Sonochemical Preparation and Size-Dependent Properties of Nanostructured $CoFe_2O_4$ Particles

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Nanostructured $CoFe_2O_4$ particles were prepared by a sonochemical approach, first by preparation of the amorphous precursor powders, followed by heat treatment at relatively very low temperatures. The precursor was prepared by sonochemical decomposition of solutions of volatile organic precursors, $Fe(CO)_5$ and $Co(NO)(CO)_3$, in Decalin at 273 K, under an oxygen pressure of 100−150 kPa. The amorphous nature of these particles was confirmed by various techniques, such as scanning and transmission electron microscopy (SEM and TEM), electron microdiffraction, and X-ray diffractograms. Magnetic measurements, Mössbauer, and electron paramagnetic resonance (EPR) spectral studies indicated that the as-prepared amorphous particles were superparamagnetic. The Mössbauer parameters and the significantly low (45 emu/g) observed saturation of magnetization of the annealed sample, compared to that of the bulk sample (72 emu/g), reflected its nanocrystalline nature.

Introduction

Ferrites−the transition metal oxides having a spinel structure−are technologically important because of their interesting magnetic and electrical properties. They are used in magnetic inks[1] and magnetic fluids[2] and for the fabrication of magnetic cores of read/write heads for high-speed digital tapes or for disc recording.[3] Nanostructured materials are now being studied intensively due to their novel physicochemical properties, which are quite different from those of the bulk materials.[4,5] A variety of methods have been used to prepare nanosized ferrite particles. The conventional high-temperature ceramic method for the preparation of ferrites can result in the loss of their fine particle nature. The wet chemical methods include coprecipitation,[6−8] spray drying,[9] and hydrothermal[10] and microemulsion processes.[11,12] The fine ferrite particles are also produced by ball milling, i.e., grinding coarse powders of high-purity bulk material in the presence of kerosene and oleic acid (organic surfactant).[13]

Bulk $CoFe_2O_4$ is a ferrimagnetic material with a partially inverse spinel structure, with the formula $(Co_xFe_{1-x})[Co_{1-x}Fe_{1+x}]$, where the parentheses and square brackets indicate A and B sites, respectively. The site occupancy ratio, Fe(A)/Fe(B), depends on the preparation procedures. They vary from 0.61 to 0.87 for the rapidly quenched and slowly cooled samples.[14] The work on ferrimagnetic materials with sizes less than 10 nm is scanty. Davies et al.[15] have reported the hydrothermal preparation of $CoFe_2O_4$ nanoparticles with sizes of about 3 nm, while Pileni and co-workers[16] have prepared nanoparticles with sizes of about 5 nm by the inverse micellar process. We discuss here a new approach, the sonochemical decomposition method for the preparation of nanostructured (<5 nm) $CoFe_2O_4$ powders. In the sonochemical process, the mechanism is the cavitation phenomenon, and the reaction occurs inside a microbubble equivalent to a microreactor

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(1) Charles, S. W.; Popplewell, J. *Ferromagnetic Materials*; Wolfarth, E. P., Ed.; North-Holland: Amsterdam, 1980; Vol. 2, p 509.
(2) Mehtha, R. V.; Upadhyay, R. V.; Dasanacharya, B. A.; Goyal, P. S.; Rao, K. S. *J. Magn. Magn. Mater.* **1994**, *132*, 153.
(3) Kuliokowski, J.; Lenniewski, A. *J. Magn. Magn. Mater.* **1980**, *19*, 117.
(4) Ozin, G. A. *Adv. Mater.* **1992**, *4*, 612.
(5) Gleiter, H. *Adv. Mater.* **1992**, *4*, 474.
(6) Sui, Y.; Xu, D. P.; Zheng, F. L.; Su, W. H. *J. Appl. Phys.* **1996**, *80* (2), 719.
(7) Morrish, A. H.; Haneda, K. *J. Appl. Phys.* **1981**, *52* (3), 2496.
(8) Bee, A.; Massart, R.; Neveu, S. *J. Magn. Magn. Mater.* **1995**, *149*, 6.
(9) Yu, H.-F.; Gadalla, A. M. *J. Mater. Res.* **1996**, *11* (3), 663.
(10) Pannaparayil, T.; Marande, R.; Komarneni, S. *J. Appl. Phys.* **1991**, *69* (8), 5349.
(11) Moumen, N.; Veillet, P.; Pileni, M. P. *J. Magn. Magn. Mater.* **1995**, *149*, 67.
(12) Kommareddi, N. S.; Tata, M.; John, V. T.; McPherson, G. L.; Herman, M. F.; Lee, Y.-S.; O'Connor, C. J.; Akkara, J. A.; and Kaplan, D. L. *Chem. Mater.* **1996**, *8*, 801.
(13) Kodama, R. H.; Berkowitz, A. E.; McNiff, E. J., Jr.; Foner, S. *Phys. Rev. Lett.* **1996**, *77* (2), 394.
(14) Haneda, K.; Morrish, A. H. *J. Appl. Phys.* **1988**, 63 (8), 4258.
(15) Davies, K. J.; Wells, S.; Upadhyay, S. V.; Charles, S. W.; O'Grady, K.; El Hilo, M.; Meaz, T.; Morup, S. *J. Magn. Magn. Mater.* **1995**, *149*, 14.
(16) Moumen, N.; Bonvilee, P.; Pileni, M. P. *J. Phys. Chem.* **1996**, *100*, 14410.

