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Superparamagnetic Properties of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ Nanoparticles

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Nanoparticles $Ni_{0.7}Zn_{0.3}Fe_2O_4$ is fabricated by a sol-gel method. The magnetic and structural properties of powders were investigated with XRD, SEM, Mössbauer spectroscopy, and VSM. $Ni_{0.7}Zn_{0.3}Fe_2O_4$ powders annealed at 300 °C have a spinel structure and behaved superparamagnetically. The estimated size of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ nanoparticle is about 11 nm. $Ni_{0.7}Zn_{0.3}Fe_2O_4$ annealed at 400 and 500 °C has a typical spinel structure and is ferrimagnetic in nature. The isomer shifts indicate that the iron ions were ferric at the tetrahedral (*A*) and the octahedral (*B*). Blocking temperature (T_B) of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ nanoparticle is about 260 K. The magnetic anisotropy constant of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ annealed 300 °C were calculated to be 1.7×10^6 ergs/cm^3. Also, temperature of the sample increased up to 43 °C within 7 minutes under AC magnetic field of 7 MHz.

Key words : Superparamagnetism, Nanoparticle, Mössbauer spectroscopy, Magnetic anisotropy constant

1. Introduction

Superparamagnetic nanoparticles have been used in biomedicine and biotechnology as contrast agents in magnetic resonance imaging (MRI) and as drug carriers for magnetically guided drug delivery [1, 2]. superparamagnetism has been extensively studied in the nanoparticles of pure metals such as Fe, Co, and Ni [3, 4]. However, these metallic nanoparticles are chemically unstable. Thus, their applications are very limited. On the other hand, abundant and diverse magnetic metal-oxides offer great opportunities for developing superparamagnetic nanoparticles with desirable properties. The nanoparticles of metal oxides such as spinel ferrites possess great potentials for applications.

Many methods are successfully used for the preparation of particulate oxide materials, the ceramic method, the co-precipitation method, the sol-gel method, the crystallization with a melting method and so on. But among them the sol-gel method has many advantages. One of the advantages of using the sol-gel method is the lower annealing temperature that enables to make smaller grained powders be grown (e.g., nanocrystalline particles). A few sol-gel methods for ultrafine cobalt, barium ferrite powders have been introduced [5, 6]. However, Zn-doped Ni-Zn ferrite nanoparticles have not yet been investigated to a great extent.

In this study, a sol-gel procedure was used for the preparation of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ nanoparticles powders and their magnetic and structural properties as a function of annealing temperature were characterized by using x-ray diffractometry (XRD), Mössbauer spectroscopy, and vibrating sample magnetometry (VSM) as well as scanning electron microscopy (SEM), alcoholic thermometer.

2. Experimental Procedures

Nanoparticles $Ni_{0.7}Zn_{0.3}Fe_2O_4$ were synthesized by a sol-gel method. The raw materials utilized in the present study were $Ni(CH_3CO_2)_2 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$. These were dissolved in a mixed solvent system (ethanol : distilled water : acetic acid = 6 : 1 : 1). The solution was refluxed at 50 °C for 12 h. Afterwards, it was dried in an oven at 100 °C for 72 h and then oven-dried powders were milled and finely powdered. The dried powder was ground and annealed at temperatures ranging from 200 to 500 °C for 3 h in air. These compositions of samples annealed at various temperatures were identified by XRD with Cu*Ka* radiation. The mean particle size was confirmed by SEM (JSM-6700F). The Mössbauer spectra were recorded using a conventional Mössbauer spctrometer of the electromechanical type with a 30 mCi ^{57}Co source in an Rh matrix [7]. The

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saturation magnetization and coercivities of the powders were measured with a VSM (LakeShore 7300) at a maximum applied field of 10 kOe from 60 to 350 K. Also, the exothermic characteristics of the sample was measured with a alcoholic thermometer at a 400 Oe and 7 MHz of AC magnetic field.

3. Results and Discussion

XRD patterns of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ powders fired at various temperatures are shown in Fig. 1. The XRD measurement shows that all peaks of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ powders annealed at and above 300 °C are consistent with those of a standard pattern of a Ni-Zn ferrite [8]. In addition, the increase in the annealing temperature yields an increased sharpness of the major peak (311), that is, the growth of the larger grain size of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ powders and improved crystallization. In Fig. 1, the formation of crystalline $Ni_{0.7}Zn_{0.3}Fe_2O_4$ ferrite is seen to start at and above 300 °C, however, the considerable broadening of all diffraction peaks of the sample fired at 300 °C suggests that the sizes of the Ni-Zn ferrite particles are relatively small.

