Magnetic properties and Mössbauer studies of nanosized NiFe$_2$O$_4$ particles

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In recent years, nanosized spinel ferrite particles have attracted considerable attentions for their variation of physical and chemical properties markedly different from their bulk counterparts. Quite new and striking magnetic properties have been reported [1–10]. It is well known that spinel ferrites have the general molecular formula $(M_{1-x}Fe_x)[M_xFe_{2-x}]O_4$, where M represents divalent metal, x is inversion parameter, round and square bracket are the cations occupying tetrahedral (A) and octahedral (B) interstitial positions of the fcc lattice formed by oxygen ions. The magnetic properties of these oxides depend on the type of cations and their distribution among the two interstitial positions. ZnFe$_2$O$_4$ is a normal spinel with the Zn^{2+} and Fe^{3+} ions at A and B sites, and it exhibits antiferromagnetic ordering below 10 K. But, when the particle size is reduced to nanometer level, ZnFe$_2$O$_4$ shows magnetic ordering and a large moment that is attributed to the cation redistribution from the normal to the mixed spinel [1–5]. In contrast to ZnFe$_2$O$_4$, NiFe$_2$O$_4$ is an inverse spinel with Ni^{2+} ions at B sites and Fe^{3+} ions equally distributed among A and B sites. Most of the previous studies on NiFe$_2$O$_4$ nanoparticle focused on its magnetic properties and surface effects [8–12], where a core-shell model was proposed to explain the unusual magnetic properties of NiFe$_2$O$_4$ nanoparticles. Only a few reports [6, 7], to the best of our knowledge, elaborate on the cation distribution. Šepelák *et al.* [6] produced NiFe$_2$O$_4$ nanoparticles by high-energy milling coarse powders of high-purity commercial NiFe$_2$O$_4$. Chinnasamy *et al.* [7] have synthesized the nanocrystalline NiFe$_2$O$_4$ by conventional ceramic method followed by a ball milling process. High-energy milling was taken as an important reason to induce a redistribution of cations between A and B sites. In order to gain insight into the effect of various methods of synthesis on the properties of NiFe$_2$O$_4$ nanoparticles, we prepared NiFe$_2$O$_4$ nanoparticle samples by sol–gel method, which has a lower crystallization temperature compared to the ceramic method, and mainly investigated their cation redistribution.

A solution of metallic salts containing Ni^{2+} and Fe^{3+} ions in the ratio of 1:2 was made by dissolving nickel and iron nitrates into a certain amount of deionized water. Polyvinyl alcohol (PVA) was used to make a gel. The aqueous PVA solution was added to the nitrate solution. After stirring for half an hour, the homogeneous solution was put into an oven to be dehydrated at 80 °C. The precursor was calcined for 2 hr at different temperatures to obtain NiFe$_2$O$_4$ nanoparticles with size ranging from 12–110 nm.

X-ray diffraction (XRD) with Cu Kα radiation was used to examine the crystal structure and the phase purity. Room temperature and low field magnetization measurements were made using a vibrating sample magnetometer while low temperature and high field magnetization measurements were made by means of a commercial superconducting quantum interference device (SQUID) magnetometer. The Mössbauer spectra (MS) were recorded in constant acceleration mode with a ^{57}Co in Rh radioactive source. The spectrometer was calibrated using α-Fe.

The X-ray diffraction patterns of nanocrystalline NiFe$_2$O$_4$ powders annealed at different temperatures are shown in Fig. 1. The result shows that the reflections in all the cases are characteristic of the spinel structure without any impurity phases. The increase in sharpness of XRD peaks with increasing heat treatment temperature indicates the growth of crystallite size. Table I shows the calcination temperature, the integrated intensity ratio of (220) and (222) peaks and the average diameter of the crystallites evaluated from the width of the peaks using Scherrer formula. It is noted that the integrated intensity ratio of (220) and (222) peaks apparently decreases with the reduced particle size. In the spinel structure, the integrated intensity of the (220) reflection depends exclusively on the cations occupying the A sites, and the (222) reflection depends on the B site cations only [6]. Thus, the XRD measurements of the variation of the integrated intensity ratio I(220)/I(222) provide information about the variation of cation distribution in the spinel NiFe$_2$O$_4$ of different sizes. However, more quantitative estimates are impossible because the X-ray atomic scattering factors of nickel and iron cations differ insufficiently to allow an accurate evaluation.