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(reverse micelles) in the microemulsion technique. Hence, only a small concentration of the reagents is needed. In contrast, in the hydrothermal process, an initial large concentration of reagents is required.

Amorphous materials, obtained by rapid quenching of the melt, have many important applications. Iron-based amorphous oxides exhibiting a ferromagnetic character, with a Curie point higher than room temperature and a relatively high saturation magnetization, are of great importance because of their unique electronic and magnetic properties. They can be used in magnetooptical devices such as optical isolators, optical switches, etc.[17] Amorphous ferrites, in flake form, have been prepared by rapidly quenching the molten mixtures of bulk mother ferrite with one or two kinds of glass formers, such as P_2O_5, V_2O_5, MoO_3, SiO_2, Bi_2O_3, etc., as additives to prevent crystallization.[18,19]

Acoustic cavitation, i.e., the formation, growth, and implosive collapse of a bubble in an ultrasonically irradiated liquid, generates a transient localized hot spot, with an effective temperature of 5000 K and a nanosecond lifetime.[20−22] The rapid cavitational cooling rate ($>10^9$ K s^{-1}) is much greater than that obtained by the conventional melt-spinning technique[23] for the preparation of metallic glasses (10^5-10^6 K s^{-1}). Since the thermal conductivities of metal oxides are usually much lower than are those of the metals, faster cooling rates are needed to prepare amorphous metal oxides. This is the reason glass formers, which can prevent crystallization, are employed during the quenching process. Nanostructured amorphous powders of metal,[24] alloy,[25] metal oxide,[26] and metal nitride[27] have been prepared by the sonochemical method. By use of surfactants such as oleic acid, these nanosized clusters can be trapped as colloids[28] or can be deposited on silica microspheres (Stober's silica).[29]

Experimental Section

Iron pentacarbonyl (Aldrich) was used without further purification. Cobalt tricarbonyl nitrosyl, $Co(CO)_3(NO)$, was prepared by a known method.[30] Pentane (Fluka) and Decalin (Sigma) were dried with sodium metal or a 4 Å molecular sieve.

The $CoFe_2O_4$ was prepared by ultrasonic irradiation of the solution of $Fe(CO)_5$ and $Co(NO)(CO)_3$ in Decalin at 273 K, under 100−150 kPa (1−1.5 atm) of oxygen, with a high-intensity ultrasonic probe (Sonics & Materials, Model VC-600, 1.25-cm Ti horn, 20 kHz, 100 W/cm^2). After 3 h of irradiation, a black powder was obtained, which was then centrifuged and washed with dry pentane. Centrifuging and washing were repeated at least five times, and finally the product was dried under vacuum.

Powder X-ray diffractograms were recorded on a Rigaku X-ray diffractometer (Cu Kα radiation, $\lambda = 0.15418$ nm). Scanning electron micrographs and energy-dispersive X-ray analysis (EDX) were carried out on a JEOL-JSM-840 electron microscope. Transmission electron micrographs were obtained with a JEOL-JEM100SX electron microscope. Magnetization loops were measured at room temperature using an Oxford Instruments vibrating sample magnetometer. Surface area (BET method) was measured on a Micromeritics-Gemini surface area analyzer. Mössbauer spectroscopic studies were carried out using a conventional constant acceleration spectrometer with a 50 mCi ^{57}Co:Rh source and an APD DMX20 closed-cycle refrigerator system for the low-temperature measurements. Variable-temperature ESR spectra were recorded on a Bruker ER 041 spectrometer operating at X-band frequency ($\nu = 9.42$ GHz) with a 100 kHz magnetic field modulation.