The SEM micrographs of the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ powders are shown in Fig. 2. The SEM micrographs indicate the distribution of grains uniform with really spherical shape. The powders present average particle sizes of 11, 15, 21 nm for sample as obtained and annealed at 300, 400, 500 °C, respectively, which shows that the particle size increases with increasing annealing temperature.

Mössbauer absorption spectra measured at various temperatures from 13 to 400 K for $Ni_{0.7}Zn_{0.3}Fe_2O_4$ powders annealed at different temperatures are shown in Fig. 3 and Fig. 4, respectively.

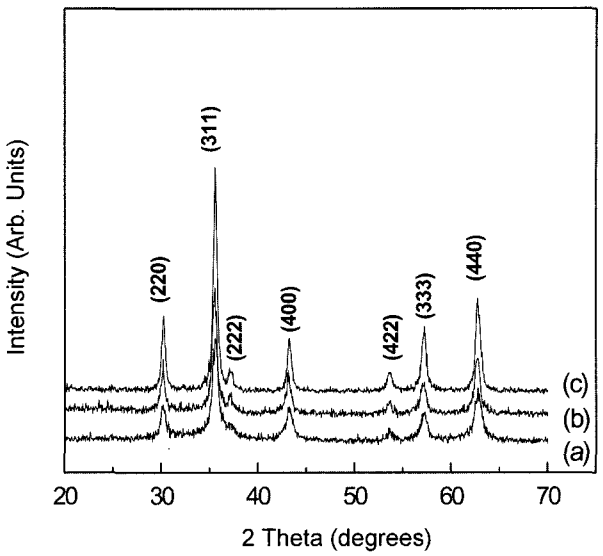

Fig. 1. X-ray diffraction patterns of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ samples annealed at (a) 300 °C, (b) 400 °C, (c) 500 °C.

Mössbauer parameters obtained from least square fits of the spectra [9]. The room temperature Mössbauer spectrum (Fig. 3) of sample annealed at 200 °C shows a paramagnetic phase. Also, spectra of samples annealed at 400 and 500 °C can be fitted with two six-line subpatterns that are assigned to *A*-ions in tetrahedral sites and *B*-ions in octahedral sites of a typical cubic spinel ferrite. However, the Mössbauer spectra (Fig. 4) for the sample

Table 1. Analyzed results of Mössbauer spectra for $Ni_{0.7}Zn_{0.3}Fe_2O_4$ annealed at 300 °C. H_{hf} is the magnetic hyperfine field, E_Q the quadrupole splitting, δ the isomer shift relative to iron at room temperature and the area ratio for sextet / doublet.

Temperature (K)	Mössbauer parameter	fitted spectrum			sextet / doublet	Magnetism
		sextet		doublet		
		B-site	*A*-site			
13	H_{hf}(kOe)	523	499	–	–	ferrimagnetic
	E_Q (mm/s)	0.01	-0.02			
	δ(mm/s)	0.34	0.30			
77	H_{hf}(kOe)	520	493	–	–	ferrimagnetic
	E_Q (mm/s)	0.00	-0.01			
	δ(mm/s)	0.33	0.26			
260	H_{hf}(kOe)	463	416	–	1.0	superparamagnetic
	E_Q (mm/s)	0.01	0.00	0.68		
	δ(mm/s)	0.23	0.18	0.22		
295	H_{hf}(kOe)	440	406	–	0.8	superparamagnetic
	E_Q (mm/s)	0.00	0.00	0.69		
	δ(mm/s)	0.21	0.16	0.24		

