Journal of the Korean Ceramic Society
Vol. 39, No. 1, pp. 12~15, 2002.

Magnetization of Ultrafine Cadmium Ferrite Particles

Eun Jung Choi†

Department of Neo-material Science, Konyang University, Chungnam 320-711, Korea
(Received October 19, 2001; Accepted November 27, 2001)††

ABSTRACT

Ultrafine cadmium ferrite particles have been investigated by X-ray diffractometry, transmission electron microscopy and SQUID magnetometry. All peaks of X-ray diffraction patterns are broad, but correspond to a cubic spinel structure with the lattice constant of 8.65 Å. The average particle size determined by TEM is 9.7 nm and the size distribution of particles is not normal, but lognormal. The maximal magnetization measured at 5 K was 17.7 emu/g. The experimental data show a transition from a disorder ferrimagnetic phase to a spin-glass phase (i.e. reentrant behavior) with a freezing temperature (T_f) of 30 K. Superparamagnetic behavior of the particles is confirmed by the coincidence of the plots of M vs. H/T for 100 and 300 K.

Key words : Ultrafine particles, Particle size distribution, Magnetization, Superparamagnetism

1. Introduction

Recently, research into ultrafine materials and their properties has been given much attention because of the wide range of potential applications, including magnetic recording media, ferrofluids, catalysts, medical diagnostics, drugdelivery systems, and pigments in paints and ceramics.[1] The physical properties of the disordered system of such particles differ from those of the free atoms or molecules themselves as well as from the properties of the bulk solids. These ultrafine particles have been also widely studied in the field of gas sensors in recent years.[2-4] Wet chemical methods, such as co-precipitation and hydrothermal oxidation, and ball-mill grinding method have been used to yield ultrafine ferrite particles ranging from 10 to 100 nm. Many publications by these technique are available in literatures.[5-7] These synthesis methods are of particular interest because of the low-temperature processing techniques. The physical properties of ultrafine particles prepared by these methods are drastically different from their bulk counterparts because the size of particles is sufficiently reduced. The interparticle spacing and surface-to-volume ratio in particles play a predominant role in influencing the material properties. Small particles structurally differ from bulk solids, in that a large fraction of atoms resides at the surface. These surface atoms have lower coordination number than the interior ones.

Cadmium ferrite is a specially interesting material for magnetic investigation. The bulk material of cadmium ferrite is known as completely normal spinel in which tetrahedral or A-sites are almost exclusively occupied by Cd^{2+} ions, and octahedral or B-sites by Fe^{3+} ions. This material is classified as an antiferromagnetic material with the Néel temperature of 10 K due to B-B interaction. The saturation magnetization is 4.2 emu/g at 300 K and 12 emu/g at 6 K.[8] Cadmium ferrite also shows a high sensitivity and selectivity to C_2H_5OH gas, and then is expected to find wide applications in the traffic management, food ferment, wine making and medical processes.[9]

However, recent investigations have suggested that the cation distribution of ultrafine cadmium ferrite particles is partially inverted and the saturation magnetization of them is remarkably different from that of the bulk material. Yokoyama *et al.*[10] have found that ultrafine cadmium ferrite particles with average size of 8 nm exhibited ferrimagnetic behavior with a net magnetization of 89 emu/g at 6 K in an applied field of 1 T, which corresponds to 4.6 μ_B/molecular. Their X-ray diffraction study showed that 6% and 13% of the A-sites were occupied by Fe^{3+} ions in the bulk material and ultrafine particles, respectively. On the other hand, Chinnasamy *et al.*[11] observed a smaller saturation magnetization 22 emu/g at 5 K even in an applied field of 9 T. The average particle size by prepared by them is 7 nm. These extraordinary magnetic behavior may be related to the ferrimagnetic cluster formation of Fe^{3+} ions that is relevant to cation distribution, the particle size distribution and the preparation method. However, there is no detailed information about the magnetic properties of cadmium with regard to Fe^{3+} ion distribution not only in ultrafine particles but also in bulk material.