Results and Discussion

Ferrite composition was determined by elemental and EDX analyses. Since the atomic numbers of Co and Fe are similar, the ratio of the X-ray intensities from these elements approximates their composition. The intensity ratio of Fe:Co as detected by the EDX is 2:1. Since these particles are much smaller than the free path for X-ray transmission through solids, i.e., 100 nm, the X-ray intensities need not be corrected for absorption and fluorescence effects.

The elemental analysis shows that the amorphous $CoFe_2O_4$ powder has trace amounts of carbon (<3%) impurities. The presence of carbon is presumably a result of the decomposition of alkane solvents or adsorbed CO during ultrasonication, and this probably plays an important role in stabilizing the amorphous structure.[25,26]

The amorphous nature of the particles was confirmed by various techniques, such as scanning and transmission electron microscopy (SEM and TEM), electron microdiffraction, and X-ray diffractograms. A scanning electron micrograph of $CoFe_2O_4$ powder shows coral-like features typical for noncrystalline materials.[31] The TEM images of the as-prepared and heat-treated samples of $CoFe_2O_4$ are shown in Figures 1−3. Figure 1 gives no evidence of crystallite formation and shows that the as-prepared material is composed of agglomerates of nanoparticles with diameters <5 nm. Because most of the particles are aggregated, it is difficult to determine the precise particle size. The TEM microdiffraction pattern (inset) only shows diffuse rings characteristic of amorphous materials. However, Figure 2, the TEM micrograph of the heat-treated sample at 450 °C in air, clearly shows nearly uniform spherical ferrite particles with sizes less than 5 nm. The ED pattern (inset) indicates that these nanoparticles are crystallized. In Figure 3, the well-crystallized particles that are less than 10 nm in size can be clearly seen. The ED pattern shows well-defined rings and spots characteristic of nanocrystalline materials. The XRD pattern for the

(17) Tanaka, K.; Hirao, K.; Soga, N. *J. Appl. Phys.* **1991**, *69* (11), 7752.
(18) Sugimoto, M.; Hiratsuka, N. *J. Magn. Magn. Mater.* **1983**, *31−34*, 1533.
(19) Sugimoto, M.; *J. Magn. Magn. Mater.* **1994**, *133*, 460.
(20) Suslick, K. S. *Science* **1990**, *247*, 1439.
(21) Flint, E. B.; Suslick, K. S. *Science* **1991**, *253*, 1397.
(22) Atchley, A. A.; Crum, L. A. In *Ultrasound, Its Chemical, Physical and Biological Effect*; Suslick, K. S., Ed.; VCH Press: NewYork, 1988.
(23) Greer, A. L. *Science* **1995**, *267*, 1947.
(24) Koltypin, Yu.; Katabi, G.; Cao, X.; Prozorov, R.; Gedanken, A. *J. Non-Cryst. Solids* **1996**, *201*, 159.
(25) Shafi, K. V. P. M.; Gedanken, A.; Goldfarb, R. B.; Felner, I. *J. Appl. Phys.* **1997**, *81* (10), 6901.
(26) Cao, X.; Koltypin, Yu.; Kataby, G.; Prozorov, R.; Gedanken, A. *J. Mater. Res.* **1995**, *10*, 2952.
(27) Koltypin, Yu.; Cao, X.; Prozorov, R.; Balogh, J.; Kaptas, D.; Gedanken, A. *J. Mater. Chem.* **1997**, *7* (*12*), 2453.
(28) Shafi, K. V. P. M.; Prozorov, R.; Gedanken, A. *Adv. Mater.* In press.
(29) Ramesh, S.; Koltypin, Yu.; Prozorov, R.; Gedanken, A. *Chem. Mater.* **1997**, *9*, 546.
(30) Job, R.; Rovang, J. *Synth. React. Inorg. Met.−Org. Chem.* **1976**, *6* (5, 6), 367.
(31) Suslick, K. S.; Choe, S.-B.; Cichowlas, A. A.; Grinstaff, A. A. *Nature* **1991**, *353*, 414.

