研 究

Hydrothermal Synthesis and Magnetic Properties of Zinc Ferrite Nanocrystals

Katsuhisa Tanaka^{☆1}, Makoto Katsuta^{☆2}, Seisuke Nakashima^{☆1} and Koji Fujita^{☆1}^{☆1}Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510.^{☆2}Department of Chemistry and Materials Technology, Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585.

Received June 23, 2004

SYNOPSIS

Magnetic properties have been examined for zinc ferrite nanocrystals synthesized via hydrothermal reaction. The hydrothermal reaction has been carried out at 200 °C using an aqueous suspension containing zinc hydroxide and iron hydroxide. X-ray diffraction analysis indicates that the resultant specimens are composed of single phase of ZnFe_2O_4 , independent of the reaction time. The size of crystal, which is smaller than 10 nm, is apt to increase as the reaction time is increased, as revealed from transmission electron micrographs as well as linewidth at half maximum of X-ray diffraction lines. A single phase of ZnFe_2O_4 is still observed in X-ray diffraction patterns after heat treatment at 300 °C in air. The present ZnFe_2O_4 nanocrystals exhibit high magnetization even at room temperature. The temperature dependence of magnetization manifests superparamagnetic behavior with a blocking temperature of several tens K under external magnetic field of 500 Oe. The magnetization is apt to decrease with a decrease in temperature below the blocking temperature even when field cooling is carried out, suggesting that there is strong magnetic interaction among nanocrystals so that the magnetization of nanocrystals is oriented randomly with each other.

KEY WORDS

zinc ferrite, nanocrystal, ferrimagnetism, superparamagnetism, hydrothermal synthesis

1 Introduction

A stable phase of zinc ferrite (ZnFe_2O_4) possesses normal spinel structure, because there exists a strong tendency that Zn^{2+} ion prefers tetrahedral coordination in oxide crystals with spinel structure. Hence, Fe^{3+} ions occupy octahedral sites, and the superexchange interaction among Fe^{3+} ions governs magnetic properties of ZnFe_2O_4 . Since this superexchange interaction works at the bond angle of 90°, the magnetic interaction among Fe^{3+} ions in the ZnFe_2O_4 with normal spinel structure is rather weak. In addition, the sign of this superexchange interaction is negative. Consequently, the ZnFe_2O_4 manifests antiferromagnetic properties with Néel temperature of 10 K or so.

In contrast, a metastable phase of ZnFe_2O_4 is known to exhibit curious magnetic properties. For instance, Pavljukhin et al.¹⁾ reported that magnetic order is observed at temperature much higher than the Néel temperature, e.g., at 78 K, for ZnFe_2O_4 fine particle derived by mechanical pulverization of bulk ZnFe_2O_4 crystal. They also demonstrated that only surface region of the fine particles of ZnFe_2O_4 contributes to the magnetic ordering. Chinnasamy et al.²⁾ revealed the relation between magnetic

properties and size of crystal for ZnFe_2O_4 fine particle obtained by mechanical milling. According to them, magnetization at 300 K monotonically increases with a decrease in size of crystal from 90 to 11 nm. Also, a fine particle of ZnFe_2O_4 crystal synthesized via co-precipitation method exhibits high magnetization at room temperature as well^{3,4)}. The magnetization at 4.2 K was reported to increase with a decrease in size of crystal down to 8 nm⁴⁾. Tanaka et al. reported that high magnetization at room temperature is observed for ZnFe_2O_4 crystal prepared by a rapidly quenching method using a twin-roller^{5,6)}. For these ZnFe_2O_4 crystals, some of the tetrahedral sites are occupied by Fe^{3+} as well as Zn^{2+} ions. Subsequently, there exists strong superexchange interaction between Fe^{3+} ions in tetrahedral and octahedral sites, leading to ferrimagnetic properties accompanied by high magnetization at room temperature. Previous studies using extended X-ray absorption fine structure (EXAFS) measurements confirmed that some of the Zn^{2+} ions occupy octahedral sites in addition to normal tetrahedral sites^{7,8)}.

