Mössbauer and magnetic study of CoxFe3–xO4 nanoparticles

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Abstract

Magnetic nanoparticles of cobalt ferrites CoxFe3-xO4 (x=1 or 2) have been obtained either by mechanical milling or thermal treatment of pre-prepared layered double hydroxide carbonate x-LDH–CO3. Mechanical milling of the 1-LDH–CO3 leads to the large-scale preparation of nearly spherical nanoparticles of CoFe2O4, the size of which (5 to 20 nm) is controlled by the treatment time. Core-shell structure with surface spin-canting has been considered for the nanoparticles formed to explain the observed hysteresis loop shift (from ZFC–FC) in the magnetic properties. Annealing treatment of the 2-LDH–CO3 below 673 K results in the formation of nearly spherical pure Co2FeO4 nanoparticles. At 673 K and above, the LDH decomposition leads to the formation of a mixture of both spinels phases Co2FeO4 and CoFe2O4, the amount of the latter increases with annealing temperature. Unusually high magnetic hardness characterized by a 22 kOe coercive field at 1.8 K has been observed, which reflects the high intrinsic anisotropy for Co2FeO4.
Key words CoxFe3-xO4 (x =1, 2) nanoparticles . ferrite spinel . high energy ball-milling . high coercivity . Mössbauer Nano-sized materials are currently of great technological importance and consequently, one of the research subjects under intense investigation for their mechanical, electrical or chemical properties due to the fact that the properties of the nanophases being very different from those of the bulk material. Nanoparticles of materials are likely to improve dramatically the properties of the resulting material. Consequently, the synthesis of spinel ferrite nanoparticles has been intensively studied in recent years due to their potential application in high-density magnetic recording, microwave devices and magnetic fluids.

2 Experimental

Cobalt ferrite powders (CoxFe3-xO4, x=1 or 2) were prepared from co-precipitation of layered iron–cobalt hydroxide carbonates x-LDH–CO3, by high-energy ball-milling or annealing thermal treatment. The starting materials used were Fe(NO3)3·9H2O (purity 99%), Co(NO3)2·6H2O (purity 96%) and Na2CO3.

The powder X-ray diffraction (XRD) patterns were recorded by use of a TUR M62 diffractometer with Co-Ka radiation (.=1.789 Å). The observed patterns were crossmatched with those in the JCPDS database. Transmission Electron Microscopy (TEM) investigations were made using a Topcon 002B electron microscope operating at 200 kV with a point-to-point resolution r=1.8 Å. The samples were sonicated in ethanol and deposited on a pre-deposited polymer on a copper grid. Mössbauer spectra of nano-size cobalt ferrite particles were recorded at 295 and 77 K on a Wissel electromechanical Mössbauer spectrometer (Wissenschaftliche Elektronik GmbH, Germany) working in a constant acceleration mode. A 57Co/Cr (activity.10 mCi) source and an a-Fe standard were used. The experimental spectra were treated using the least squares method. The parameters of hyperfine interaction such as isomer shift (IS), quadrupole splitting (QS) and effective internal magnetic field (Heff) as well as the line widths (FWHM) and the relative weight (G) of the partial components of the spectra were determined. Temperature and field dependences of the magnetization of the cobalt ferrite were measured on a Quantum Design MPMS-XL SQUID operating in the temperature range 2–400 K and an applied field up to 5 T. In order to avoid sample rotation in the applied field the nanoparticles were embedded in a polymer matrix, PMMA (poly methyl methacrylate).

3 Results and discussion

Nearly spherical CoFe2O4 nanoparticles were obtained by high energy ball milling of the 1-LDH-CO3. X-ray powder diffraction and Transmission Electron Microscopy show that the average size of the particles increases (ca. 5, 8 and 20 nm) with milling time (ca. 5, 10 and 15 h). The increase in size is also evidenced by the reduction of the microstrain that is commonly associated with a diminution of structural defects. It is interesting to note that the process of crystallization continues as a function of treatment time and at later stages is accompanied by the reduction to cobalt. Similarly, Menzel et al. have shown that highenergy milling of nickel ferrite spinels induces the formation of metallic iron [1].

