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Fe_xO_y-SiO_2 nanocomposites studied by Mössbauer spectroscopy

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Fe_xO_y-SiO_2 nanocomposites were obtained via the sol-gel method, by using three different precursors for the silica matrix. The morphology and the iron phase composition is strongly influenced by the precursors. The presence of magnetically ordered goethite and fayalite is evidenced by low temperature Mössbauer spectroscopy. Subsequent annealing treatments performed on the initial samples have induced the formation of hematite nanoparticles in the silica matrix, mainly on the account of the goethite decomposition. The total amount and the size distribution of the hematite nanoparticles can be controlled via the initial precursors and the subsequent annealing conditions. The simultaneous analysis of the iron phase composition and of the local magnetic interactions in the analysed samples is performed.

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1. Introduction

Materials consisting of nanosized magnetic grains embedded in various matrices are subject of intense current research. Magnetic nanocomposites have been investigated for their potential applications in magnetic recording and magneto-optics [1,2], color imaging [3], bioprocesing [4], catalysis [5] and ferrofluids [6].

One of the most reliable methods for the preparation of the nanocomposites is the sol-gel procedure. Iron oxide nanoparticles can be embedded in an inert, inorganic, transparent and temperature resistant silica matrix, within a wide range of experimental conditions [7-10]. Following this procedure, α-FeOOH appears as an intermediate compound during the thermal processing. The thermal behavior of α-FeOOH is reported in literature [11,12,13]. The above mentioned studies have shown that the final product of the thermal induced decomposition of α-FeOOH is α-Fe_2O_3 and that the crystallographic and the magnetic properties of the final product depend on the annealing conditions and the degree of the crystalline order of the initial material. This paper presents the influence of the different SiO_2 sources on the structural, morphological and local magnetic properties of the iron phases in iron oxide- silica nanocomposite materials prepared by the sol-gel method. The influence of different annealing treatments is also emphasized.

2. Experimental

Three samples of Fe_xO_y-SiO_2 nanocomposites have been prepared using the alkoxide route of the sol-gel method. Tetraethoxysilan (TEOS), from Merck, methyltriethoxysilan (MTEOS), from Fluka, and phenyltriethoxysilan (PTEOS), from Aldrich, were used as SiO_2 sources. Regarding the iron source, this was a common one for all samples, respectively the Fe(II) salt, $FeSO_4\cdot7H_2O$, from "Reactivul". The preparation and the structural characterization of the iron oxide-silica nanocomposites have been detailed in our previous papers [14,15]. The syntheses were carried at well controlled temperature with permanent magnetic stirring. The relative amount of iron oxide to SiO_2 was 3 wt.% in all cases. The initial gels were dried at 110 °C for 24 h, giving rise to samples T, M and P, respectively (according to the silica sources in the above mentioned order). The compositions and the preparation conditions of the synthesized samples are presented in Table 1.

Table 1. The chemical compositions and the experimental conditions of the prepared Fe_xO_y-SiO_2 nanocomposites.

Sample	Silica precursor	Molar ratio				Conditions of reaction	
		$\frac{ROH}{SiO_2}$	$\frac{H_2O}{SiO_2}$	$\frac{Fe^{2+}}{SiO_2}$	$\frac{NH_4OH}{SiO_2}$	T (°C)	t (h)
T	TEOS	4	13.375	0.033	0.008	65	1
M	MTEOS	8	13.375	0.033	0.008	65	3
P	PTEOS	8	13.375	0.033	0.008	65	6

Subsequently, amounts of each of the three initial samples (T, M and P) were thermally treated at 550 °C and 1000 °C, respectively, for 1 hour, giving rise to samples with expected different properties as compared with the initial ones.

The Fe_xO_y-SiO_2 nanocomposites were previously characterized by DTA/TG analysis [10,14,16,17], XRD [14,17], IR spectroscopy [10,14], TEM [10,17], and by the BET method for surface area determinations [10,14,17].