The purpose of this work is to report the magnetization and superparamagnetic phenomenon of ultrafine cadmium ferrite particles.

†Corresponding author : ejchoi@kytis.konyang.ac.kr
††This paper was accepted as an on-site paper at the submitted 2001 fall technical meeting of the Korean Ceramic Society.

2. Experimental Procedure

Ultrafine cadmium ferrite particles were prepared by the coprecipitation method. Iron chloride solution (0.2 mol/l) and cadmium sulfide solution (0.1 mol/l) as starting materials were mixed. Ammonium carbonate solution was added to the mixed solution until a pH of 6.5 was attained. The product was washed with deionized water, filtered and then dried at 60°C. X-ray powder diffraction patterns of the particles were obtained by using Cu-$K\alpha$ radiation in the $25° \leq 2\theta \leq 70°$ range. Transmission Electron Microscopy(TEM) was used to determine the particle shape and the average particle size. A SQUID magnetometer was used to study the magnetic properties of the particles in the temperature range of 5-300 K and in the field up to 50 kOe. In the field of 50 kOe the so-called Zero-Field-Cooled(ZFC) and Field-Cooled(FC) magnetizations were also obtained by using the following procedure: first, the sample was cooled from room temperature to a low temperature in zero applied field, after which a field H=50 kOe was applied, then the variation of magnetization with temperature (ZFC process) was measured in the temperature-increasing process until T=300 K. Second, the sample was cooled again, keeping the same applied field to the same low temperature; then the temperature was increased, and again, the variation of magnetization with temperature (FC process) was measured.

3. Results and Discussion

The X-ray diffraction patterns of ultrafine cadmium ferrite particles were taken at a slow scanning speed, i.e., 0.02° advance in 2θ per min., and shown in Fig. 1. X-ray diffraction patterns corresponding to the sample consist of broad lines. The broadening of all diffraction peaks indicates that the average size is very small. There is no evidence of extra crystalline or amorphous phases present. Each peaks in the patterns are broad, but can be indexed on the basis of a cubic spinel structure. The lattice constant a_0 was found to be 8.65 Å, which is smaller than that of the bulk cadmium ferrite(8.70 Å[12]), by plotting $a_0(\theta)$ versus the Nelson-Riley function and extrapolating to θ=90°. In general, the lattice constant of the ultrafine particles is smaller than that of the bulk material. The present difference in the lattice constant between the fine particles and the bulk material of cadmium ferrite can be explained by the difference of cation distribution between them[13] and the possible contraction because of the deformation of the Fe^{3+}[B]-O^{2-}-Fe^{3+}[B] bonds as observed by Sėpelak *et al.*[14]

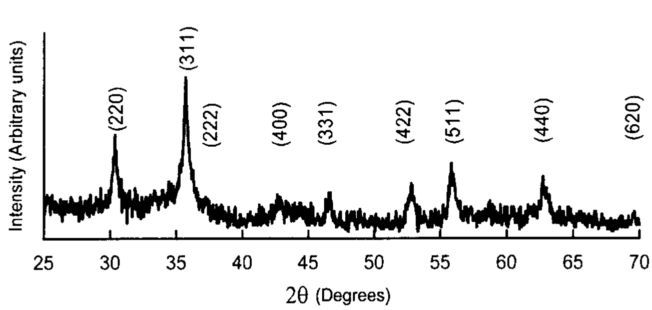

Fig. 1. X-ray diffraction pattern for ultrafine cadmium ferrite particles.