Hydrothermal synthesis, through which a material in solid-state is fabricated in a liquid medium under a high

pressure like 10 atm or so, is useful to prepare a crystal possessing a diameter of several nanometers. The hydrothermal synthesis has been utilized for the preparation of ferrites including ZnFe_2O_4 ⁹⁻¹¹⁾. Nonetheless, the ferrimagnetic properties of ZnFe_2O_4 nanocrystal derived by hydrothermal synthesis has been little focused. In the present investigation, we have hydrothermally synthesized ZnFe_2O_4 nanocrystals, and examined magnetic properties of the resultant specimens. We demonstrate that the ZnFe_2O_4 nanocrystal hydrothermally synthesized exhibits high magnetization even at room temperature.

2 Experimental procedure

2.1 Preparation of specimens

Nanocrystalline ZnFe_2O_4 was synthesized via hydrothermal reaction as mentioned above. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as starting materials. They were weighed so that the molar ratio of Zn to Fe was 1 : 2, and dissolved in water. Then, $\text{NH}_3(\text{aq})$ was added to adjust the pH of the solution to be 9.0. At this step, precipitation was observed. The resultant aqueous solution containing the precipitate was subjected to hydrothermal reaction in an autoclave. After the solution with the precipitate was kept at 100 °C for 40 min in the autoclave, the temperature was raised to 200 °C, at which the hydrothermal reaction proceeded. The reaction time was varied from 1 to 24 h. After the reaction, precipitate formed in the solution was filtrated and dried at 120 °C for 2 h. Some of the specimens thus obtained were heat-treated at 300 °C for 10 min in air. Both as-prepared and heat-treated specimens were subjected to measurements of magnetization.

2.2. Measurements

X-ray diffraction analysis with $\text{CuK}\alpha$ radiation (Rigaku RINT2500V) was carried out for resultant specimens to identify crystalline phase. Lattice constant was calculated from the positions of diffraction lines, and size of crystal was evaluated from linewidth at half maximum of the lines using Scherrer's equation. Transmission electron microscopy (JEOL JEM2010) was performed to examine morphology as well as size of crystal for the specimens.

Measurements of magnetization were carried out for powder specimens of about 0.1 g using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS). Room temperature magnetization was measured at an external magnetic field applied up to 1 T. Temperature dependence of magnetization was also explored at 300 K to 5 K. Both field cooling and zero-field cooling were performed.

3 Results

Fig. 1 (a) and (b) show X-ray diffraction patterns for as-prepared and heat-treated specimens, respectively. The values in the figures denote the reaction time; 0 h in Fig. 1 (a) corresponds to the precipitate before hydrothermal reaction, which manifests halo pattern characteristic of amorphous state. All the specimens obtained by the hydrothermal reaction and the heat-treated specimens exhibit diffraction lines all of which are assigned to spinel-type ZnFe_2O_4 . In other words, a single phase of ZnFe_2O_4 is precipitated under all the preparation conditions except the case that the amorphous phase is obtained before hydrothermal reaction and heat treatment. The lattice constant evaluated from the position of diffraction lines is summarized along with the value in the literature (JCPDS card) in Table 1. It is clear that the lattice constant of the present specimens is almost coincident with the value for ZnFe_2O_4 reported previously. It should be noted that the lattice constant for specimens obtained by hydrothermal synthesis for shorter reaction time contains more significant error because the intensity of X-ray diffraction lines is so low and the linewidth is so broad for those specimens as indicated in Fig. 1. Fig. 2 shows size of crystal estimated using Scherrer's equation from the linewidth at half maximum of the diffraction lines. The size of the crystal depends on the preparation condition; it is apt to increase with an increase in reaction time. The size of the crystal lies in a range of 3 to 10 nm. These values are in agreement with those estimated from transmission electron microscopy (TEM). As an example, transmission electron micrograph of the as-prepared specimen after hydrothermal reaction for 24 h is shown in Fig. 3. The size of crystal is roughly estimated to be 5 to 10 nm, coincident with the results of X-ray diffraction analysis. A similar result was obtained for the other specimens.