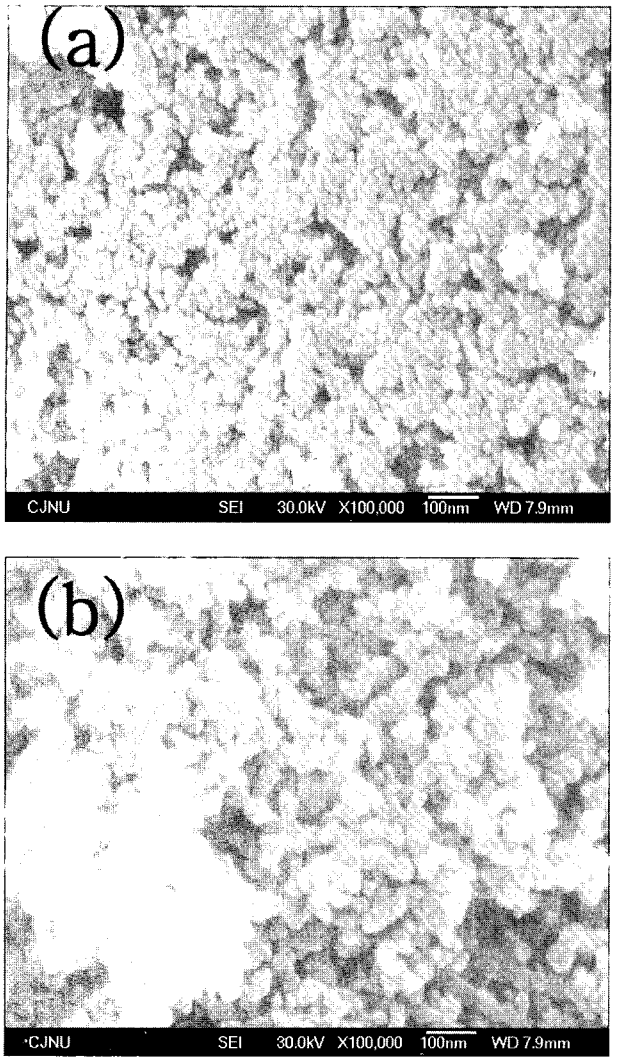

Fig. 2. SEM micrographs of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ samples annealed at (a) 300 °C, (b) 500 °C.

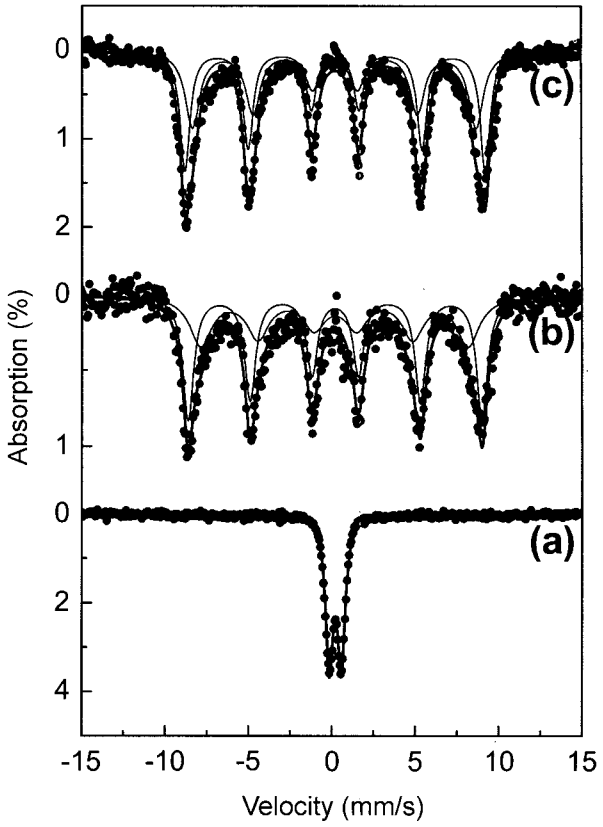

Fig. 3. Room temperature Mössbauer spectra of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ samples annealed at (a) 200 °C, (b) 400 °C, (c) 500 °C.

annealed at 300 °C exhibit a quadrupole doublet at the center of the spectrum superimposed a magnetically split component spread across the spectrum. The coexistance of both quadrupole and magnetic splitting is due to size distribution in the nanocomposite. At room temperature, the quadrupole doublet dominates the magnetic splitting, and hence the sample becomes superparamagnetic. The intensity of quadrupole splitting decreases with temperature. At 13 K, only the magnetic splitting is present and the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ powder is completely ferrimagnetic. The results of the computer analysis of the spectra at some typical temperatures are presented in Table 1. The hyperfine fields at 13 K for the *A* and *B* patterns are found to be 523 and 499 kOe, respectively. The isomer shifts at room temperature for the *A, B* site and doublet patterns were found to be 0.16, 0.21 and 0.24 mm/s relative to the Fe metal, respectively, which are consistent with high-spin Fe^{3+} charge states [9].