The Mössbauer spectra were acquired by using a constant acceleration spectrometer with symmetrical waveform and a ^{57}Co source (1.4 MBq) in a Rh matrix. Measurements at 5 K have been performed with the samples in a liquid He bath cryostat. A close cycle He cryostat was used for Mössbauer measurements above 20 K. The spectra were least-squares fitted by using the computer program “NORMOS” by Brand [18]. All isomer shift values are given relative to bcc Fe at RT.

3. Results and discusion

The Mössbauer spectra of samples T, M, P collected at 5 K are shown in Fig. 1 and the corresponding Mössbauer parameters in Table 2.

The Mössbauer spectrum of sample T shows three components. The first component is a central paramagnetic doublet with a small isomer shift, IS=0.40 mm/s, and quadrupole splitting, QS=0.70 mm/s. This component suggest the presence of not interacting magnetic moments of Fe and is tentatively attributed to the Fe^{3+} ions diffused uniformly in silica matrix. The second component, consists in a very broad sextet with a relatively low hyperfine magnetic field, B_{hf}, but with a large isomer shift. Tacking into account the values of the hyperfine parameters, namely B_{hf} = 28T, IS=0.90 mm/s and QS = 0.31 mm/s, this component was assumed to belong to Fe_2SiO_4 in a magnetic relaxation regime, as will be subsequently detailed. The third component consists in a pretty well shaped sextet with a hyperfine field B_{hf} = 49T, a small isomer shift IS=0.40 mm/s and a quadrupole splitting QS = 0.30 mm/s. This position was attributed by its hyperfine parameters to the α-FeOOH phase [19]. The α-FeOOH (goethite) presents an antiferromagnetic behavior at room temperature and has a Néel temperature, T_N, of approximately 400 K and an hyperfine magnetic field of about 50 T, for well formed particles of mezoscopic size. Lower hyperfine fields are expected for particles of smaller mean size, due to the presence of a relatively higher fraction of Fe surface positions.

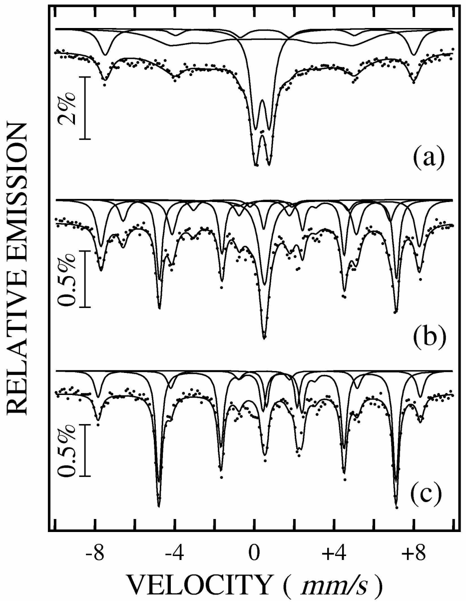

Fig. 1. Mössbauer spectra collected at 5 K on samples T (a), M (b) and P (c).