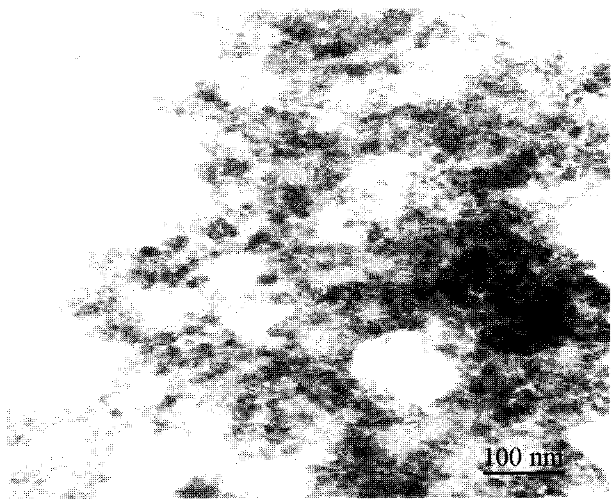

Fig. 2. TEM micrograph of ultrafine cadmium ferrite particles.

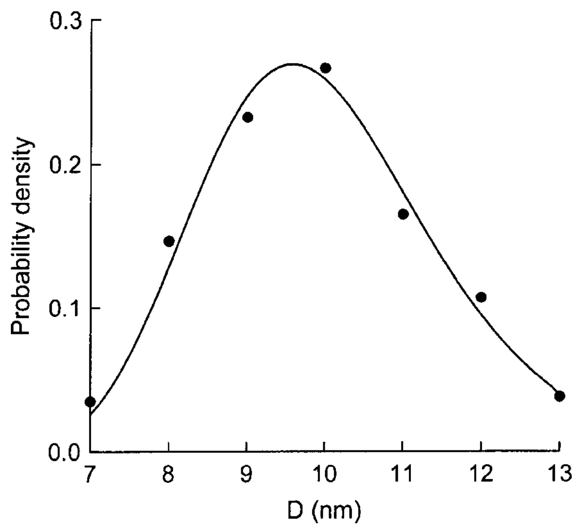

Fig. 3. Particle size distribution for ultrafine cadmium fertie particles.

Fig. 2 shows electron micrograph of ultrafine cdmium ferrite particles taken by TEM. Either a distribution of particle diameter, volume or number can be obtained form a study of this microscopy. Probability density of ultrafine cadmium ferrite particles measured from this micrograph is shown in Fig. 3 (dot points). The distribution of particles may be fitted to a well-known analytical Gaussian normal distribution. However, it has been recently recognized and confirmed experimentally that the size distribution of ultrafine particles is not normal, but lognormal.[15,16] The lognormal distribution f(ln x) , where x represents diameter of particles, is represented as follows:

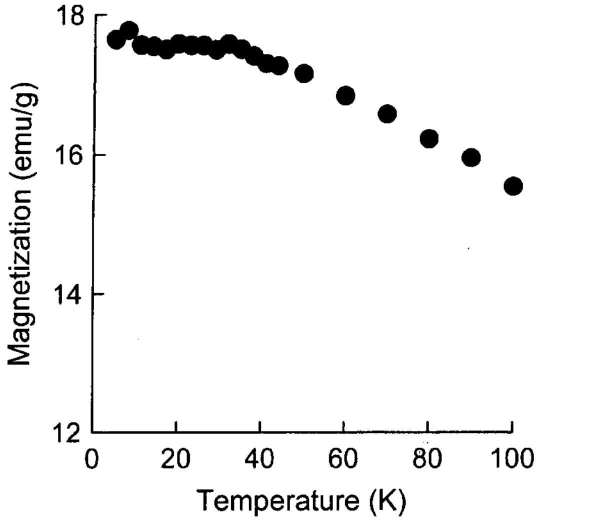

Fig. 4. Temperature dependence of the magnetization obtained in the FC process with applied field H=50 kOe.

$$f(\ln x)\, d(\ln x) = \frac{\exp(-(\ln x - \overline{\ln x})^2/2\sigma^2)}{\sqrt{2\pi}\,\sigma} d \ln x$$

where $\overline{\ln x}$ is the mean of the ln x and σ is the standard deviation of ln x. It follows that

$$f(x)\, d(x) = \frac{\exp(-\ln(x - x_m)^2/2\sigma^2)}{\sqrt{2\pi}\,\sigma x} d\, x$$

where x_m is the median of x and $\overline{\ln x} = \ln (x_m)$.