Mössbauer spectroscopy is a powerful technique to characterize magnetic nanoparticles undergoing superparamagnetic relaxation. The superparamagnetic relaxation time, τ is the average time that it takes the particle magnetization to jump from one direction to another. The relaxation time τ depends on the size of the particles and the temperature, which is approximated by Néel as

$$\tau = \tau_0 \exp(KV/k_BT), \quad (1)$$

where K is the anisotropy constant of the particle, V the particle volume, k_B the Boltzman constant, T the temperature, and τ_0 is a constant usually taken as $\tau_0 \cong 10^{-10}$ s [10]. The superparamagnetic relaxation of a single domain magnetic nanoparticle may be observed by a technique with [11]

$$T_B = KV/[k_B \ln(\tau_s/\tau_0)]. \quad (2)$$

Mössbauer spectra show can record the sextet hyperfine

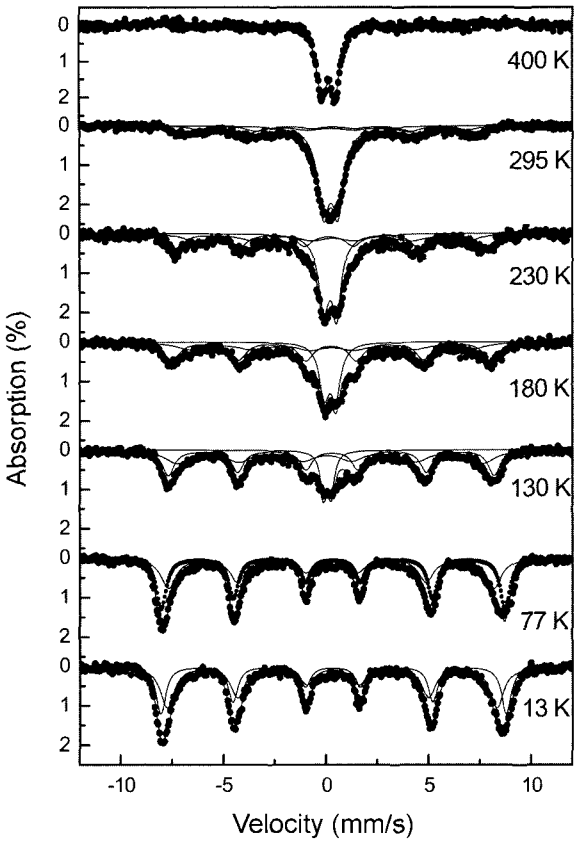

Fig. 4. The Mössbauer spectra of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ annealed at 300 °C measured at various temperatures.

structure if the magnetization of the nanoparticles does not flip during one Larmor precession. Since the Larmor precession time τ_s is about 10^{-8} s for ^{57}Fe, the hyperfine sextet will be observed when the relaxation time of the superparamagnetic nanoparticles is longer than 10^{-8} s. Above the blocking temperature, the relaxation time $\tau \ll \tau_s$, only a quadrupole doublet in the Mössbauer spectra is observed. Below the blocking temperature, $\tau \gg \tau_s$ a characteristic sextet Mössbauer pattern is observed. Near the T_B when $\tau \sim \tau_s$, a partially collapsed sextet with broad lines is seen. The area ratio of the sextet to the doublet spectra, $R(T)$ can be represented as $R(T) = [C\text{-}P(T)]/P(T)$ where C is the total population [12]. The numerator $[C\text{-}P(T)]$ represents the population of the nanoparticles responsible for the hyperfine sextet. The enominator $P(T)$ is the population responsible for the doublet absorption. Fig. 5 shows the temperature dependence of $R(T)$ for $Ni_{0.7}Zn_{0.3}Fe_2O_4$ at annealed 300 °C. The blocking temperature is the temperature at which $R(T)$=1 corresponds to 50 % of the total population. As a result, blocking temperature $T_B = 260$ K from Mössbauer spectroscopic measurements. With sets of the relaxation time and the