The Mössbauer spectrum of sample M obtained at 5 K shows four different components: a singlet and three magnetic sextets. The paramagnetic component, represented by a singlet with IS= 0,51 mm/s, has been attributed again to Fe^{3+} ions uniformly diffused into the silica matrix. Compared with sample T (with TEOS precursor) showing a distorted Mössbauer pattern (doublet) for the diffused ions, the presence of the singlet with negligible quadrupole splitting, proves a much lower distortion of the silica matrix in sample M. The second component of the spectrum, represented by a magnetic sextet with high quadruole shift, corresponds to a Fe^{2+} phase. The hyperfine parameters are specific to one of the sextets belonging to fayalite, Fe_2SiO_4 (IS=1.28 mm/s, QS = 2.55 mm/s and B_{hf}=33T) [20]. It is worth mentioning that Fe_2SiO_4 is one of the most abundant minerals in Earth’s upper mantle and therefore it has been extensively studied in the last decades [20,21]. Its magnetic structure has been studied by Mossbauer spectroscopy and neutron diffraction and is reported to have a noncollinear antiferromagnetic structure below the Neel temperature of about 66 K [22,23]. Two iron positions giving rise to two magnetic patterns with quite different hyperfine fields (about 32 T and 12 T, respectively) are generally reported for the low temperature Mössbauer spectra of this compound [20-23]. However, in the present case, the fit quality of the Mössbauer spectrum gave strong indications for only one spectral component assigned to fayalite. This could suggest a very defected orthosilicate compound formed at the interface of the iron oxide with the silica matrix, with mainly one crystallographic site occupied by Fe^{2+} ions. In the previous sample, T, the broad sextet with a large isomer shift, suggesting Fe^{2+} ions, and assigned also to fayalite, has an atypical low quadrupole shift and hyperfine field. The overall shape of those component reminds a magnetic relaxation regime, which in this case is most probably due to the low size of the fayalite particles. For a mean size in the nanometric range, the blocking temperature decreases rapidly much below the Neel temperature of only 66 K and a relaxation regime could be I work also at 5 K. Accordingly, the hyperfine magnetic field could be 5-6 T lower than the hyperfine magnetic field in the static regime and the quadrupole shift could loss the meaning from the time independent perturbations. The third component in the Mössbauer spectrum is a magnetic sextet with a hyperfine field of 50T and IS=0.40 mm/s, specific to goethite, α-FeOOH. Finally, the fourth component (magnetic sextet) is assigned to an iron oxihydroxide with B_{hf}=42T and IS=0.48 mm/s and is supposed to belong to γ- FeOOH. The low dimensionality of the particle could be again the cause of a smaller hyperfine magnetic field as compared with the bulk value (42 T as compared with 46 T in the bulk). Sample M is definitely better crystallized than sample T, as directly suggested by the lower line-widths of the Mössbauer components. The Mössbauer absorptions of the very broad sextet in sample T resembles to the ones corresponding to fayalite in sample M, but the lower hyperfine field can be explained only via a magnetic relaxation regime, specific to nanosized particles. Fe phases of lower dimensionality in sample T is also suggested by the lower hyperfine field of goethite in this sample (49 T in sample T as compared with the typical value of 50 T in sample M).

The Mössbauer spectrum of sample P gives evidence for Fe^{2+} ions in intermediate spin configuration, diffused in the SiO_2 matrix, and the presence of the fayalite and the goethite phases.

Table 2. The Mössbauer parameters (the hyperfine magnetic field, B_{hf}, the isomer shift, IS, and the quadrupole splitting, QS) of the initial samples T, M and P. The relative content of the various iron phases corresponds to the relative area of the Mössbauer components.

Sample	Component	B_{hf} (T)	IS (mm/s)	QS (mm/s)	Aria (%)
T	Fe^{3+}	-	0.40	0.70	38
	Fe_2SiO_4	28	0.90	0.31	41
	α–FeOOH	49.5	0.40	0.25	21
M	Fe^{3+}	-	0.50	-	18
	Fe_2SiO_4	34.0	1.28	2.55	38
	α–FeOOH	50	0.40	0.20	31
	γ– FeOOH	42	0.48	0.72	11
P	Fe^{2+}	-	1.38	1.53	10
	Fe_2SiO_4	37.13	1.28	2.45	71
	α–FeOOH	50	0.37	0.24	19

The Mössbauer spectra of sample T taken at 20K and room temperature (RT) after the annealing treatment of 1 h at 1000 °C are presented in Fig. 2.

The 20 K and RT Mössbauer spectra of sample T (not annealed) confirm the presence of three Fe phases, assigned as previously, to α-FeOOH, Fe_2SiO_4 and isolated Fe^{3+} ions dispersed in the silica matrix. Moreover, the evolution of the spectra versus the temperature provides additional evidence for magnetic relaxation phenomena due to the low dimensionality of both the fayalite and the goethite phases (see the collapsing behavior of the magnetic sextets in Fig. 2 (b)).