Room temperature magnetization as a function of external magnetic field is shown for as-prepared and heat-treated specimens in Figs. 4 and 5, respectively. The values in the figures represent hydrothermal reaction time. The as-prepared specimen indicated by 0 h, which is the precipitate before hydrothermal reaction and is amorphous as mentioned above, manifests a small magnetization even at 1 T. In addition, the magnetization varies almost linearly with magnetic field. For the other specimens, the magnetization tends to be slightly saturated at a high magnetic field. The magnetization is apt to increase after heat treatment. This tendency is more evident for specimens synthesized for shorter reaction time. In particular, the magnetization of the specimen indicated by

Fig.1 X-ray diffraction patterns for (a) as-prepared and (b) heat-treated specimens. The values in the figures represent the reaction time. The reaction time of 0 h denotes the specimen before hydrothermal reaction.

Table 1 Lattice constant of ZnFe_2O_4 obtained via hydrothermal reaction and heat-treatment after the reaction

Hydrothermal reaction time (h)	Lattice constant (nm)	
	As-prepared	Heat-treated
1	0.8451	0.8448
2	0.8444	0.8391
4	0.8442	0.8437
8	0.8444	0.8445
12	0.8437	0.8440
24	0.8445	0.8428
ZnFe_2O_4 (JCPDS card)	0.8441	

0 h is drastically increased by the heat treatment. The magnetization at 1 T is 10 emu/g or so for heat-treated specimens.

Temperature dependence of magnetization is shown in Fig. 6 for the specimen prepared by hydrothermal synthesis for 0 h and heat treatment at 300 °C. Open and closed circles denote the field cooling and zero-field cooling, respectively. The zero-field cooling manifests a maximum of magnetization at around 66 K, although a plateau is

Fig.2 Relation between hydrothermal reaction time and size of ZnFe_2O_4 crystal obtained via hydrothermal reaction and heat-treatment after the reaction. Open triangles and closed squares denote as-prepared and heat-treated specimens, respectively.

Fig.3 Transmission electron micrograph of as-prepared ZnFe_2O_4 . The hydrothermal reaction time is 24 h.

Fig.4 Dependence of magnetization on external magnetic field at room temperature for as-prepared ZnFe_2O_4 nanocrystals. The values in the figure denote hydrothermal reaction time.

observed in a temperature range from 50 to 80 K. Below this temperature range, the magnetization drastically decreases with a decrease in temperature. In contrast, the magnetization is almost constant below this temperature range when field cooling is carried out. Fig. 7 shows

Fig.5 Dependence of magnetization on external magnetic field at room temperature for heat-treated ZnFe_2O_4 nanocrystals. The values in the figure denote hydrothermal reaction time.

Fig.6 Dependence of magnetization on temperature for ZnFe_2O_4 nanocrystal prepared by hydrothermal reaction for 0 h and heat treatment at 300°C . Open and closed circles represent the field cooling and zero-field cooling, respectively. The external magnetic field is 500 Oe.

temperature dependence of magnetization for the specimen prepared by hydrothermal synthesis for 24 h and heat treatment at 300°C . Open and closed circles denote the

Fig. 7 Dependence of magnetization on temperature for ZnFe_2O_4 nanocrystal prepared by hydrothermal reaction for 24 h and heat treatment at 300°C . Open and closed circles represent the field cooling and zero-field cooling, respectively. The external magnetic field is 500 Oe.

field cooling and zero-field cooling, respectively. The change of magnetization with temperature is similar to the behavior observed in Fig. 6, although the magnetization decreases with a decrease in temperature below the temperature of maximum magnetization even when the field cooling is performed.

Fig. 8 shows temperature dependence of magnetization for the specimen prepared by hydrothermal synthesis for 1 h and heat treatment at 300°C . Both field cooling and zero-field cooling were carried out at varied external magnetic field of 50 to 1500 Oe. In this figure, open triangles, closed triangles, open circles, and closed circles denote the data obtained under the external field of 50, 250, 500, and 1500 Oe, respectively. The temperature of maximum magnetization observed in the zero-field cooling is decreased as the external magnetic field is increased.