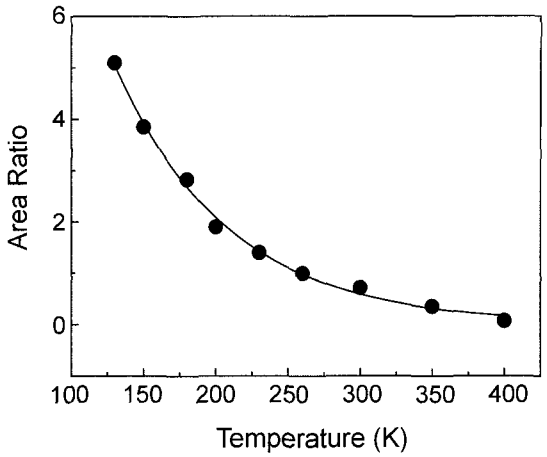

Fig. 5. Temperature dependence for the area ratio of the sextet to the doublet of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ nanoparticle. The closed circles are the data collected by the Mössbauer spectrometer and the solid line is the fit using the exponential function.

corresponding blocking temperature, magnetic anisotropy constant is calculated directly from Eq. (2). The result shows a value of 1.7×10^6 ergs/cm^3 as the magnetic anisotropy constant of the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ nanoparticles with a size of 11 nm.

Magnetic properties of the superparamagnetic nanoparticle $Ni_{0.7}Zn_{0.3}Fe_2O_4$ annealed at 300 °C were investigated with VSM from 60 to 350 K. According to the Stoner-Wohlfarth theory [14], the coercivity H_C of a single-domain particle is the following: $H_C = 2K/\mu_0 M_S$, where μ_0 is a universal constant of permeability in free space and M_S is the saturation magnetization of the nanoparticle. Above the blocking temperature, the

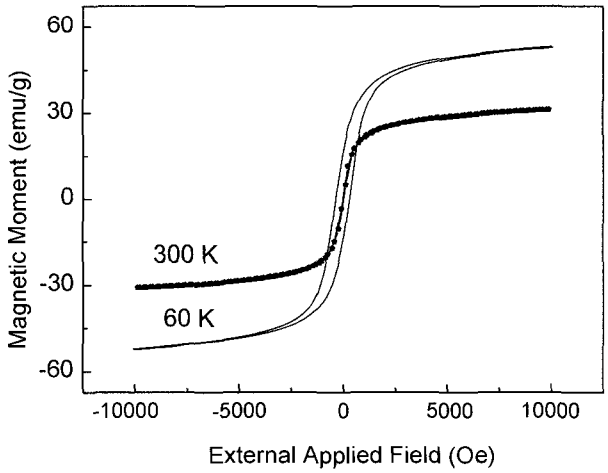

Fig. 6. Magnetization vs applied magnetic field curve of the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ annealed at 300 °C. The solid and dotted lines were measured at 60 and 300 K, respectively.

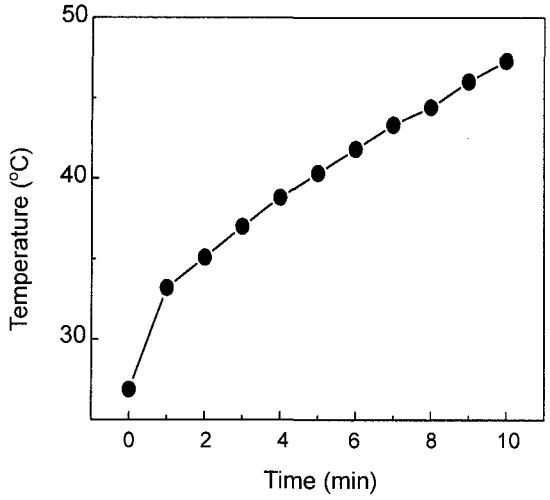

Fig. 7. Change of temperature of the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ under AC magnetic field at 7 MHz.

magnetocrystalline anisotropy is overcome by thermal activation, and K can be considered as zero. The nanoparticles do not display any magnetization hysteresis behavior with $H_C = 0$. Figure 6 shows the magnetization versus magnetic field curves of the sample annealed at 300 °C, measured at 60 K (solid line) and 300 K (dotted line). At low temperatures, the sample annealed at 300 °C, exhibits a hysteretic behavior, indicating that it has a ferrimagnetic phase. However, at room temperature, the ferrimagnetic hysteresis seems to have disappeared. As a typical blocking behavior of superparamagnetic nanoparticles, the $Ni_{0.7}Zn_{0.3}Fe_2O_4$ nanoparticles show a different magnetization process when the sample is cooled below the blocking temperature with an external magnetic field. The saturation magnetization M_S of 60 and 295 K were 31 and 53 emu/g, respectively.

