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Influence of annealing temperature on structural and magnetic properties of $MnFe_2O_4$ nanoparticles

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Abstract. Nanoparticles of manganese ferrite were obtained by the impregnation of highly ordered mesoporous MCM-41 silica support. The investigated sample contained 20% wt. Fe. The obtained nanocrystallites were strongly dispersed in silica matrix and their size was about 2 nm. The sample annealing at 500°C led to increase of particle size to about 5 nm. The Mössbauer spectroscopy investigations performed at room temperature show on occurrence of $MnFe_2O_4$ nanoparticle in superparamagnetic state for the sample annealed in all temperatures. The coexistence of superparamagnetic and ferromagnetic phase was observed at liquid nitrogen temperature. The sample annealed at 400°C and 500°C has bigger manganese ferrite particle and better crystallized structure. One can assign them the discrete hyperfine magnetic field components.

Key words: manganese ferrite • MCM-41 porous silica • Mössbauer effect • superparamagnetic nanoparticles

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Introduction

The design, synthesis, and characterization of nanocomposite materials are the subject of intense research. One of the more interesting and advanced materials dedicated to the creation of modern nanocomposite is mesoporous silica MCM-41. This material discovered by Mobil oil researchers [1] has large surface area often exceeding 1000 m^2/g and uniform pore distribution with diameters changing from 2 to 10 nm depending on method of preparation. This material can be used as a chemically, physically or biologically active-particle carrier. The nanosized particles have huge specific surface area and can be used as highly active catalysts [2, 3]. Sometimes, the physical properties of nanomaterials are essentially different from those of the bulk counterparts and often exhibit new and surprising phenomena. In bulk materials, domain walls are created through minimization of the magnetic stray energy. In small particles with diameters of tens of nanometers and less, each grain may be a magnetic single domain. In this case, the magnetic anisotropy energy is proportional to the volume of the grain, which may give paramagnetic behavior, even if the material is in the magnetic-ordered state, so-called superparamagnetism. Thermal fluctuations cause the direction of magnetization undergoes to random reorientation. The transition from ferro or ferromagnetic to superparamagnetic behavior depends on particle size, temperature, and also timescale used in the chosen instrument for the investigation.

Nanosized manganese ferrites exhibit interesting structural and magnetic properties. They have wide applications, ranging from fundamental research to industrial applications. The possible applications of manganese ferrite nanoparticles are in magnetic storage, as precursors for ferrofluids, contrast-enhancing agents in magnetic resonance imaging (MRI), efficient catalyst for degradation of dye pollutants and magnetically guided drug-delivery agents [4–6].

Manganese ferrite, $MnFe_2O_4$ is one of the magnetic oxides, where oxygen has fcc close packing structure and Mn^{2+} and Fe^{3+} ions can occupy either tetrahedral or octahedral interstitial sites. The spinel ferrite is a very promising candidate for understanding and controlling the magnetic properties of nanoparticles at the atomic level.

The aim of the present study is to determine the influence of annealing temperature on the nanocrystallite size, crystal structure, and magnetic properties of the highly disparaged manganese ferrites nanoparticles supported on the MCM-41 silica mesoporous materials.

Experiment

Highly dispersed manganese ferrites were obtained by the impregnation of mesoporous silica matrix characterized by regular-ordered pores arrangement of 3 nm diameter. The synthesis of silica support MCM-41 was accomplished using the procedure described in [7]. In order to prepare manganese ferrites, alcoholic iron and cobalt nitrate solutions were mixed in constant 2:1 molar ratio and then used for impregnation of the MCM-41 silica material. The sample so prepared contained 20% wt. Fe. The sample was then dried at 423 K for 1 hour and then was annealed in differed temperatures from 100°C to 500°C for 3 hours.

The X-ray diffraction (XRD) and Mössbauer spectroscopy (MS) measurements were performed for the sample annealed at different temperature. XRD patterns were measured by means of a Philips X'Pert PW 3040/60 using diffractometer with CuKα radiation at room temperature. They were fitted using the X'Pert High Score Plus program for Rietveld refinement method.

The ^{57}Fe Mössbauer spectra were measured in transmission geometry at room temperature (RT) and at temperature of liquid nitrogen (LN) using a constant acceleration spectrometer with a $^{57}Co/Rh$ source. The isomer shift (IS) was calibrated against a metallic iron foil at RT.

Results

In order to investigate the influence of annealing temperature on growth process and structural properties of $MnFe_2O_4$ nanoparticles embedded in MCM-41 silica matrix, the XRD measurements were carried out.

