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Fe₂O₃/SiO₂ Hybrid Nanocomposites Studied Mainly by Mössbauer Spectroscopy

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Magnetic nanocomposites exhibit promising applications in many areas, for example optics, electronics, biology, medicine, etc. The main goal of this study was to synthesize magnetic ϵ -Fe₂O₃ nanoparticles embedded in amorphous SiO₂. These materials were prepared by the help of ultrasonic activation and subsequent annealing in nitrogen atmosphere or air with concentrations of iron oxide of about 20 and 30 wt.%. The structure and properties of the final product were analysed by the Mössbauer spectrometry as well as by X-ray diffraction, scanning electron microscopy, and high resolution transmission electron microscopy. They strongly depend on the initial conditions of preparation.

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1. Introduction

Nanostructured materials are the subject of an intense research during the past ten years [1, 2]. The nanocomposite phases with the dimensions less than 100 nm exhibit extraordinary material characteristics, including mechanical, chemical, structural, optical, and electric/magnetic properties.

The effects of ultrasonic cavitation (sonocatalysis) upon the precursors give rise to materials with new properties. This process creates a unique environment

for sol-gel reactions leading to particular features in the resulting gels: high density, fine texture, homogeneous structure, etc. All these properties are affected by the evolution of sonogels and the structure of the final nanomaterial.

2. Experimental

$\text{Fe}_2\text{O}_3/\text{SiO}_2$ magnetic nanocomposites with various phase compositions were prepared by the sol-gel method. Sonohydrolysis of tetraethoxysilane (teos) with Fe^{3+} added as alcoholic solution of inorganic salt was followed by exchanging liquid phase of wet gel with acetone and drying at 60°C for 10 hours. Subsequently, these xerogel samples were annealed at 1000°C under moderate oxidation conditions (air), and in an inert atmosphere (nitrogen). The resulting concentrations of iron oxide in magnetically inert matrix were 20 wt.% and 30 wt.% (see also Table I).

TABLE I

Description of the samples studied. V12 = silica matrix — SiO_2 — (TEOS+ H_2O + $\text{C}_2\text{H}_5\text{-OH}$); F20, F30 = Fe_2O_3 concentration of 20 and 30 wt.%, respectively; US2 = the liquid iron nitrate was impregnated in silica matrix under sonication in ultrasonic bath (USB); n = without sonification; T = not thermostatic; V1S10 = hybrid silica matrix (90 wt.% SiO_2 + 10 wt.% PVA), calculated for the dried gel.

The symbol of the sample	The condition of the preparation (annealed in N_2)	Sonification regime	The symbol of the sample	The condition of the preparation (annealed in air)	Sonification regime
$\text{Fe}_2\text{O}_3/\text{SiO}_2$ nanocomposites					
3T N	V12F20	n	3T	V12F20	n
$\text{Fe}_2\text{O}_3/\text{SiO}_2$ nanocomposites (hybrid matrix)					
21T N	V1S10F20	n21T	V1S10F20	n	
22T N	V1S10US2F20T	USB	22T	V1S10US2F20T	USB
23T N	V1S10F30	n	23T	V1S10F30	n

X-ray diffraction (XRD), Mössbauer spectroscopy, scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) were used for detailed sample characterization and to study the influence of preparation conditions upon the resulting properties of the samples.

SEM and HRTEM images were acquired using the Jeol JEM 3010.

Phase composition and size of the magnetic iron oxide particles were determined by X-ray powder diffraction with Bruker D8 diffractometer using $\text{Cu } K_\alpha$ line and Sol-X energy dispersive detector.

^{57}Fe Mössbauer spectra (MS) were acquired in transmission geometry using a $^{57}\text{Co}/\text{Rh}$ source mounted on a standard constant acceleration spectrometer. The spectra were measured at 300 K and some of them also at 4 K.

3. Results and discussion

According to HRTEM observations, particles of about 5–10 nm in size are supposed to belong to ϵ -Fe₂O₃, hematite, and magnetite phases (Fig. 1).

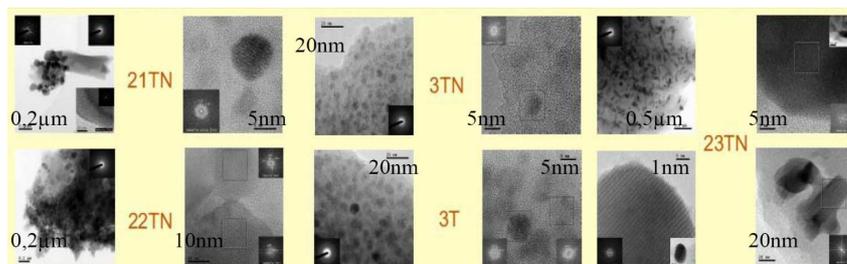


Fig. 1. HRTEM images of iron oxide particles of various samples.