Figure 7 represents the rise in temperature of the Ni-Zn ferrite under 400 Oe and 7 MHz of AC magnetic field. It can be seen that sample is heated up to 43 °C, which is the effective hyperthermic temperature for cancer treatment, by 7 minutes after the magnetic field is applied.

For biomedicine application, such as hyperthermia, drug delivery system (DDS), and so on, magnetic fluid carrier should not lump for the smooth circulation of the blood and should not be sharp for the prevention of a hurt [15]. Therefore, they should be superparamagnetic and have the spherical shape. It is considered that $Ni_{0.7}Zn_{0.3}Fe_2O_4$ annealed at 300 °C, are available for biomedical applications such as hyperthermia and drug delivery system as a magnetic fluid carrier because it has spherical shape, narrow particle distribution, chemical stability, and superparamagnetic behavior.

4. Conclusion

$Ni_{0.7}Zn_{0.3}Fe_2O_4$ powder annealed at 300 °C has a spinel structure and behaves superparamagnetically. The estimated size of superparammagnetic $Ni_{0.7}Zn_{0.3}Fe_2O_4$ nanoparticle is about 11 nm. The hyperfine fields at 13 K for the A and B patterns were found to be 499 and 533 kOe, respectively. The blocking temperature (T_B) of superparammagnetic $Ni_{0.7}Zn_{0.3}Fe_2O_4$ nanoparticle is about 260 K. The magnetic anisotropy constant of $Ni_{0.7}Zn_{0.3}Fe_2O_4$ annealed at 300 °C was calculated to be 1.7×10^6 ergs/cm^3. The saturation magnetization M_S were 31 emu/g at 60 K, and 53 emu/g at room temperature (295 K) under an applied field of 10 kOe. Temperature of the sample increased up to 43 °C within 7 minutes under AC magnetic field of 7 MHz. It is considered that $Ni_{0.7}Zn_{0.3}Fe_2O_4$ powder annealed at 300 °C is available for biomedicine application such as hyperthermia and drug delivery system as a magnetic fluid carrier.

References

[1] S. H. Im, T. Herricks, Y. T. Lee, and Y. Xia, Chem. Phys. Lett. **401**, 19 (2005).
[2] S. W. Lee, K. W. Woo, and C. S. Kim, J. of Magnetics. **9**, 83 (2004).
[3] S. K. Khanna and S. Linderoth, Phys. Rev. Lett. **67**, 742 (1991).
[4] Qi Chen and Z. J. Zhang, Appl. Phys. Lett. **73**, 3156 (1998).
[5] J. G. Lee, H. M. Lee, C. S. Kim, and Y. J. Oh, J. Magn. Magn. Mater. **177-181**, 900 (1998).
[6] V. K. Sankaranarayana, Q. A. Pankhurst, D. P. Dickson, and C. E. Johnson, J. Magn. Magn. Mater. **125**, 199 (1998).
[7] S. W. Lee, Y. G. Ryu, K. J. Yang, K. D. Jung, S. Y. An, and C. S. Kim, J. Appl. Phys. **91**(10), 610 (2002).
[8] S. W. Lee and C. S. Kim, J. of Magnetics. **10**(1), 5 (2005).
[9] H. N. Ok, K. S. Baek, H. S. Lee, and C. S. Kim, Phys. Rev. B **41**, 62 (1990).
[10] Q. Chen , Adam J. Rondinone, Bryan C. Chakoumakos, Z. John Zhang, J. Magn. Magn. Mater **194**, 1 (1999).
[11] B. K. Nath, P. K. Chakrabarti, S. Das, U. Kumar, P. K. Mukhopadhyay, and D. Das, Eur. Phys. B **39**, 417 (2004).
[12] Adam J. Rondinone, Anna C. S. Samia, and Z. J. Zhang, Appl. Phys. Lett. **76**(24), 3624 (2000).
[13] S. W. Lee, S.Y. Yoon, S. Y. An, W. C. Kim and C. S. Kim, J. of Magnetics **4**, 115 (1999).
[14] S. Chikazumi, *Physics of Ferromagnetism*, 2nd ed. (Oxford University Press, New York, 1997), p. 510.
[15] S. Y. An, I. B. Shim, and C. S. Kim, J. Appl. Phys. **97**(10), 10Q909 (2005).