Fig. 3 shows the least-square fit (solid line) of the above lognormal distribution to the measured points obtained from transmission electron micrographs. From these results, the average particle size was found to be 9.7 nm.

Fig. 4 shows Field-Cooled (FC) magnetization curve with an applied field H=50 kOe. The experimental curve of the sample is different from that of ultrafine cobalt ferrite particles[17] in that the curve of the ultrafine cadmium ferrite particles appears as the plateau of the field-cooled magnetization below 30 K. These features are typical of a transition from a disorder ferrimagnetic phase to a spin-glass phase (i.e. reentrant behavior), with a freezing temperature T_f=30 K.[18] The random cadmium substitution of magnetic ions on A and B sites induced a deterioration of magnetic interactions inside and between the magnetic sub-lattices, and so favors spin-glass state at low temperature.

Fig. 5 illustrates the magnetization curves measured at 5, 100 and 300 K in fields up to 50 kOe. It is evident that the maximal applied field of 50 kOe is not enough to saturate the sample. The maximal magnetizations measured at 5, 100 and 300 K are 17.7, 15.6 and 13.3 emu/g, respectively. These values are smaller than those observed by Yokoyama *et al.*[10] and Chinnasamy *et al.*,[11] but are still larger than those of the bulk material (12 emu/g at 6 K and 4.2 emu/g at 300 K). This enhancement of magnetization in the ultrafine

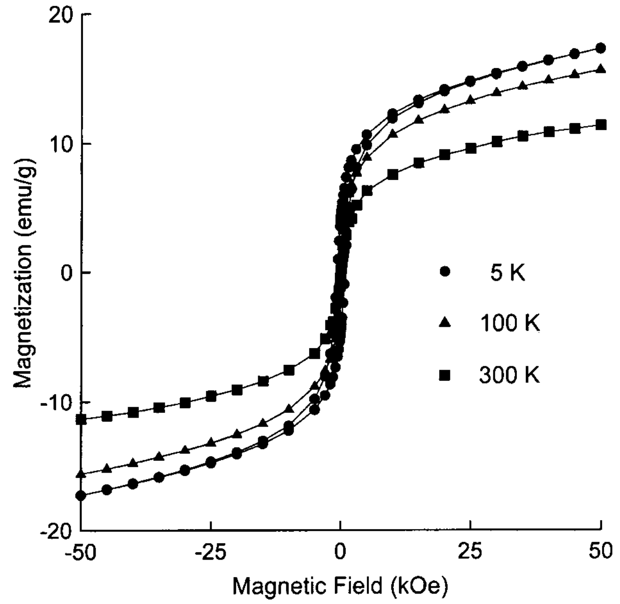

Fig. 5. Magnetization curves measured at 5, 100 and 300 K.

cadmium ferrite particles may be attributed to the magnetic cluster formation caused by the deviation in cation distribution from the normal spinel structure, which is pronounced in restricted geometry.

The present ultrafine cadmium ferrite particles show a typical superparamagnetic behavior. This behavior can be observed from the following aspects[19]:

