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Magnetic properties of nanosized $MnFe_2O_4$ particles

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Abstract

Nanosized $MnFe_2O_4$ particles were prepared by chemical ultrasonic emulsion method. The as-prepared sample was found to be in amorphous state and showed spin-glass behavior at low temperature. The Curie temperature of the annealed sample is 160 K higher than that of the bulk material, which is thought to be due to finite-size scaling and also may be related to a nonequilibrium cation distribution.

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Keywords: Nanostructures; Chemical synthesis; Spin-glass behavior; Finite-size scaling

1. Introduction

Nanosized magnetic particles have attracted much interest not only due to unusual properties different from their corresponding bulk materials, but also from their promising technological applications such as magnetic recording media, ferrofluids, permanent magnets, etc. [1,2]. The general question is what happens to the bulk properties of a macroscopic body as one or more of its dimensions is reduced to atomic size. Of fundamental importance is the ferromagnetic systems or the spin-freezing temperature in spin-glass systems, which in all studies has been found to be significantly lower than in the bulk. Some work has been done on Mn-ferrite particles, where a significant increase in T_c (relative to the bulk value) in particles was found [3,4]. Some claimed that this effect was due to finite-size scaling [3,4] while others attributed it to the particle-size-dependent changes in the cation distribution [5–10]. In this article, we show a more detailed study of the magnetic properties of $MnFe_2O_4$ nanoparticles synthesized by ultrasonic emulsion method.

2. Experimental

Nanosized $MnFe_2O_4$ particles were prepared in water-in-oil (W/O) microemulsions, which composed of water droplets surrounded by a layer of

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surfactant molecules and dispersed in the oil phase. These water droplets can be used as nanopools to control the growth of particles. First, appropriate amounts of aqueous solutions of Mn^{2+} and Fe^{3+} nitride salts were added into proper amounts of dodocal benzene sulfuric acid sodium salt (DBS) solution to generate mixed solution. Then appropriate amounts of toluene were added into the above mixed solution and the W/O microemulsion was generated under continuous stirring. After 10 min stirring, the microemulsion was ultrasonated for half an hour, then appropriate amounts of NaOH were added into it. The acoustic cavitation of ultrasound can make the particles disperse evenly. Finally, $MnFe_2O_4$ sols were formed. By washing and distilling the sols, the sample of $MnFe_2O_4$ nanoparticles coated with DBS was obtained (sample A). The fresh specimen was annealed at 400°C in vacuum with a pressure of 5×10^{-4} Pa for 1 h (sample B).

Structural characterization was performed by X-ray diffraction (XRD, Cu $K_{\alpha 1}$ radiation $\lambda =$ 1.5405 Å). The size and shape of the particles were studied by transmission electron microscopy (TEM). A mean size of the spherical particles was about 5.6 nm for the annealed sample. Magnetization measurements were carried out by using extracting sample magnetometer in the temperature range from 3 to 300 K. A magnetic balance was used to determine the Curie temperature of the particles. All samples were kept in a vacuum of 1×10^{-4} Pa to resist oxidation during the heating process.

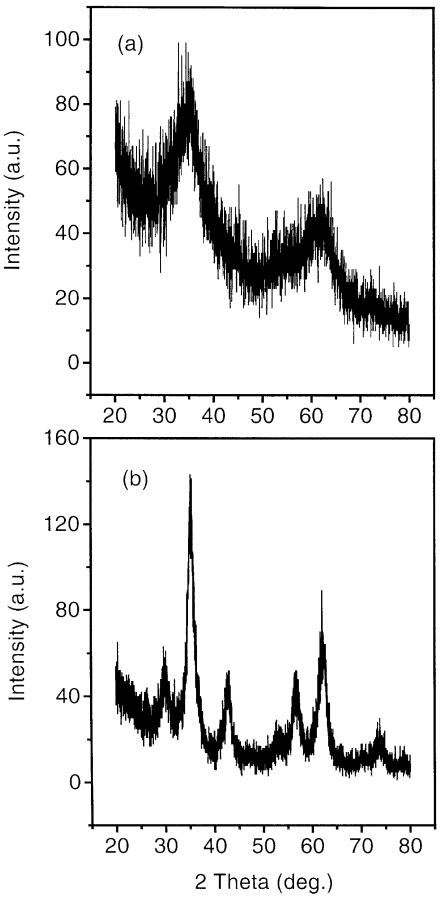

Fig. 1. X-ray-diffraction pattern for as-prepared sample (a) and annealed sample (b).