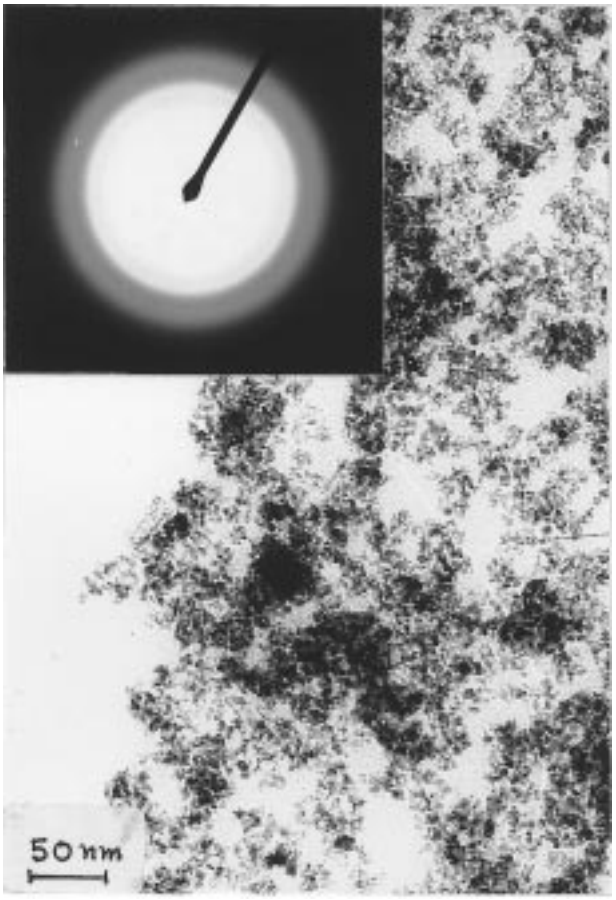

Figure 1. TEM image with microdiffraction (inset) for amorphous $CoFe_2O_4$.

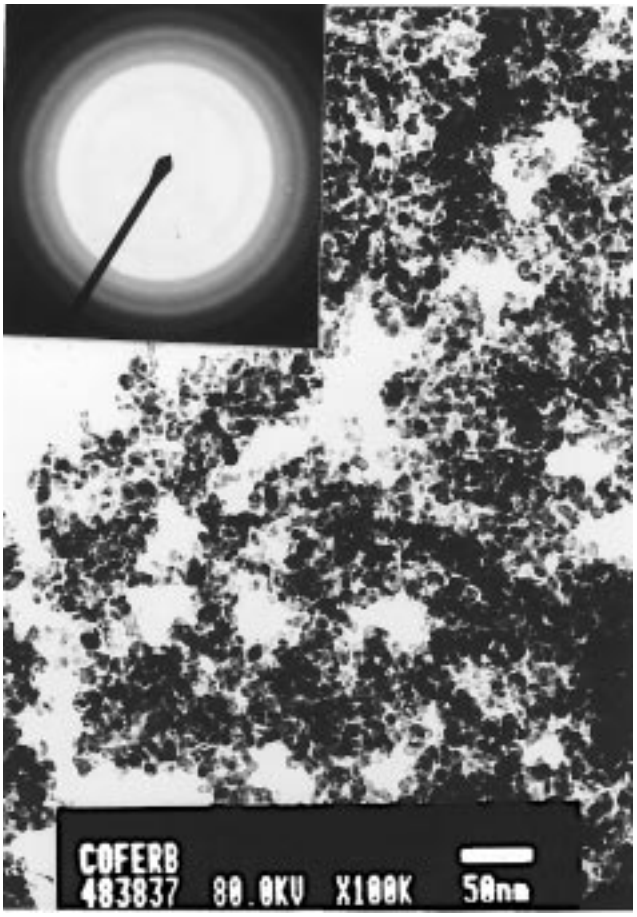

Figure 2. TEM image with microdiffraction (inset) for crystalline $CoFe_2O_4$ annealed at 450 °C.

amorphous as well as the heated samples of $CoFe_2O_4$ are shown in Figure 4. The X-ray diffractogram of the amorphous solid (Figure 4a) does not show any sharp diffraction patterns characteristic of crystalline phases. After heating at 450 °C for 5 h in air to induce crystallization, peaks characteristic of $CoFe_2O_4$ start to appear (Figure 4b). The broad nature of the peaks is an indication of the small particle size. These peaks become narrow and sharp in the XRD of the sample heated at 700 °C (Figure 4c), and the pattern clearly shows that these nanoparticles have a pure spinel structure, with all major peaks matching the standard pattern of bulk $CoFe_2O_4$ (JCPDS 22-1086).