4 Discussion

As revealed by X-ray diffraction analysis and TEM observation, single phase of ZnFe_2O_4 crystal the size of which was several nanometers to 10 nm was obtained via hydrothermal reaction and heat-treatment after the reaction. In addition, it is clear that these ZnFe_2O_4 nanocrystals exhibit ferrimagnetic or strictly speaking, superparamagnetic behavior at room temperature as found in the relation between magnetization and external magnetic field. The

Fig. 8 Dependence of magnetization on temperature for ZnFe_2O_4 nanocrystal prepared by hydrothermal reaction for 1 h and heat treatment at 300°C . Both field cooling and zero-field cooling were performed. Open triangles, closed triangles, open circles, and closed circles correspond to external fields of 50, 250, 500, and 1500 Oe, respectively.

Fig. 9 Relationship between room temperature magnetization at 1 T and size of crystal for as-prepared (open circles) and heat-treated (closed circles) ZnFe_2O_4 nanocrystals.

magnetization at 1 T lies in a range of about 5 to 10 emu/g depending on the synthesis condition. Fig. 9 shows relationship between room temperature magnetization at 1 T and size of crystal for as-prepared and heat-treated specimens. For both as-prepared and heat-treated

Fig.10 Dependence of inverse magnetization on temperature for ZnFe_2O_4 nanocrystals prepared by hydrothermal reaction for 0 h and heat treatment at 300°C (open circles) and prepared by hydrothermal reaction for 24 h and heat treatment at 300°C (closed circles).

specimens, the magnetization takes a maximum when the size of crystal is 4 nm, and decreases with an increase in size of crystal above 4 nm. A similar tendency, i.e., the behavior that the magnetization increases, takes a maximum, and then decreases as the size of crystal increases was observed for nanocrystalline ZnFe_2O_4 prepared by co-precipitation method^{3,4)}. For the ZnFe_2O_4 derived by the co-precipitation method, the magnetization at 4.2 K manifests a maximum when the size of crystal is 8 nm⁴⁾. This behavior is explainable in terms of metastable ferrimagnetic structure characteristic of nanocrystal as well as superparamagnetism. When the size of crystal is very small, superparamagnetism is dominant, leading to a decrease in magnetization. On the other hand, the structure of ZnFe_2O_4 is converted from metastable to stable phase as the size of crystal is increased. Namely, the magnetic structure where antiferromagnetism is stable is preferred in a crystal of larger size.

In Fig. 9, the magnetization for as-prepared specimen is smaller than that for heat-treated specimen when the size of crystal is small (see the data for 3 and 4 nm). This is simply because the as-prepared specimen of smaller crystallite size includes amorphous hydroxides which reduce magnetization. In fact, thermogravimetric analysis in air for as-prepared specimens with smaller crystallite size, i.e., specimens hydrothermally synthesized for shorter

reaction time manifests a drastic weight loss at around 300°C . This is due to the conversion of amorphous hydroxides of zinc and iron into ZnFe_2O_4 accompanied by removal of H_2O . Since the magnetization in Fig. 9 is the value per mass (weight), the inclusion of amorphous phase which is not ferrimagnetic and is the origin for the removal of H_2O drastically reduces the magnetization.

The temperature dependence of magnetization shown in Figs. 6 to 8 also indicates that the present ZnFe_2O_4 nanocrystals exhibit magnetic behavior different than that observed for bulk ZnFe_2O_4 with the normal spinel structure. Magnetic transition reflected by the maximum of magnetization is observed at around 66 and 32 K for the specimens obtained by heat-treatment after hydrothermal reaction for 0 and 24 h, respectively. The relation between inverse magnetization and temperature for these two specimens is shown in Fig. 10. Clearly, the relationship can not be described in terms of the Curie-Weiss law, suggesting that the magnetic structure above the magnetic transition temperature is not paramagnetic but superparamagnetic. This magnetic structure is naturally expected considering that the size of the ZnFe_2O_4 crystal lies in a range of several nanometers.

The magnetic transition at which maximum magnetization is observed can be depicted in terms of the magnetic structure for an assemblage of superparamagnetic nanocrystals. As shown in Figs. 6 and 7, the magnetization tends to decrease with a decrease in temperature below the magnetic transition temperature, i.e., the superparamagnetic blocking temperature, even when the field cooling is performed. In addition, as revealed in Fig. 8, the superparamagnetic blocking is observed at higher temperature when the external magnetic field is smaller. These facts indicate that magnetic interaction among nanocrystals acts at low temperatures so that the magnetic structure where the magnetization of each of nanocrystals is randomly oriented is frozen. In other words, the interaction among the nanocrystals accompanies the superparamagnetic transition for the present system of assemblage of ZnFe_2O_4 nanocrystals.