3. Results and discussion

Fig. 1a and Fig. 1b shows the XRD pattern for samples A and B. It indicates that the as-prepared sample (A) is in an amorphous state while the annealed sample (B) crystallizes well. The pattern of Fig. 1b fits Mn-ferrite well with the lattice constant almost the same as that of bulk $MnFe_2O_4$ given by the ASTM card value (0.856 nm for our sample while 0.85 nm for bulk $MnFe_2O_4$). The Scherrer formula has also been used to determine the crystal size from the width of the XRD (3 1 1) line. The mean size of the particles is about 6.2 nm, which approximately agrees with that obtained by TEM.

Fig. 2 shows the hysteresis loop of samples A and B measured at 1.5 and 300 K, respectively. At 1.5 K, sample A is ferromagnetic with $\sigma_s = 15.27$ emu/g. But it changes to paramagnetic when the temperature reaches 300 K. The DC susceptibility of sample A measured in an applied field of $H = 5000$ Oe is shown in Fig. 3, where the curves correspond to both the zero-field cooled (ZFC) and the field cooled (FC), respectively. Namely, in the case of ZFC operation, the sample was cooled first from 300 to 1.5 K without H, then measured with H, while for the case of FC the measurement was made on heating routing after the sample was

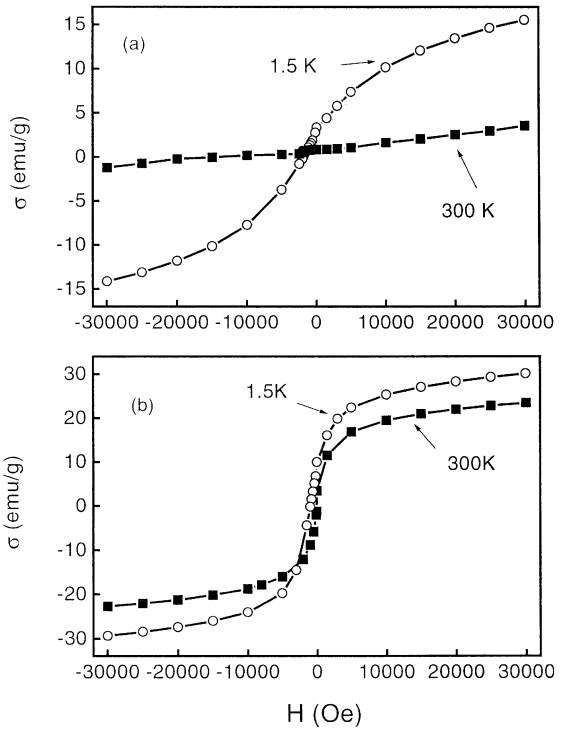

Fig. 2. Magnetization hysteresis loops of as-prepared sample (a) and annealed sample (b), which were measured in 1.5 K (○) and 300 K (■).

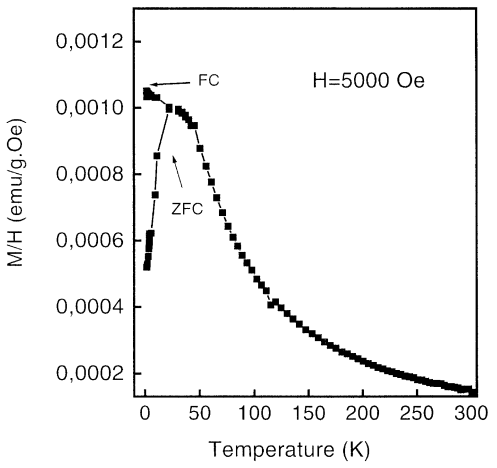

Fig. 3. Direct-current susceptibility of as-prepared $MnFe_2O_4$ particles measured under field-cooling and zero-field-cooling conditions.