Figure 5 shows room-temperature magnetization curves of the as-prepared amorphous, as well as the annealed, samples of $CoFe_2O_4$, heated for 5 h at 450 and 700 °C, respectively. The curve of the amorphous samples does not reach saturation, even at a magnetic field of 15 kG, and no hysteresis is found, indicating that the as-prepared (amorphous) particles are superparamagnetic. The magnetization (M) vs field (H) curve is not found to be a pure Langevin type, owing to the distribution of particle sizes and the randomly oriented anisotropy axes. The observed values of magnetization of the annealed samples, 22 and 45 emu/g (heated at 450 and 700 °C, respectively), at a high enough field of 15 kG, are significantly lower than that of the reported[14] multidomain bulk $CoFe_2O_4$ materials (72 emu/g), and this reflects the nanocrystalline nature of our sample. The BET surface area of the amorphous sample is 176 $m^2\ g^{-1}$ while those of the annealed samples are 74 and 52 $m^2\ g^{-1}$ for sample heated at 450 and 700 °C, respectively. The decrease in the surface area of the heated sample is due to the increase in particle size because of sintering that occurs on heating. Specifically, the difference in the magnetization value between the bulk and our nanosized materials can be attributed to the small particle size effect. It is known that the magnetic properties of nanoparticles, such as saturation magnetization and magnetic hyperfine field value, are much smaller than are those of the corresponding bulk materials.[24,25,32−34] The energy of a magnetic particle in an external field is proportional to its size or volume via the number of magnetic molecules in a single magnetic domain. When this energy becomes comparable to kT, thermal fluctuations will significantly reduce the total magnetic moment at a given field. Cobalt ferrite, $CoFe_2O_4$, an inverse spinel, has a collinear ferrimagnetic spin structure in the bulk form. The decrease in the saturation magnetization can also be explained in terms of its noncollinear spin arrangement at or near the surface of the particle.[14] Such a noncollinear structure attributed to a surface effect is more

(32) Pannaparayil, T.; Marande, R.; Komarneni, S.; Sankar, S. G. *J. Appl. Phys.* **1988**, *64* (10), 5641.
(33) Morup, S.; Dumesic, J. A.; Topsøe, H. In *Mössbauer Spectroscopy, Applications*; Cohen, R. L., Ed.; Academic Press: New York, 1990; p 1.
(34) Jiang, X.; Stevenson, S. A.; Dumesic, J. A.; Kelly, T. F.; Casper, R. J. *J. Phys. Chem.* **1984**, *88*, 6191.

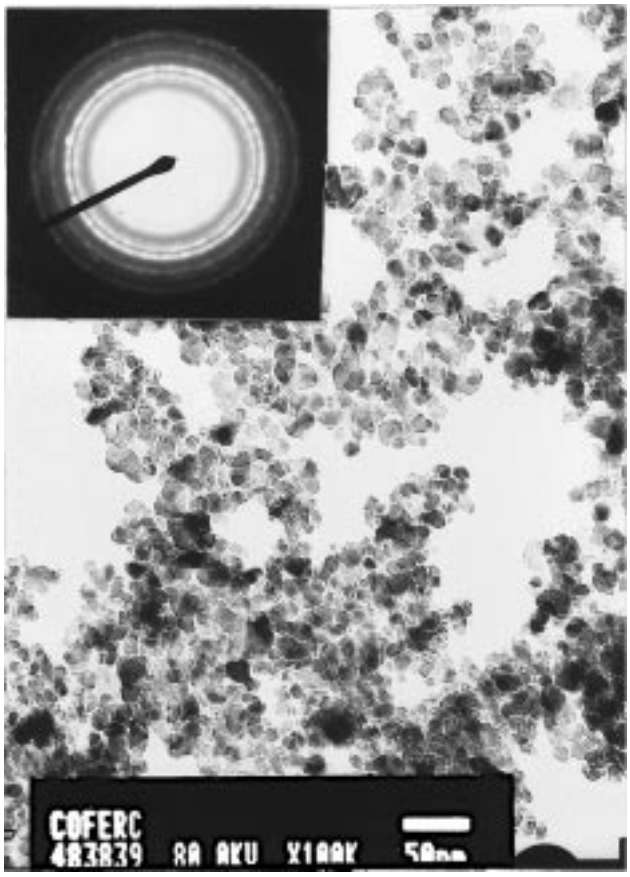

Figure 3. TEM image with microdiffraction (inset) for crystalline $CoFe_2O_4$ annealed at 700 °C.