Magnetic hysteresis loops for NiFe$_2$O$_4$ particles with different sizes at 300 K are shown in Fig. 2. With the exception of sample 5, all the other samples are not saturated because of the superparamagnetic effect. Fig. 3 shows the hysteresis loops obtained at 2 K after the NiFe$_2$O$_4$ samples were cooled in zero field. The magnetization was improved in comparison with the value at 300 K. Saturation magnetization (M_s) values of 63.3, 50.1, 43.3, 41.2 and 50.8 emu/g, for sample 5 to sample 1, respectively, have been obtained by using the Langevin function [13], by extrapolating the M values to the limit of 1/H = 0. Two values attracted

TABLE I Particle size and intensity ratio of NiFe$_2$O$_4$ samples annealed at different temperatures

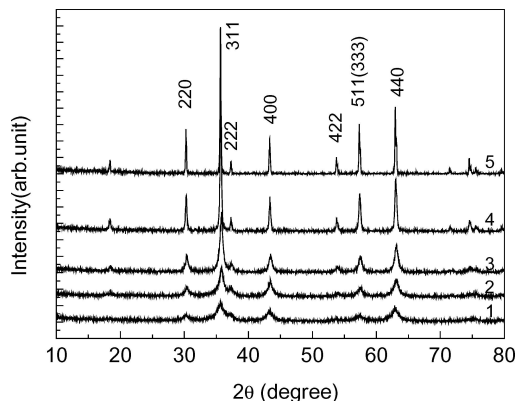| Sample	1	2	3	4	5
T (K)	673	773	823	1073	1373
D (nm)	12	21	24	46	114
I(220)/I(222)	0.8	1.1	2.1	2.9	3.6

Figure 1 XRD patterns of nanocrystalline NiFe$_2$O$_4$ sample 1 to sample 5.
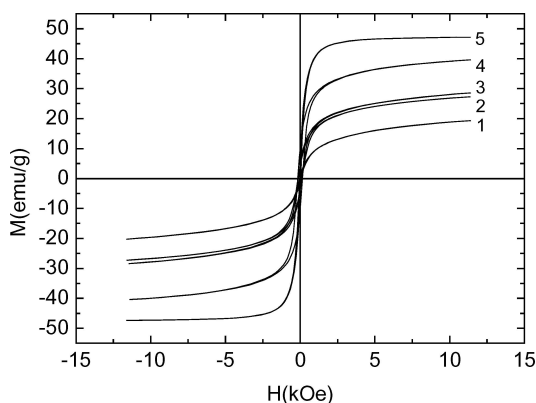
Figure 2 Magnetic hysteresis loops at 300 K for NiFe$_2$O$_4$ samples with different sizes.
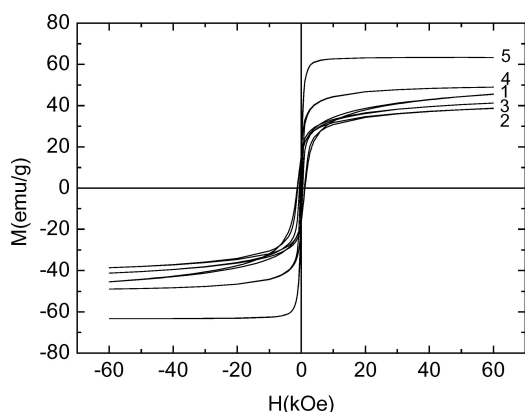

Figure 3 Magnetic hysteresis loops at 2 K for NiFe$_2$O$_4$ samples with different sizes.