On the other hand, the Mössbauer spectra collected at 20 K and RT for sample T treated at 1000 °C for 1 h, consist of only two Mössbauer components: a magnetic sextet and a paramagnetic/superparamagnetic doublet. The hyperfine parameters of these components suggest only the presence of Fe^{3+} based phases. The most complete information about the phase composition of the sample is obtained in the magnetic static regime corresponding to 20 K. Accordingly, the sextet can be undoubtedly assigned to the α-Fe_2O_3 phase (hematite). About 45% of the total iron belongs to this magnetic phase, whereas the rest of 55% is attributed to paramagnetic Fe^{3+} ions in silica matrix. The RT Mössbauer spectrum of sample T annealed at 1000^{0}C evidences only 14% of magnetic phase with hyperfine parameters typical to hematite. This result suggests that the central doublet at RT (86% relative area) involve both isolated Fe^{3+} ions dispersed uniformly in silica matrix and small superparamagnetic particles of α-Fe_2O_3. That is in agreement with a bimodale size distribution of the hematite particles, with a significant fraction of very fine nanoparticles (mean size lower than 5 nm [24]).

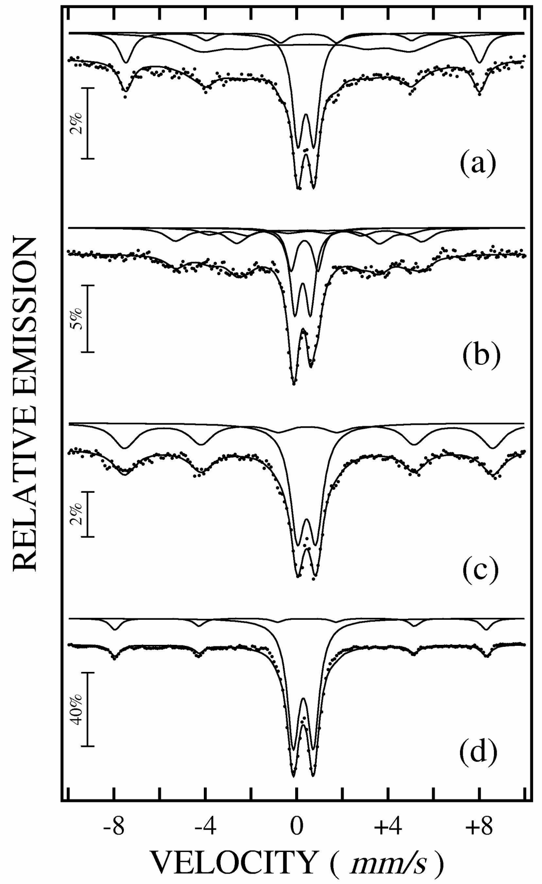

Fig. 2. Mössbauer spectra of sample T collected at different temperatures before and after annealing at 1000^{0}C: (a) spectrum collected at 20 K on sample T before annealing, (b) spectrum collected at RT on sample T before annealing, (c) spectrum collected at 20 K on sample T after annealing, (d) spectrum collected at RT on sample T after annealing.

The Mössbauer spectra of samples M, as prepared and heated at 550 °C and at 1000 °C respectively, are presented in Fig. 3. The 80 K spectrum of the initial sample M (as prepared) gives clear evidence for only a weak magnetic component assigned to α-FeOOH (14% relative contribution) and intense paramagnetic patterns assigned to Fe^{3+} (43% relative area of the central doublet and the central singlet) and Fe^{2+} (43% relative area of the doublet with large quadrupolle splitting and positive isomer shift) species. The 80 K Mössbauer spectrum of sample M heated at 550^{0}C shows three different components. The corresponding Mössbauer parameters suggest that the sextet with the largest magnetic splitting belongs to hematite (α-Fe_2O_3) whereas the second sextet (with lower magnetic splitting) belongs to goethite (α-FeOOH). The third component is attributed to Fe^{3+} diffused in silica matrix. At RT the whole spectrum becomes paramagnetic-like, suggesting the superparamagnetic behavior of the hematite and the goethite particles.