The XRD patterns obtained for the $MnFe_2O_4$ in MCM-41 silica at various annealed temperatures

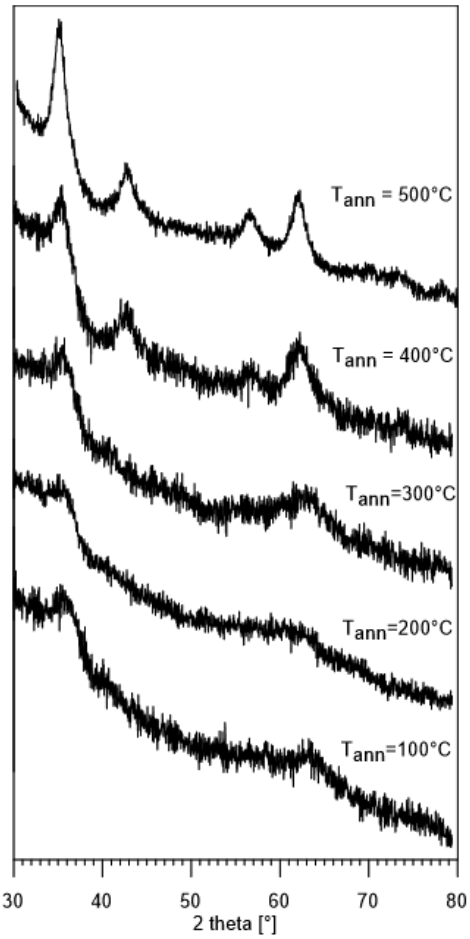

Fig. 1. The XRD diffraction patterns of $MnFe_2O_4$ in MCM-41 silica support annealing at different temperatures. XRD: X-ray diffraction.

are presented in Fig. 1. The pattern obtained for unannealed sample has very broad and hardly visible Bragg reflection. It suggests that the size of manganese ferrite particles is very small and this is on the detection limit of the XRD method.

The average particle diameter (d_{XRD}) was calculated using the Williamson–Hall relation in order to consider the possible contribution from the internal strain [8]

$$\beta_{total} = \beta_{size} + \beta_{strain} = \frac{K\lambda}{d_{XRD}\cos\theta} + 4\eta \cdot \tan\theta$$

where β_{total} is the full width at half-maximum (FWHM) of the XRD peak, K is the Debye–Scherrer constant (~0.94 for spherical nanoparticles), λ is the incident X-ray wavelength, θ is the diffraction angle, and η is the microstrain parameter. The obtained values of crystallites sizes, the microstrain parameter, and lattice constant are presented in Table 1.

The sample annealing up to 300°C causes only slight crystallite growth. The patterns obtained for sample annealed above 300°C have visible diffraction peaks. However, the diffraction lines are very broad in relation to the pattern obtained for the bulk materials.

The XRD measurements show that all peaks of $MnFe_2O_4$ nanocrystallite are consistent with those of standard pattern of manganese ferrite [9].

Table 1. Particle size and lattice constant derived from XRD patterns obtained for of $MnFe_2O_4$ in MCM-41 silica support annealing at different temperatures. XRD: X-ray diffraction

Annealing temperature [°C]	Crystallite size [Å]	Strain [%]	Lattice constant [Å]
100	28.3	0.19	8.37(6)
200	29.0	0.32	8.48(4)
300	29.1	0.33	8.58(4)
400	35.2	0.62	8.44(1)
500	52.1	0.92	8.44(1)

Mössbauer studies were performed in order to study the superparamagnetic nature and some magnetic properties of the manganese ferrite nanoparticles annealing at different temperatures. In the lattice of spinel compound (AB_2O_4), there are two kinds of oxygen polyhedral (octahedron and tetrahedron). Manganese ferrites belong to ferrites with partially inverse spinel structure where both cation sublattices are occupied by manganese and iron. The degree of inversion depends on the preparation method and on thermal treatment [10]. Generally, the Mössbauer spectra should consist of two sets of the sextets related to existence of the ^{57}Fe ions at the two nonequivalent sites. However, as Fig. 2 shows, the Mössbauer spectra recorded at RT for different annealing temperatures consist of only two doublets components with different contributions and quadrupole splitting. The doublet is due to superparamagnetic relaxation of finite size particle. The first doublet (QS1) with lower QS value (0.72 mm/s) corresponds to iron atoms located in core of nanoparticle, the second doublet (QS2) can be the result of free recoil absorption in ^{57}Fe probes located on the surface or close to the surface of nanoparticles. Average value QS2 for annealing sample at different temperatures is equal to about 1.16 mm/s. Although the X-ray measurements show that the increase in annealing temperature leads to the growth of nanocrystallite size, Mössbauer results indicate that all nanocrystallites in sample annealing up to 500°C are in superparamagnetic state.

