

x	M_S / μ_B at 5 K	M_S / μ_B at 300 K
0	1.48	0.79
0.2	3.04	1.49
0.4	3.35	1.25
0.6	2.96	0.75
0.8	2.55	0.47

the particle, k is the Boltzmann constant, and T is the temperature. The different M_S values at 5 K and 300 K are considered to reflect the large effect of thermal fluctuations because the particles are nanoscopic. This makes sense because thermal fluctuations become larger at higher temperatures. Fig. 5 shows the rate of decrease in M_S from 5 K to 300 K. In this figure, the rate of decrease increases as the amount of doped Zn^{2+} ions increases. This phenomenon reflects the fact that the magnetization becomes susceptible to thermal fluctuations because the anisotropy of the magnetic spins in the particles decreases. The largest magnetization value was observed when $x = 0.4$ for 5 K and when $x = 0.2$ for 300 K, as shown in Fig. 4. It is believed that the rate of decrease in M_S for $x = 0.4$ is

Fig. 4 Dependence of maximum magnetization M_S on Zn^{2+} ion composition and temperature.

Fig. 5 Rate of decrease in M_S from 5 K to 300 K, which drastically depends on the Zn^{2+} ion contents.

larger than that for $x = 0.2$ because the thermal fluctuations are larger at 300 K. Thus, the magnetization value varies depending on the particle content, and quite interesting phenomena were observed in the MgFe_2O_4 nanoparticle system.

4. CONCLUSIONS

Zn^{2+} -doped pluralistic ferrite nanoparticles with compositions $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$) encapsulated with amorphous SiO_2 were prepared by a wet chemical method. The average particle size of all samples was estimated approximately to be 4.5 nm. From the temperature dependence of the magnetization under the FC and ZFC conditions, the values of T_B were

observed to be between 20 and 60 K. T_B shifted to lower temperature as the Zn^{2+} ion contents increased. It is confirmed that ferromagnetic behavior below T_B and superparamagnetic or paramagnetic behavior above T_B from the magnetization curves. The M_S varied drastically depending on the Zn^{2+} ion contents.

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