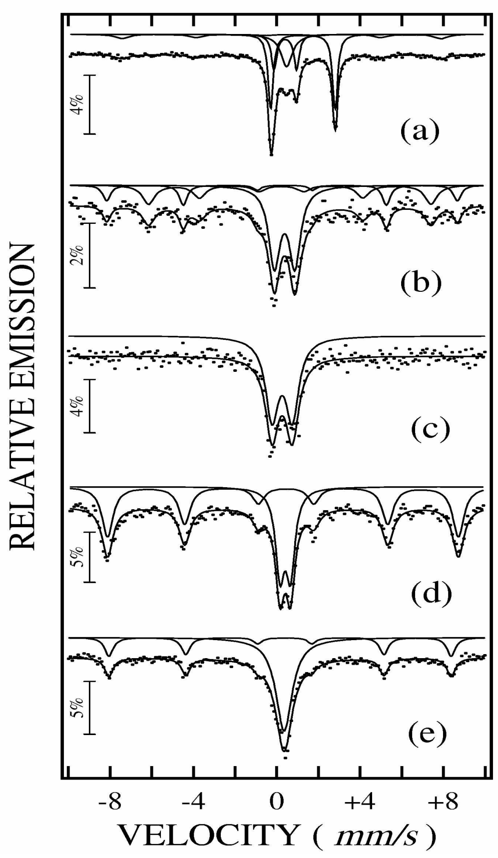

Fig. 3. Mössbauer spectra of sample M collected at different temperatures in the as prepared and annealed states: (a) spectrum of the as prepared sample M collected at 80K, (b) spectrum of sample M annealed at 550 °C and collected at 80 K, (c) spectrum of sample M annealed at 550 °C and collected at RT, (d) spectrum of sample M annealed at 1000 °C and collected at 80 K, (e) spectrum of sample M annealed at 1000 °C and collected at RT.

The 80 K Mössbauer spectrum of sample M annealed at 1000 °C show only two components. The first one, represented by a paramagnetic central doublet with a small isomer shift (IS = 0.40 mm/s) and quadrupole splitting (QS = 0.50 mm/s) is attributed to Fe^{3+} ions dispersed in silica matrix. The second component is a magnetic sextet with hyperfine parameters typical for hematite. The relative area of the sextet belonging to hematite decreases from about 61% at 80 K to about 32% at RT, in conditions of a very weak decrease of the hyperfine field. That is again a direct proof that the hematite particles present a bimodal size distribution also in sample M.

4. Conclusions

Mainly fayalite and goethite are obtained as magnetic phases dispersed in the silica matrix in samples prepared by the sol-gel method and using tetraethoxysilan (TEOS), methyltriethoxysilan (MTEOS) and phenyltriethoxysilan (PTEOS) as precursors for the silica and $FeSO_4 \cdot 7H_2O$ as iron source. The highest amount of goethite is observed in the sample prepared with MTEOS whereas the sample prepared with PTEOS shows the highest amount of fayalite. Annealing treatments of 1 h at 1000 °C performed on the initial samples induce the formation of hematite nanoparticles in the silica matrix. The highest amount of hematite corresponds to the initial sample presenting the highest amount of goethite. A bimodal size distribution of the hematite nanoparticles is evidenced from the evolution of the Mössbauer spectra versus temperature. The nanoparticles with the lower mean size are in the superparamagnetic state at room temperature. Annealing treatments for 1 h at 550 °C induce only the formation of an incipient hematite and increase the size of the goethite particles. All hematite nanoparticles formed in these conditions are in the superparamagnetic state at room temperature.

References

[1] S. Onodera, H. Kondo, T. Kawana, MRS Bull. **21**, 35 (1996).