our attention: One is the M_s of sample 5 (63.3 emu/g), which is 13% larger than 55 emu/g reported for the bulk NiFe$_2$O$_4$ [14]. The increase in the value of M_s could be understood only if the cation distribution for nanocrystalline NiFe$_2$O$_4$ changes

from the well-known inverse spinel type to a mixed spinel one. In the inverted spinel structure the net magnetization comes from the Ni^{2+} moments in the B sites alone as the Fe^{3+} moments from the A and B sites cancel each other. In the mixed spinel type, Ni^{2+} ions occupy the A sites and hence the net magnetization should be higher than that for the inverse spinel structure as the Ni^{2+} magnetic moment (2 μ_B) is smaller than that of the Fe^{3+} magnetic moment (5 μ_B). The other significant value is 50.8 emu/g, the M_s for sample 1. At room temperature, it is obvious that magnetization decreases monotonously as the particle size decreases due to the superparamagnetic effect. But, at a low temperature of 2 K, sample 1 with the smallest particle size exhibits an anomalous increase in magnetization. This could be explained as follows: at a low temperature 2 K, superparamagnetism is restrained. Two main factors influencing the macroscopic magnetic behavior of nanoparticles are spin disorder in the shell around the core and cation distribution. The former factor reduces the magnetization. The latter increases the net magnetization. As the particle size decreases, both factors contribute strongly to the total magnetization. Which is dominant to the final net magnetization depends on its degree of strength. In our case, when the particle size is larger than 20 nm, the surface effect is the dominant factor, and when the particle size is further reduced, the cation distribution is dominant. It is likely that a large fraction of nickel ions in sample 1 transports from B sites to A sites.

In order to verify the variation of cation distribution discussed above on the basis of macroscopic magnetic measurement, Mössbauer spectra of sample 5 and sample 1 were recorded at 9 K in an applied field of 70 kOe parallel to the direction of gamma rays. As seen in Fig. 4, the outer lines of spectra are resolved, which yields reliable relative intensities for the sextets. Relative population of Fe^{3+} ions on the A sites and B
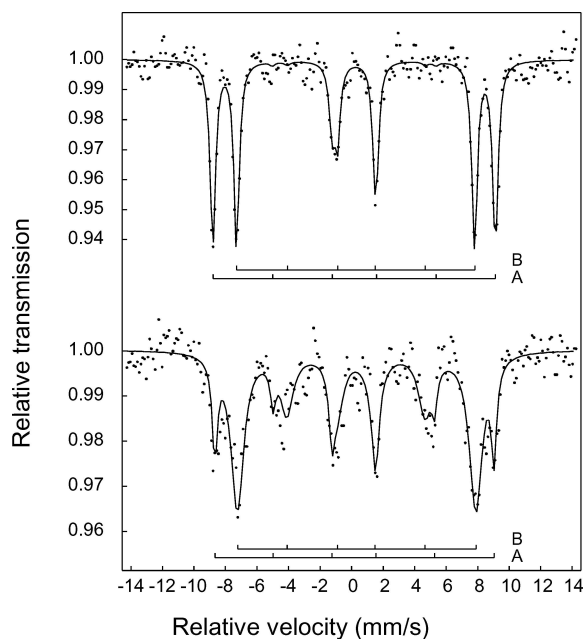

Figure 4 Mössbauer spectra taken in an longitudinal external field of 70 kOe at 9 K for NiFe$_2$O$_4$ sample 5 (top) and sample 1 (bottom).

sites were estimated from the relative intensity of their corresponding subspectrum. For sample 5 and sample 1, the number of Fe^{3+} ions on A and B sites is 49.0 and 51.0, 31.3 and 68.7%, respectively. This means 37.4% of Ni^{2+} ions in sample 1 is likely to occupy A sites, a structure formula like $(Ni_{0.37}Fe_{0.63})[Ni_{0.63}Fe_{1.37}]O_4$ can be obtained. It is evident that the inversion parameter x reduces as the particle size decreases, i.e. there are more Ni^{2+} ions occupying A sites in smaller $NiFe_2O_4$ nanoparticles. This is consistent with the result of magnetization measurement.

In the present study, we have seen the cation redistribution in nanosized nickel spinel ferrite prepared by sol–gel method. This suggests that the evolution of an inverse spinel structure to a mixed spinel structure is size dependent rather than a mechanically induced cation transportation.

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