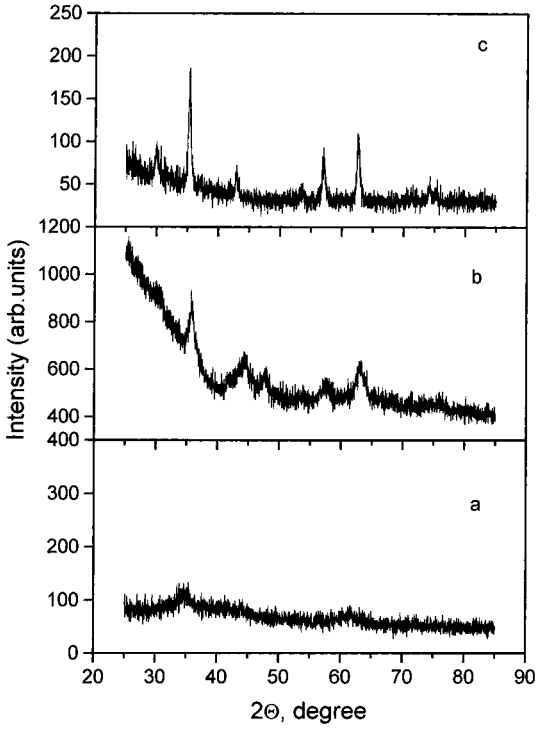

Figure 4. XRD patterns for $CoFe_2O_4$: (a) amorphous, (b) heated at 450 °C, and (c) heated at 700 °C.

pronounced for the smaller particle size of our sample (<10 nm). On the other hand, the difference in magnetization for the two samples annealed at 450 and 700 °C can be attributed to the increase of the particle size

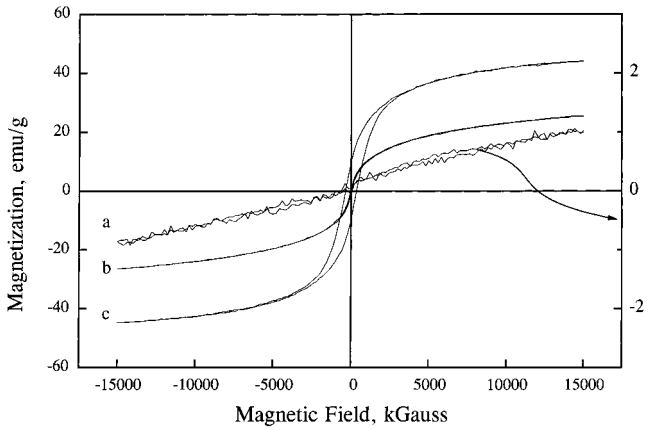

Figure 5. Room-temperature magnetization curves of $CoFe_2O_4$: (a) amorphous, (b) heated at 450 °C, and (c) heated at 700 °C.

for the sample annealed at 700 °C. This can be readily seen by the low value of surface area and the narrow XRD peaks, compared to those of the sample annealed at 450 °C. The presence of small quantities of amorphous impurities in the sample annealed at 450 °C also reduces its total magnetization. The disordered spins in the amorphous system lead to a dispersion in the exchange constant, which can suppress the magnetic moment. The large surface-to-volume ratio for small particles is another factor. The magnetic molecules on the surface lack complete coordination, and the spins are likewise disordered. Finally, the small impurities of metal carbides can also decrease the total magnetization.

Mössbauer spectra of the as-prepared sample and that of the one heat-treated at 450 °C are shown in Figure 6. The room-temperature Mössbauer spectrum of the as-prepared amorphous sample shows a fully paramagnetic state in accordance with the magnetization results. The quadrupole splitting (Q) and the isomer shift (IS) are 0.82 and 0.31 mm/s, respectively. A small fraction of the sample remains superparamagnetic even at 12 K. The paramagnetic component (Q = 0.69 and IS = 0.10 mm/s) has about an 18% area fraction in the spectrum. The magnetic component was fitted by two sextets with hyperfine fields (H) of 42.8 and 47.9 T. These values are significantly lower than those observed in the bulk samples.[14] The broad line width of the magnetic sextets and the reduced hyperfine fields, as compared to the bulk values, can be attributed both to the amorphous structure and to the observed superparamagnetic behavior.[33] The sample heat-treated at 450 °C shows mixed behavior at room temperature. About 18% of the Fe atoms contribute to a magnetically split spectrum (H = 44.5 T), while 36% of the Fe atoms are in a paramagnetic state (Q = 0.88 mm/s, IS = 0.35 mm/s). The rest gives rise to a very broad relaxation-type spectrum. At 77 K, the sample is fully magnetic; however, it is better fitted by a distribution of hyperfine fields than by the two sextets[14] characteristic of bulk $CoFe_2O_4$. If we compare the calculated average hyperfine field (49.4 T) at 77 K and the thermal behavior of the sample to those measured in cobalt ferrite magnetic fluids,[16] it can be concluded that the particle size distribution is in the 3−5 nm range when the sample is heat-treated at 450 °C. This value is in accordance with the TEM results. The low value of the saturation