[2] H. Guerrero, G. Rosa, M.P. Morales, F. Del Monte, E. M. Moreno, D. Levy, R. Pérez del Real, T. Belenguer, C. J. Serna, Appl. Phys. Lett. **71**, 2698 (1997).

[3] R. F. Ziolo, E. P. Gionnelis, B. A.Weinstein, M. P. O'Horo, B. N. Ganguly, V. Metrotra, M. W. Russel, D. R. Huffman, Sience **257**, 219 (1992).

[4] L. Nixon, C. A. Koval, R. D. Noble, G. S. Staff, Chem.Mater. **4**, 117 (1992).

[5] C. R. F. Lund, J. A. Dumesic, J. Phys. Chem. **86**, 130, (1982).

[6] S. W. Charles, in Studies of magnetic properties of fine particles and their relevance to materials science, ed. J. L. Dormann and D.Fiorani. Elsevier Science, Amsterdam, (1992).

[7] S. Bruni, F. Cariati, M. Casu, A. Lai, A. Musinu, G.Piccaluga and S. Solinas, NanoStructured Materials **5**(11), 573 (1999).

[8] G. Garçon, P. Gosset, F. Zerimech, B. Grave-Descampiaux, P. Shirali, Toxicology Letters **2**(150), 179 (2004).

[9] K. Woo, H. J. Lee, J. M. M .M. **272-276**, e1155 (2004).

[10] A. Jitianu, Maria Crisan, Aurelia Meghia, Ileana Rau, Maria Zaharescu, J. Mater. Chem. **12**, 1401 (2002).

[11] U. Schwertmann, R. M. Cornell, Iron oxide in the Laboratory, VCH, Weintheim, (1991).

[12] D. G. Klissurski, V. N. Bluscov, Mater. Chem. **5,** 67 (1980).

[13] S. Goni-Elizalde, M. E. Garcia-Clavel Thermochim. Acta **124**, 359 (1980).

[14] M. Zaharescu, M. Crisan, A. Jitianu, D. Crisan, A. Meghia, I. Rau, J. Sol-Gel Sci. Technol. **19**, 631. (2000).

[15] I. Peleanu, M. Zaharescu, I. Rau, M. Crisan, A. Jitianu, A. Meghia, J. Radioanal. Nucl. Chem. **246**, 557 (2000).

[16] M. Crişan, A. Jitianu, D. Crişan, M. Bălăşoiu, N. Drăgan, M. Zaharescu, J. Optoelectronics Adv. Mater. **2**, 339 (2000).
[17] A. Jitianu, M. Răileanu, M. Crişan, M. Zaharescu, L. Stanciu, Proceedings of the 14th Conference on Glass and Ceramics, Eds. B. Samuneva, S. Bachvarov, I. Gutzov, Y. Dimitriev, "Marin Drimov" Academic Publishing House, Sohia, in print, (2002).
[18] R. A. Brand, Nucl. Instr. Methods Phys. Res. B **28**, 398 (1987); the NORMOS program is available from WISSEL GmbH, D-82319 Starnberg, Germany.
[19] N. N. Greenwood, T. C. Gibb, Mossbauer Spectroscopy, Chapman and Hall Ltd-London, (1971).
[20] W. Kündig, J. A. Cape, R. H. Lindquist, G. Costabaris, J. Appl. Phys. **3**(38), 947 (1967).
[21] M. Cococcioni, A. Dal Corso, S. De Gironcoli, Phys. Rev. B **1**(67), 094106-1 (2003).
[22] W. Lottermoser, H. Fuess, Phys. Stat. Sol. A **2**(109), 589 (1988).
[23] W. Lottermoser, K. Forcher, G. Amthauer, H. Fuess, Phys. Chem. Minerals **22**, 259 (1995).
[24] W. Kündig, H. Bömmel, G. Constabaris, R. H. Lindquist, Physical Review **2**, 142 (1966).

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