Cobalt ferrite bulk material (CoFe2O4) is known to be a ferrimagnetic material with very high cubic magnetocrystalline anisotropy leading to high theoretical coercivity: 25.2 kOe at 5 K (maximum observed at 2 K is 22 kOe) and 5.4 kOe at 300 K, and a saturation magnetization of 93.9 emu/g at 5 K and 80.8 emu/g at 300 K [2–4].
Concerning our samples, the absence of coercivity, remanence and saturation at 295 K for the sample milled during 5 h suggests that this material behaves as a superparamagnet at room temperature. This superparamagnetic character is confirmed by Mössbauer spectrometry, two doublets arising from the two possible iron environments in spinels are observed at room temperature. At lower measuring temperatures, these doublets tend to disappear to

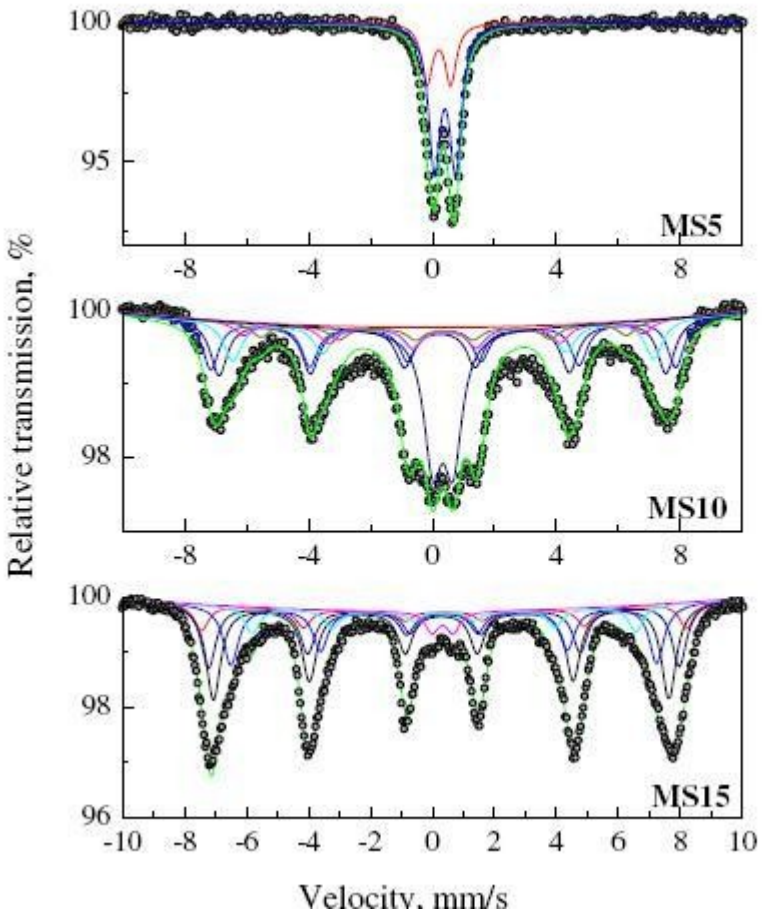


Figure 1 Mössbauer spectra of CoFe2O4 at 295 K for different milling time.

the benefit of sextets. The blocking temperature TB associated to the maximum in the Zero Field Cooling curve increases (ca. 200, 310 and 390 K) with milling time (ca. 5, 10 and 15 h) indicating that the samples milled for 10 or 15 h are blocked at room temperature. Magnetic splitting is evidenced on room temperature. Mössbauer spectra of the samples milled for 10 and 15 h confirm the presence of ferrimagnetic species (Figure 1). Saturation of the magnetization is never reached (in the magnetic field range explored (±5 T) for all the samples and measuring temperatures (Figure 2). However, saturation magnetization