Mössbauer spectra (see Fig. 2) were fitted with the help of the NORMOS program [3]. They consist of 2–4 sextets and 1–2 doublets [4]. The latter ones correspond to Fe in paramagnetic (PM) and/or superparamagnetic (SPM) states. The difference in relative fractions of the doublet components at 4 and 300 K (see Table II) indicates the SPM contribution. In particular, a considerable part of the doublet for 3T sample represents superparamagnetic state of the ϵ -Fe₂O₃ phase as evidenced by an increase in its relative fraction at low temperature.

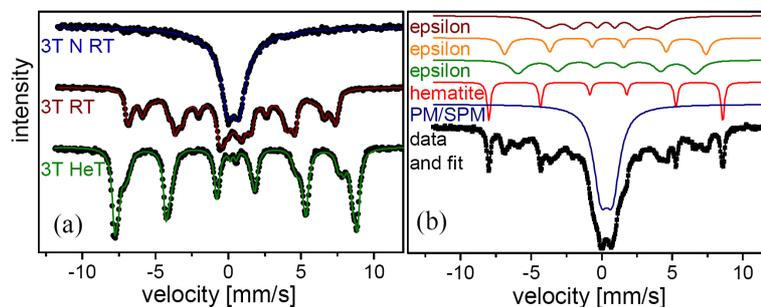


Fig. 2. Mössbauer spectra of the 3T xerogel prepared under different conditions and taken at 300 K and 4 K (a), and an example of a spectrum analysis for 22T (b).

According to the spectral parameters listed in Table III (hyperfine field, isomer shift), the sextets represent hematite, ϵ -Fe₂O₃ and/or magnetite (denoted by * in Table III). As seen from Table II, different preparation conditions lead to deviations in the relative fraction as well as type of magnetic components.

XRD patterns were analyzed with the Rietveld method by the help of the program FULLPROF. The XRD phase analysis confirmed the main features of the Mössbauer analysis (see Table II). When comparing the results of XRD with MS spectra, we have to take into consideration that the phases seen by MS need

TABLE II

The comparison of X-ray diffraction and MS analyses (* magnetite).

	XRD analysis			Mössbauer spectroscopy		
	ϵ -Fe ₂ O ₃	hematite	maghemite	ϵ -Fe ₂ O ₃	hematite	PM/SPM
3T	65%	–	35%	73%	–	27%
3T (4 K)	–	–	–	98%	–	2%
3T N	14%	–	86%	–	–	100%
21T	26%	12%	62%	42%	6%	52%
21T N	30%	10%	60%	42%	6%	52%
22T	26%	12%	62%	44%	11%	45%
22T N	77%*	7%	16%	79%*	7%	14%
23T	31%	69%	–	40%	60%	–
23T N	21%	79%	–	32%	68%	–

TABLE III

The parameters of magnetic phases components from MS (* magnetite).

	3T	21 T	21T N	22T	22T N	23T	23T N	
ϵ -Fe ₂ O ₃	44.4	44.2	44.0	44.3	49.1*	45.3	45.5	B_{hf} [T]
45 T	0.36	0.39	0.38	0.35	0.28	0.36	0.38	δ [mm/s]
ϵ -Fe ₂ O ₃	38.9	38.7	38.2	39.1	45.8*	39.7	39.9	B_{hf} [T]
39 T	0.43	0.39	0.45	0.43	0.67	0.37	0.37	δ [mm/s]
ϵ -Fe ₂ O ₃	24.8	25.4	24.3	24.3		26.3	27.1	B_{hf} [T]
26 T	0.11	0.16	0.22	0.18		0.2	0.23	δ [mm/s]
hematite		51.9	51.8	51.5	51.6	51.8	51.6	B_{hf} [T]
		0.37	0.38	0.38	0.38	0.38	0.38	δ [mm/s]

not possess translational symmetry essential for XRD, but on the other hand very small particles may be only identified as superparamagnetic by MS.

4. Conclusion

The content of iron phases, i.e. ϵ -Fe₂O₃, hematite α -Fe₂O₃, magnetite Fe₃O₄, and superparamagnetic components, in the samples depends on the conditions of preparation. However, none of the preparation conditions, such as iron oxide concentration, sonification power, temperature and/or atmosphere of annealing, led to the production of only ϵ -Fe₂O₃ phase embedded in amorphous silica matrix. Annealing atmosphere has a pronounced effect on the size and distribution of iron-oxide particles within silica matrix. Samples annealed in nitrogen contain higher amount of particles in superparamagnetic state at room temperature (particle size about 5 nm and less) than samples annealed in air.

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