The Mössbauer spectra of $MnFe_2O_4$ in MCM-41 silica support measured at liquid-nitrogen temperature (LNT) for different annealing temperature are shown in Fig. 3. All patterns can be well fitted by considering the superposition of magnetic and paramagnetic components due to superparamagnetic particles. For the unannealed sample, the area of the doublet is approximately equal to the area of

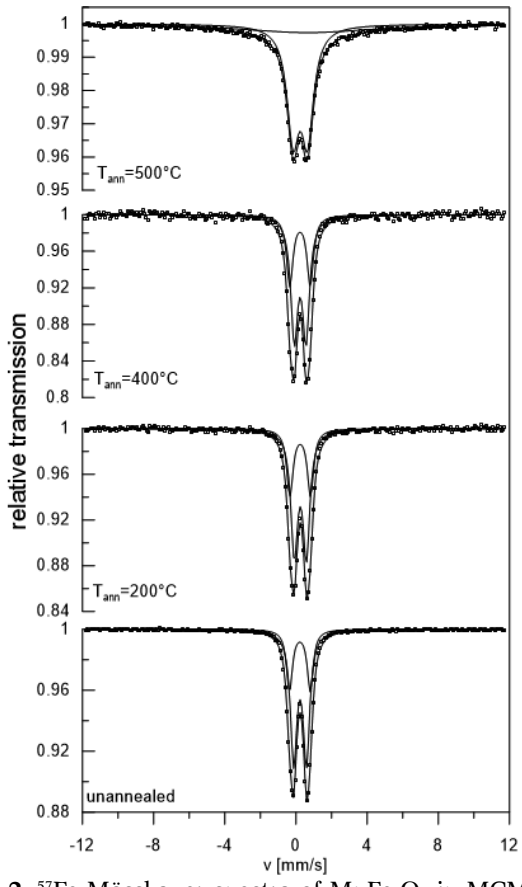

Fig. 2. ^{57}Fe Mössbauer spectra of $MnFe_2O_4$ in MCM-41 silica support measured at RT for different annealing temperature. RT: Room temperature.

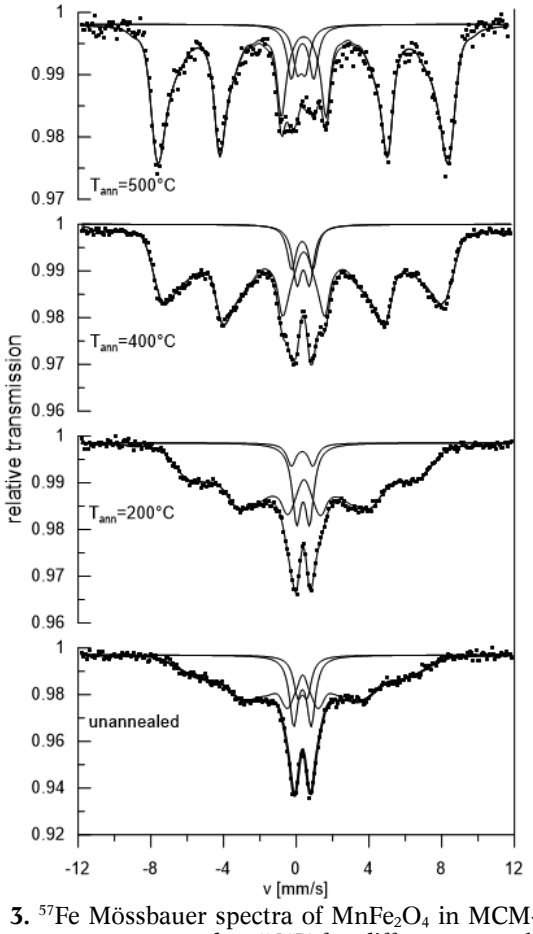

Fig. 3. ^{57}Fe Mössbauer spectra of $MnFe_2O_4$ in MCM-41 silica support measured at LNT for different annealing temperature.