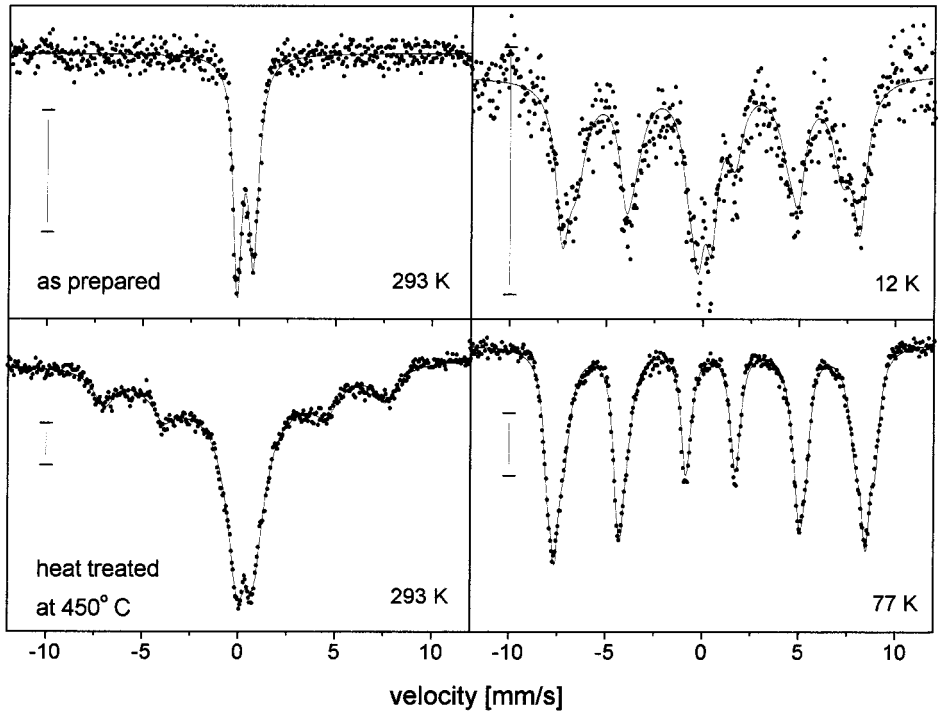

Figure 6. Mössbauer spectra of amorphous $CoFe_2O_4$ sample, measured at 293 and 12 K; and the sample heat-treated at 450 °C, measured at 293 and 77 K. The scale bar indicates the 0.5% relative transmission.

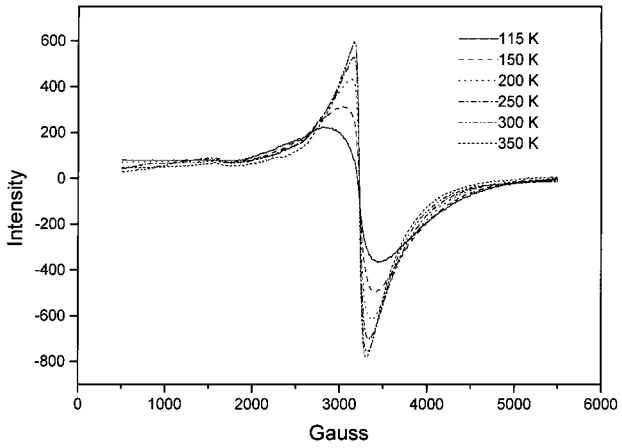

Figure 7. Variable-temperature EPR spectra of as-prepared amorphous particles.

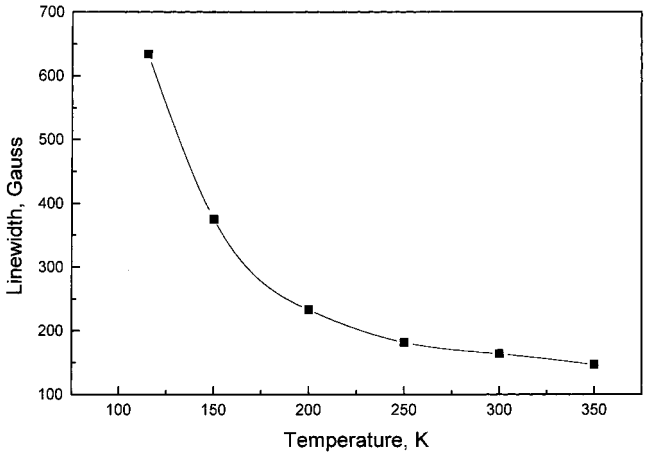

Figure 8. Temperature variation of peak-to-peak derivative line width, ΔH_{pp}, for the observed EPR spectra of the amorphous sample.

magnetization is also in accordance with the Mössbauer results and can be explained mostly by the significant fraction of the sample that is superparamagnetic at room temperature.