1. There is no hysteresis; i,e., both the retentivity and coercivity are zero.

2. Magnetization curves measured at different temperatures superimpose when M is plotted as a function of H/T.

In Fig. 5, there is hysteresis for the magnetization curve

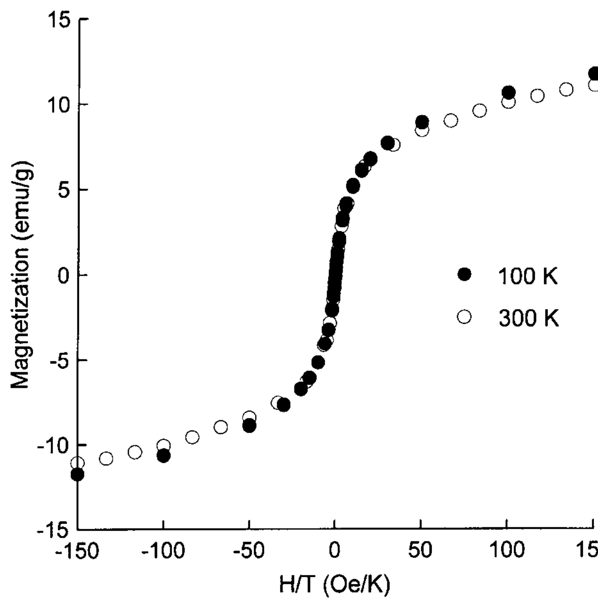

Fig. 6. Magnetization curves measured at 100 and 300 K superimposed when M is plotted as a function of H/T.

measured at 5 K: i.e., both retentivity and coercivity are not zero. This indicates that the particles behave ferrimagnetically at 5 K. But, at 100 and 300 K, the particles do not have enough thermal energy to reach a complete thermal equilibrium with the applied field during the time required for the measurement, and hysteresis does not appear. This suggests that the particles behave superparamagnetically at 100 and 300 K.

Fig. 6 shows the magnetization curves for 100 and 300 K plotted as a function of H/T. Superparamagnetic behavior of the particles can be clearly confirmed by the superimposition of the plots of M vs. H/T for 100 and 300 K. Slight discrepancies between the two curves are known as mainly related to the particle size distribution.[20]

4. Conclusion

Ultranfine cadmium ferrite particles were prepared by the coprecipitation method. All peaks of X-ray diffraction patterns can be attributed to a cubic spinel structure with the lattice constant of 8.65 Å. The average particle size determined by TEM is 9.7 nm and the size distribution of the sample is not normal, but lognormal. The maximal magnetizations measured at 5, 100 and 300 K are 17.3, 15.6 and 13.3 emu/g, respectively. Field-cooled magnetization curve with an applied field H=50 kOe appears as the plateau of the field-cooled magnetization below 30 K. These feature is typical of a transition from a disorder ferrimagnetic phase to a spin-glass phase (i.e. reentrant behavior), with a freezing temperature (T_f) of 30 K. Superparamagnetic behavior of the particles is additionally confirmed by the superimposition of the plots of M vs. H/T for 100 and 300 K.