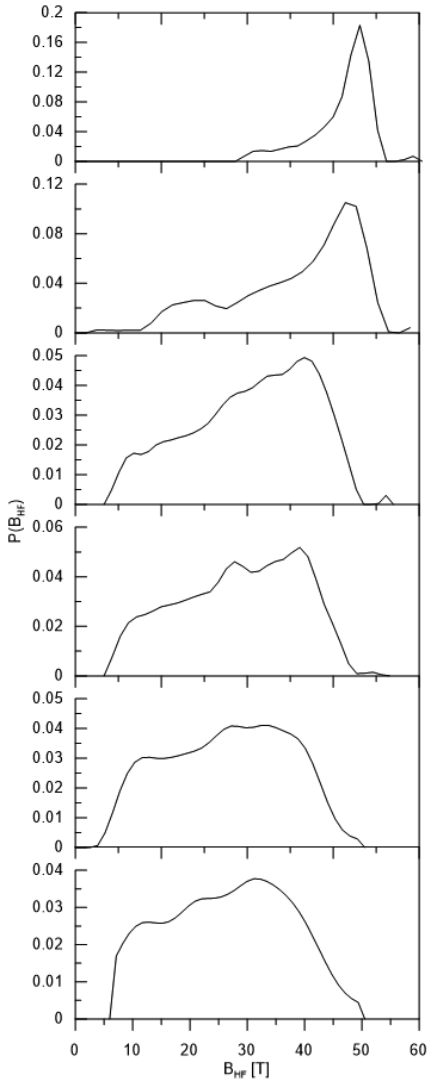

Fig. 4. The hyperfine magnetic field distribution corresponding to the continuous components of the Mössbauer spectra of sample annealing at different temperatures measured at LNT.

the sextet. It shows that half of the magnetic moments fluctuate due to the very small size of these nanoparticles.

The patterns for the unannealed and annealed samples at low temperature (up to 300°C) consist of the absorption lines connected with very narrow and not split sextet. In this case, the magnetic component can be analyzed by means of distribution of hyperfine magnetic field (Fig. 4). The continuous distribution of magnetic field comes from finite size of nanocrystallite. The size of the crystallites in unannealed and annealed sample at low temperature is equal to 3/3.5 lattice constant. The number of atoms located on the surface to the number of atoms located inside the crystallite ratio is very big. The ^{57}Fe atoms located on surface or near the surface have disordered spins due to no completed local surrounding. Moreover, near the blocking temperature, the value of the superparamagnetic relaxation time is close to the nuclear Larmor precession time and spectra with broadened lines are observed [11].

As the nanoparticles mean size increases with the increase in annealing temperature, the area of superparamagnetic doublet disappears at the expense of the sextet area; it can be observed in Fig. 2. This behavior is typical [12] of superparamagnetic relaxation and can be explained in two ways: one based on large particles, which fluctuate slowly (larger anisotropy energy), giving rise to the hyperfine sextet, and the other based on smaller particles (smaller anisotropy energy) with shorter relaxation time, yielding a quadrupole doublet.

The spectra obtained for sample annealed at 400°C and 500°C measured at LNT can be fitted using discrete model with three sextets and two doublets. Two sextets are related to the well-magnetically ordered nanoparticle core and corresponding to Fe atoms at tetrahedral and octahedral site in the spinel structure of the manganese ferrite. The third broad sextet is attributed to the surface shell of disordered spins as a consequence of the incomplete and distorted atomic surrounding at the nanoparticle surface. The hyperfine interaction parameters deduced from the fitting procedure as described above are listed in Table 2.

Conclusions

Ordered mesoporous materials of MCM-41 type can be successfully used as a support for high-density packing of magnetic nanoparticles. The prepared nanocrystallites of manganese ferrites are strongly dispersed in silica pores and exhibit a superparamagnetic behavior. The X-ray measurements show that the increase in annealing temperature leads to the growth of nanocrystallite size from 2.8 to 5.2 nm. This growth is observed in Mössbauer study. The particle of manganese ferrites annealed at 400°C and 500°C possess well-established structure of core-shell type. The atoms in the particle core have complete surrounding. In unequivocal terms, one can assign them the crystallographic position. The atoms located on the surface or near the surface have disordered spins as a consequence of the incomplete and distorted atomic surrounding at the nanoparticle surface. In

Table 2. The hyperfine interactions parameters fitted in the ^{57}Fe Mössbauer spectra of $MnFe_2O_4$ in MCM-41 silica support measured at LNT for sample annealing in temperature equal to 500°C. B – relative subspectra area

	IS [mm/s]	QS [mm/s]	H [T]	Γ [mm/s]	B
Octahedral sites	0.34	0.00	50.1	0.28	0.34
Tetrahedral sites	0.40	0.05	47.6	0.43	0.30
Disordered surface of nanoparticles	0.48	0.02	42.6	0.74	0.25
Superparamagnetic doublet I	0.31	0.32	–	0.32	0.06
Superparamagnetic doublet II	0.31	0.55	–	0.47	0.05

unannealed samples, the contribution coming from the shell atoms is predominant.

The obtained results can help us have a better understanding of the influence of pretreatment conditions and size-dependent on magnetic properties in such magnetic oxides.

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