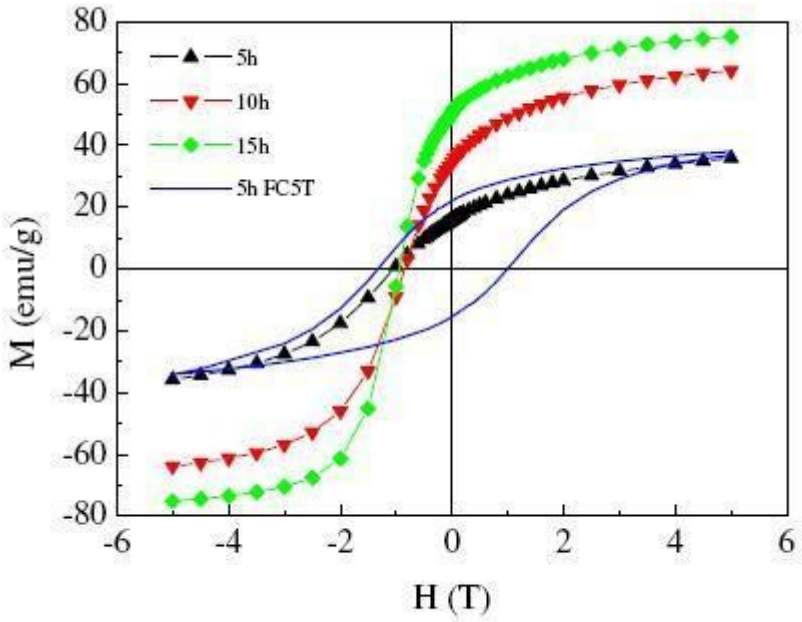


Figure 2 ZFC–isothermal magnetization(5 K) of the milled CoFe2O4 and FC (5 T) for the 5 h milled sample.