cooled from 300 to 1.5 K in H. The DC-susceptibility curve shows spin-glass behavior. The spin-freezing temperature is about 38 K. To our knowledge, this is the first measurement in the nanostructured $MnFe_2O_4$ system. The crystallized sample B is ferromagnetic both at low and room temperature. Its $\sigma_s = 24.4$ emu/g at room temperature is much lower than the bulk value (80 emu/g). The reduced saturation magnetization of $MnFe_2O_4$ particles was also found by Chen and Tang et al. [3,9]. It was explained by a magnetic dead layer on the surface of particles. Assuming the thickness of the dead layer (t) is constant, the magnetization of the particles can be expressed as

$$\sigma_s = \sigma_s(\infty)\left(1 - \frac{6t}{d}\right), \tag{1}$$

where $\sigma_s(\infty) = 80$ emu/g corresponding to the bulk value at room temperature. Fitting the data with $d = 5.6$ nm in Eq. (1), we obtained the thickness of the dead layer which is about 0.6 nm. It is the same as what Chen et al. [9] found. So our data give a further support to the dead-layer theory.

Fig. 4a shows the curve of saturation magnetization versus temperature from 300 to 1173 K for annealed sample B. The magnetization decreases with increasing temperature and reaches zero at about 733 K, corresponding to the Curie temperature. When continuously heated, the magnetization begins to increase and reaches the highest value at 1050 K, then decreases to zero. As for the peak in the high-temperature range, it is due to the segregation of iron. Our sample is covered by a layer of surfactant, the carbonization of the surfactant at high temperature can reduce the iron from the $MnFe_2O_4$ nanoparticles. The sample of nanosized $MnFe_2O_4$ particles without surfactant covering did not show the peak in σ–T curves as shown in Fig. 4b. We measured the high-angle XRD of the sample B after measuring the σ–T, which was shown in Fig. 5. It fits to α-Fe well.

The measured T_c is about 160 K higher than that of bulk material. Tang et al. [3] and Kulkarni et al. [4] also obtained 97 and 47 K rise in Curie temperature of the $MnFe_2O_4$ nanoparticles for $d = 7.5$ and 12 nm, respectively. They described it by the

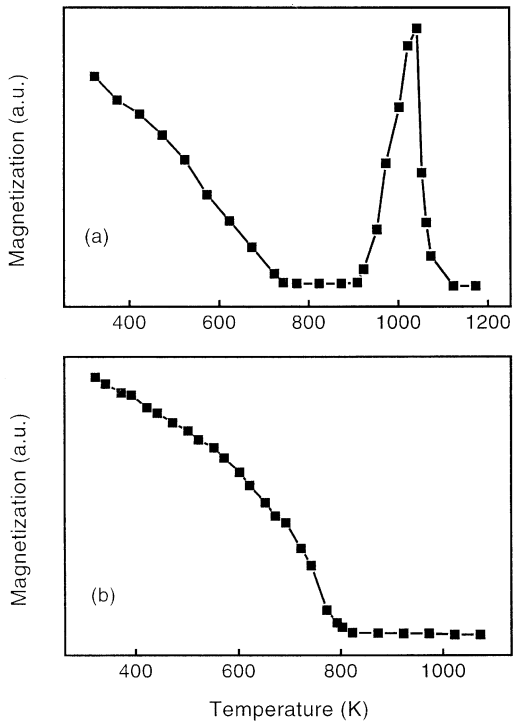

Fig. 4. Magnetization σ versus temperature for annealed $MnFe_2O_4$ particles sample (a) and $MnFe_2O_4$ particles without surfactant covering (b).