5 Conclusion

ZnFe_2O_4 nanocrystals were successfully prepared using hydrothermal synthesis. The size of them is smaller than 10 nm. The present ZnFe_2O_4 nanocrystals exhibit high magnetization even at room temperature, and manifest magnetic transition at several tens K when the external magnetic field of 500 Oe is applied. This phenomenon can be explained in terms of the superparamagnetism of

very small ZnFe_2O_4 crystals among which magnetic interaction is present. The highest magnetization at 1 T is 11 emu/g obtained for nanocrystal the size of which is 4 nm. The magnetization decreases with an increase in size of crystal above 4 nm, indicating that the metastable phase of ZnFe_2O_4 the magnetic structure of which brings about high magnetization is preferred in a smaller crystal.

Acknowledgement

This work was financially supported by Hosokawa Powder Technology Foundation.

References

- 1) Y.T.Pavljukhin, Y.Y.Medikov and V.V.Boldyrev: "Magnetic and Chemical Properties of Mechanically Activated Zinc and Nickel Ferrites", *Mater. Res. Bull.*, **18**(1983)1317-1327.
- 2) C.N.Chinnasamy, A.Narayanasamy, N.Ponpandian, K.Chattopadhyay, H.Guérault and J.-M.Greneche: "Magnetic Properties of Nanostructured Ferrimagnetic Zinc Ferrite", *J. Phys.: Condense. Matter.*, **12**(2000) 7795-7805.
- 3) T.Kamiyama, K.Haneda, T.Sato, S.Ikeda and H.Asano: "Cation Distribution in ZnFe_2O_4 Fine Particles Studied by Neutron", *Solid State Commun.*, **81**(1992)563-566.
- 4) T.Sato, K.Haneda, T.Iijima and M.Seki: "Magnetic Properties of Ultrafine ZnFe_2O_4 Particles", *Ferrites, Proc. Sixth Inter. Conf. On Ferrites, The Japan Society of Powder and Powder Metallurgy, Tokyo and Kyoto*, (1992)984-987.
- 5) K.Tanaka, Y.Nakahara, K.Hirao and N.Soga: "Structure and Magnetic Properties of a Rapidly Quenched Zn-Fe-O System", *J. Magn. Magn. Mater.*, **131**(1994)120-128.
- 6) K.Tanaka, M.Makita, K.Hirao and N.Soga: "Effect of Heat Treatment on Magnetic Properties of Ferrimagnetic Zinc Ferrite Prepared by Rapidly Quenching Method", *J. Magn. Soc. Jpn.*, **22**, Supplement, No.S1 (1998)77-79.
- 7) B.Jeyadevan, K.Tothji and K.Nakatsuka: "Local Structure Analysis of ZnFe_2O_4 by Extended X-Ray Absorption Fine Structure (EXAFS)", *J. Jpn. Soc. Powder Powder Metallurgy*, **41**(1994)109-112.
- 8) K.Tanaka, M.Makita, Y.Shimizugawa, K.Hirao and N.Soga: "Structure and High Magnetization of Rapidly Quenched Zinc Ferrite", *J. Phys. Chem. Solids*, **59**(1998)1611-1618.
- 9) T.Pannaparayil, S.Komarneni, R.Marande and M.Zadarko: "Subdomain Zinc Ferrite Particles: Synthesis and Characterization", *J. Appl. Phys.*, **67**(1990)5509-5511.
- 10) M.A.Vergés, M.Martínez and E.Matičević: "Synthesis and Characterization of Zinc Ferrite Particles Prepared by Hydrothermal Decomposition of Zinc Chelate Solutions", *J. Mater. Res.*, **8**(1993)2916-2920.
- 11) M.Rozman and M.Drofenik: "Hydrothermal Synthesis of Manganese Zinc Ferrites", *J. Am. Ceram. Soc.*, **78**(1995)2449-2455.