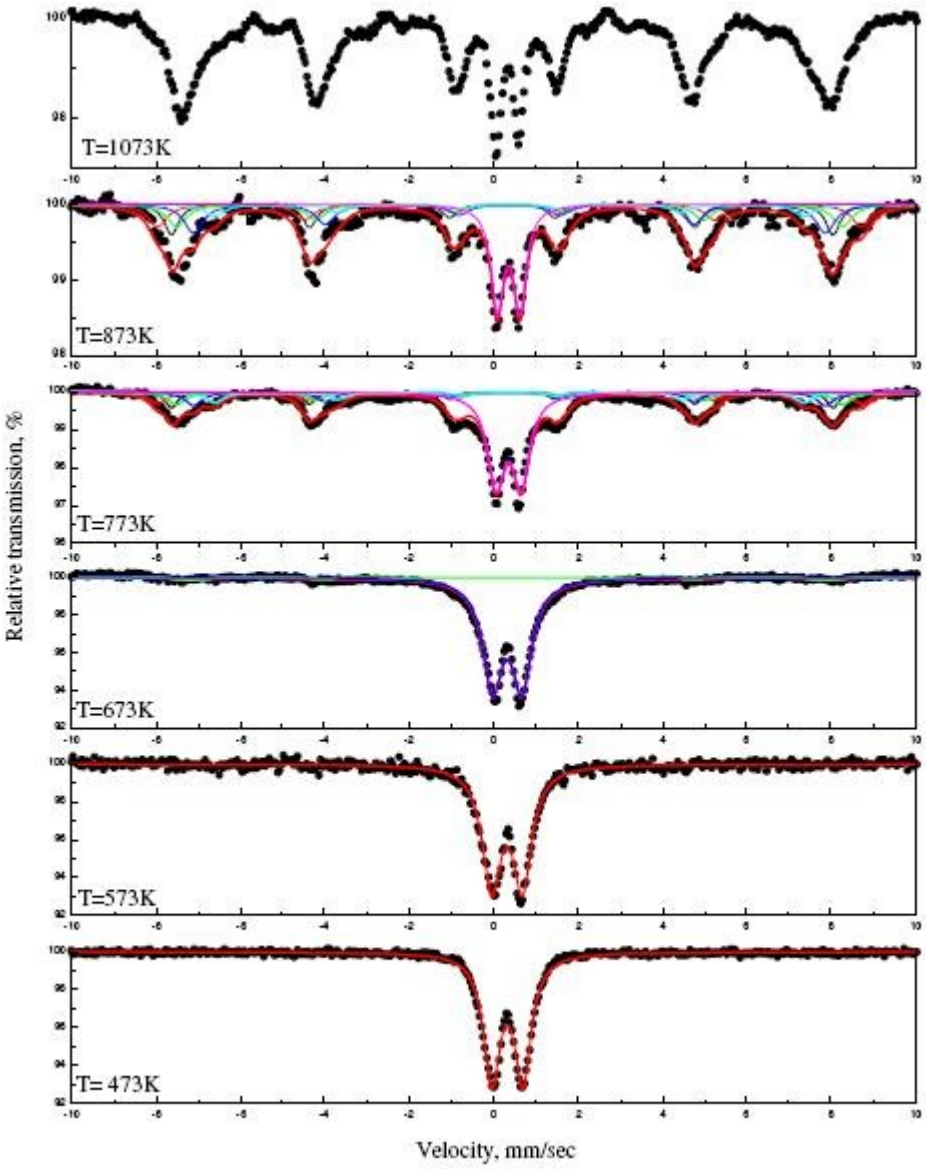
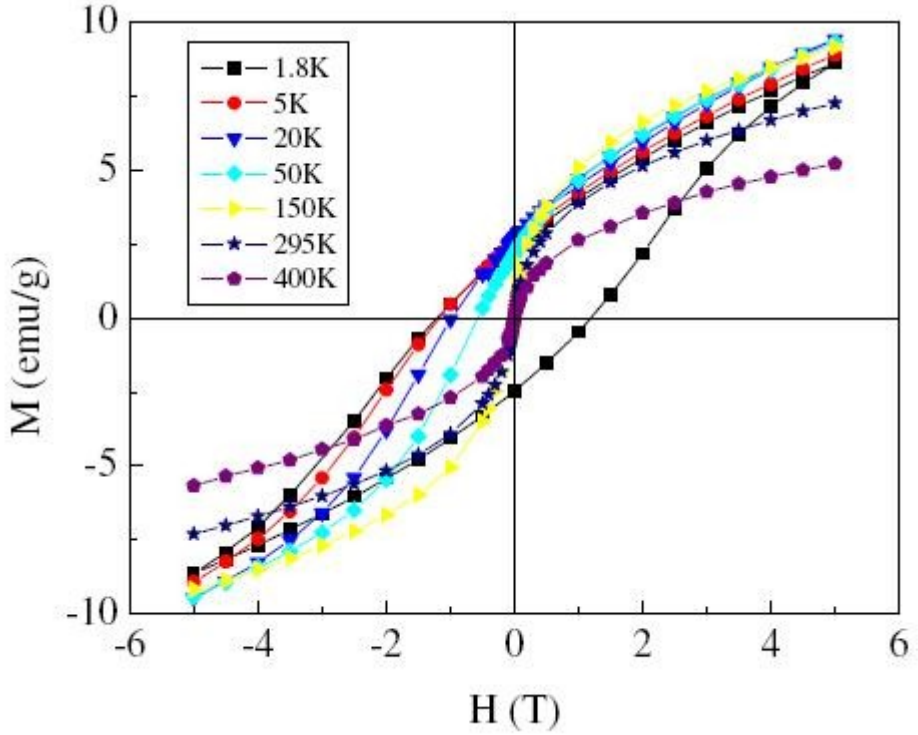


Figure 3 RT Mössbauer spectra of all synthesised Co_2FeO_4 samples.

Figure 4 Isothermal magnetization of the Co2FeO4 annealed at 573 K.



(Ms) can be estimated from zero extrapolation of M versus 1/H and the ratio Mr/Ms can be calculated [5]. Both calculated parameters increase with milling time but never reach the theoretical values [6]. This indicates that even for such long treatment time some of the ultrafine particles remain or that the objects formed are core/shell particles with a spin-glass like surface layer [5]. The later hypothesis is confirmed by the observed hysteresis loop shift (from ZFC to FC) that has been attributed to canting of the surface spins. Furthermore, Mössbauer spectra simulations show that the degree of inversion of cobalt ferrite increases with increasing milling time and approaches that of thermochemically synthesized samples.