finite-size-scaling formula [11]

$$[T_c(d) - T_c(\infty)]T_c^{-1}(\infty) = \pm (d/d_0)^{-\lambda}, \quad (2)$$

where $T_c(\infty) = 573$ K corresponds to the bulk Curie temperature, λ is related to a correlation length exponent and d_0 an order of the characteristic microscopic dimension, respectively. According to the fitting given by Tang et al., $\lambda = 1.42 \pm 0.13$ and $d_0 = 2.0$ nm are deduced. The mean diameter of particles in our $MnFe_2O_4$ sample is 5.6 nm, substituting $d = 5.6$ nm into Eq. (2) and using the above quantities of λ and d_0, the Curie temperature of our sample should be about 152 K higher than the bulk materials. It is close to our experimental data, 160 K. Fig. 6 gives the plot of T_c versus the size of the particles, in which the data of Tang et al. [3], Kulkarni et al. [4] and our data are all put together. The solid line is fitted by Eq. (2) with $\lambda = 1.42 \pm 0.13$ and $d_0 = 2.0$ nm. It seems our data can be fitted well by this formula. However, van der Zaag et al. [5,7] and Brabers [6] suggested that the increase in ordering temperature in this system is more likely to have its source in a redistribution of the iron and manganese cations over the tetrahedral (A) and octahedral (B) crystallographic sites of the spinel structure. More recent research work done by different groups [7–10]

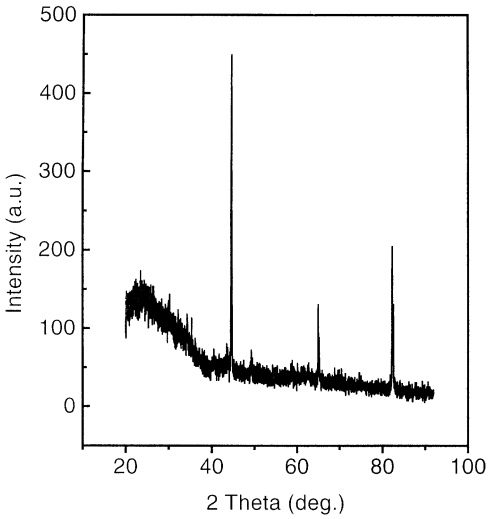

Fig. 5. X-ray-diffraction pattern of annealed sample after measuring σ–T.

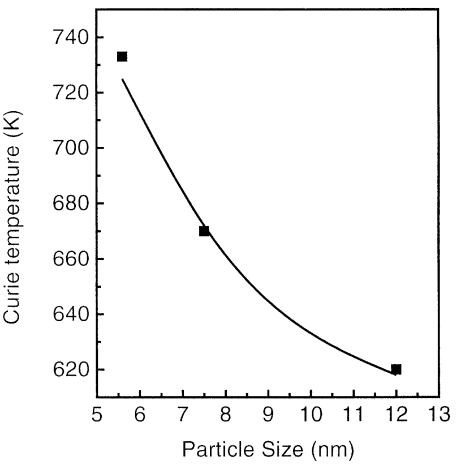

Fig. 6. Curie temperature versus particles diameter. Three data were taken from Refs. [3,4] and our experiment, respectively. Solid line is fitted by Eq. (2) with $\lambda = 1.42$ and $d_0 = 2.0$ nm.

provided more evidence on this point. Morrish et al. [8] measured Mössbauer spectra of $MnFe_2O_4$ with various particle sizes and found the cation distribution on the A and B sites depends on the particle size. They thought the increased ordering temperature is the result of an increased iron occupancy on the A sites. In addition, van der Zaag et al. [7] pointed out that oxidation of Mn^{2+} to Mn^{3+} during the determination of T_c also plays a role. This has been further confirmed by Gillot et al. [10], where thermogravimetry and FTIR spectroscopy studies have demonstrated that a change in the cation distribution takes place at $x \approx 1.50$ in $Mn_{3-x}Fe_xO_4$ fine powders. As the annealing time of our sample is long enough to ensure an equilibrium cation distribution, the 160 K rise in T_c of the annealed $MnFe_2O_4$ particles may also be caused by the cation distribution. Further studies should be done in future.

In summary, we prepared nanosized $MnFe_2O_4$ particles by chemical ultrasonic emulsion method. The as-prepared sample shows spin-glass behavior at low temperature. The Curie temperature of the annealed sample is 160 K higher than that of the bulk material. The finite-size effect and the cation redistribution during heating process may both play a role in it.

Acknowledgements

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