Figure 7 shows the variable-temperature EPR spectra of the amorphous sample, heated at 150 °C under high vacuum (2×10^{-5} Torr) for 3 h to remove the adsorbed impurities. The spectra of the heated and unheated amorphous samples looked similar, indicating that the adsorbed impurity does not play any role in the EPR spectrum. The resonance line width, ΔH_{pp} , is defined as peak-to-peak distance, and the effective g-factor is defined experimentally as $h\nu/\beta$H, where ν is the microwave frequency, H is the magnetic field at which the resonance maximum occurs, h is Planck's constant, and β is the Bohr magneton.

The spectrum of the amorphous sample at temperatures of 350 and 300 K shows a very narrow signal, with line width ΔH_{pp} = 153 G and a calculated effective g-value of 2.10. As the temperature decreases, the signal gets broadened, with no shift in the resonance magnetic field. Figure 8 shows the variation of the line width, ΔH_{pp}, with the temperature. The EPR line broadens gradually till 250 K, and below that a sharp increase in line width is observed. Magnetic crystalline anisotropy, in conjunction with the random orientations of the particles, causes line broadening in the FMR spectra of the monodomain ferromagnetic particles. However, for superparamagnetic (spm) particles, whose direction of magnetization fluctuates at a rate faster than the Larmor frequency, this results in a narrow resonance line, due to an averaging effect of this fluctuation on the magnetocrystalline anisotropy. With a decrease in the temperature, the resonance line of the spm particle broadens as the averaging effect of thermal

fluctuations is reduced and the direction of magnetization is blocked, at first in bigger, and progressively in smaller, particles. Thus, the narrow resonance line at room temperature, which progressively broadens on reduction of the temperature, once again confirms the superparamagnetic behavior of the as-prepared, amorphous $CoFe_2O_4$ sample, as noticed earlier by magnetic and Mössbauer studies. The effective *g*-value of 2.10 is in good agreement with that reported for $NiFe_2O_4$.[35] The spectrum of the Fe^{3+}-coupled pair ($Fe^{3+}-O-Fe^{3+}$) in Fe_2O_3 is known to give a resonance line with $g_{eff} = 2.0$. So the effective *g*-value, 2.10, for the as-prepared sample can be attributed to the superexchange interaction between the two sites, Fe^{3+} and Co^{2+}. A weak signal is also observed at about $g = 4.28$, in addition to the intense spectral line centered around $g = 2.10$, which can be ascribed to an isolated Fe^{3+} in the orthorhombic field.[36]

The FMR spectrum of the annealed sample shows an immeasurably broad resonance spectrum. The increased magnetic field produced by the large magnetocrystalline anisotropy, coupled with the strong interparticle interactions is the possible reason for the increased line width for FMR spectra. For ferrimagnetic particles, the intrinsic moments are large ($3.0\mu_B$ for $CoFe_2O_4$), so the magnetic dipolar interactions among these particles are strong.

(35) Shafi, K. V. P. M.; Koltypin, Yu.; Gedanken, A.; Prozarov, R.; Balogh, J.; Lendvai, J.; Felner, I. *J. Phys. Chem. B* **1997**, *101* (33), 6409.

(36) Tanaka, K.; Kamiya, K.; Yoko, T.; Tanabe, S.; Hirao, K.; Soga, N. *J. Non-Cryst. Solids* **1989**, *109*, 289.

Conclusions

Nanostructured $CoFe_2O_4$ particles of a size less than 10 nm were prepared by the new approach, i.e., first preparing the amorphous powders, followed by heat treatment at relatively very low temperatures. The amorphous powder was prepared by sonochemical decomposition of the solutions of volatile organic precursors, $Fe(CO)_5$ and $Co(NO)(CO)_3$, in Decalin at 273 K, under an oxygen pressure of 100−150 kPa. The amorphous nature of these particles was confirmed by various techniques, such as SEM, TEM, electron microdiffraction, and X-ray diffractograms. Magnetic measurements, Mössbauer, and EPR spectral studies indicated that the as-prepared amorphous particles were superparamagnetic. The Mössbauer parameters and the significantly low (45 emu/g) observed saturation of magnetization of the annealed sample, compared to that of the bulk sample (72 emu/g), reflect the ultrafine nature.

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