Heating the 2-LDH up to 673 K leads to the formation of pure cubic [a=8.19±0.01 Å] spinel Co2FeO4 nanoparticles while above this temperature a second phase (CoFe2O4)is formed [a=8.37±0.01 Å]. The amount of the latter increases at the expense of the Co2FeO4 phase upon increasing the treatment temperature. Our results surprisingly disagree with those reported by Fereira et al. [7], where the existence of two spinel phases in the temperature range 570–1070 K is discussed. The average size of the nanoparticles of Co2FeO4 increases from 3 to 22 nm by increasing treatment temperature from 473 to 1073 K. The Co2FeO4 spinel phase has not been extensively reported in the literature. According to Takahashi et al. [8] bulk Co2FeO4 has a Curie temperature around TC=425 K, saturation magnetization around Ms=15 emu/g and coercive force Hc of the order of 2 T.

For annealing temperature below 673 K, the nanoparticles formed behave as superparamagnets at room temperature. Mössbauer spectrometry indicates that only Fe3+ iron are present. The blocking temperature TB associated to the maximum in the Zero Field Cooling curve increases (ca. 45, 220 and 250 K) with annealing temperature (ca. 473, 573 and 673 K). However, for the latter temperature coercivity is observed at room temperature on magnetization curve which can be associated to the presence of small quantity of CoFe2O4 particles. Room temperature Mössbauer spectroscopy was applied to all synthesized products. Figure 3 shows the RT Mössbauer spectra of the samples obtained after treatment at different temperatures. The doublets observed in all samples can be attributed to cobalt

ferrite phase rich in cobalt (Co_2FeO_4), while the sextet component can be related with the presence of $CoFe_2O_4$. These results agree with the XRD data, where for samples annealed at temperatures higher than 673 K a second phase ($CoFe_2O_4$) is observed. When the

Mössbauer measuring temperature is decreased these doublets tend to disappear to the benefit of sextets.

Magnetization measurements have been performed, on pure Co_2FeO_4 samples immobilized in a polymer matrix (PMMA), as a function of applied magnetic field and temperature (Figure 4). Several important observations can be made from these experiments. First is the large opening of the hysteresis loop at low temperature. The coercive force can reach an unprecedented value of 2.2 T at 1.8 K for field-cooled sample. The second point is that saturation magnetization is far from being reached in the magnetic field explored. These two observations reflect the high intrinsic anisotropy for Co_2FeO_4 and one can expect higher coercivity in extended applied magnetic field. However, saturation magnetization can be estimated from zero extrapolation of M versus 1/H and the ratio Mr/Ms can be calculated. It is observed that these two parameters (Table 1) increase with annealing temperature in agreement with the increase of the average size of the particles. The estimated magnetization saturation (30 emu/g at 5 K) for the sample annealed at 673 K is higher than the value given by Takahashi et al. [8]. Our over-estimation is due to the fact that at this temperature the sample contains a small quantity of $CoFe_2O_4$. The ratio Mr/Ms obtained are far below the expected values for randomly oriented nanoparticles [9]. This is probably due to the fact that the hysteresis loops obtained in the magnetic field range explored is in fact only an inner loop. Further experiments in magnetic field up to 60 Tesla will be necessary.

Table 1 Magnetic parameters for the Co_2FeO_4 samples

Samples	Temperature (K)	Hc (T)	M_r (emu/g)	Estimated M_s (emu/g)	M_r/M_s	T_B (K)
473 K	295	0	0	6	0	45
	5	0.68	0.93	9	0.10	
573 K	295	0	0	12	0	220
	5	1.20	2.57	13	0.19	
673 K	295	0.02	0.69	23	0.03	250
	5	1.50	4.71	30	0.16	

4 Conclusion

Large-scale preparation of cobalt ferrite CoxFe3-xO4 (x=1 or 2) nanoparticles has been achieved by combining chemical precipitation of layered double hydroxide carbonate (x-LDH–CO3, x=1 or 2) and their treatments by high-energy mechanical milling or thermal decomposition. The size of the particles increases with increasing milling time or temperature. Controlled temperature treatment of 2-LDH–CO3 results in the thermodynamically less stable Co2FeO4 which is progressively transformed to the more stable CoFe2O4 at higher temperatures. Magnetic properties display finite size effects and in the case of CoFe2O4, core-shell structure with a canting of surface spins has been considered to explain the observed hysteresis loop shift (from ZFC to FC). For Co2FeO4 nanoparticles with diameter of 6 nm, unprecedented coercivity of 2.2 T has been measured at 1.8 K.

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