REFERENCES

1. S. Gangopadhyay, G. C. Hadjipanayis, B. Dale, C. M. Sorensen, K. J. Klabunde, V. Papaefthymiou and A. Kostikas, "Magnetic Properties of Ultrafine Iron Particles," *Phys. Rev. B.*, **45**(17), 9778-9787 (1992).
2. Z. Tianshu, P. Hing, Z. Jiancheng and K. Lingbing, "Ethanol-sensing Characteristics of Cadmium Ferrite Prepared by Chemical Coprecipitation," *Mater. Chem. and Phys.*, **61**, 192-198 (1999).
3. Y. Liu, W. Zhu, M. S. Tse and S. Y. Shen, "Study of a New Alcocho Gas Sensor Made from Ultrafine SnO_2-Fe_2O_3 Powders," *J. Mater. Sci. Lett.*, **14**, 1185-1187 (1995).
4. H. Suo, F. Wu, Q. Wang, G. Liu, F. Qiu, B. Xu and M. Zhao, "Study on Ethanol Sensitivity of Nanocrystalline $La_{0.7}Sr_{0.3}$ FeO_3-based Gas Sensor," *Sens. Actuators, B.*, **45**, 245-249 (1997).
5. A. Chatterjee, D. Das, S. K. Predhan and D. Chakravorty, "Synthesis of Nanocrystalline Nickel-zinc Ferrite by the Sol-gel Method," *J. Magn. Magn. Mater.*, **127**, 214-217 (1993).
6. R. Valenzuela and J. T. S. Irvine, "Domain Wall Relaxation Freqency and Magnetocrystalline Aanisotropy Constant in Ni-Zn Ferrites," *J. Magn. Magn. Mater.*, **160**, 368-387 (1996).
7. X. Y. Li, G. X. Lu and S. B. Li. "Synthesis and Characterization of Fine Particle $ZnFe_2O_4$ Powders by a Low Temperature Method," *J. Alloys Compounds*, **235**, 150-155 (1996).
8. M. Yokoyama, T. Sato, E. Ohta, T. Sato and M. Seki, "Preparation and Magnetic Properties of Cadmium," *Proc. 6th Int. Conf. Ferrites*, The Japan Society of Powder and Powder Metallurgy, 988-990 (1992).
9. Z. Tianshu, P. Hing, Z. Jiancheng and K. Lingbing, "Ethanol-sensing Characteristics of Cadmium Ferrite Prepared by Chemical Coprecipitation," *Mater. Chem. and Phys.*, **61**, 192-198 (1999).
10. M. Yokoyama, E. Ohta, T. Sato and T. Sato, "Magnetic Properties of Ultrafine Paricles and Bulk Material of Cadmium Ferrite," *J. Magn. Magn. Mater.*, **183**, 173-180 (1998).
11. C. N. Chinnasaly, A. Narayanasamy, N. Ponpandian, R. J. Joseyphus, K. Chattopadhyay, K. Shinoda, B. Jeyadevan, K. Tohji, K. Nakatsuka, H. Gureault and J-M. Greneche, "Structure and Magnetic Properties of Nanocrystalline Ferrimagnetic $CdFe_2O_4$ Spinel," *Scripta Mater.*, **44**, 1411-1415 (2001).
12. E. Wolska, W. Wolski, J. Kaczmarek, R. Riedel and D. Prick, "Defect Stuctures un Cadmium-nickel Ferrties," *Solid State Ionics*, **51**, 231-236 (1992).
13. M. Yokoyama, T. Sato, E. Ohta and T. Sato, "Magnetization of Cadmium Prepared by Coprecipitation," *J. Appl. Phys.*, **80**(2), 1015-1019 (1996).
14. V. Sepelak, K. Tkacova and A. I. Rykov, "Rietveld Analysis of Mechanically Activated Powdered Zinc Ferrite," *Crystal. Res. Tech.*, **28**, 53-59 (1993).
15. J. Popplewell and L. Sakhnini, "The Dependence of the Physical and Magnetic Properties of Magnetic Fluids and Particle Size," *J. Magn. Magn. Mater.*, **149**, 72-78 (1995).
16. R. V. Upadhyay, K. J. Davies, S. Wells and S. W. Charles, "Preparation and Characterisation of Ultra-fine $MnFe_2O_4$ and $Mn_xFe_{1-x}O_4$ Spinel Systems: II. Magnetic Fluids," *J. Magn. Magn. Mater.*, **139**, 249-254 (1995).
17. Y. Ahn, E. J. Choi, S. Kim and H. N. Ok, "Magnetization and Mössbauer Study of Cobalt Ferrite Paricles from Nanophase Cobalt Iron Carbonate," *Mater. Lett.*, **50**, 47-52 (2001).
18. I. A. Campbell, H. Hurdequint and F. Hippert, "Observation of the Volume Discontinuity in the Insulator-to-metal Transition in CsI in X-ray Diffraction Experiments," *Phys. Rev. B*, **33**, 3540-3542 (1986).
19. B. D. Cullity, *Introduction to magnetic materials*, Addison Wesley, London, 410-413 (1972).
20. Y. Ahn, E. J. Choi and S. Kim, "Crystallographic and Magnetic Properties of Nanocrystalline Cobalt Ferrite Particles," *J. Kor. Ceram.* Soc., **5**(3), 303-305 (1999).