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Synthesis of magnetic nanoparticles via the sol-gel technique

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Magnetic nanopowders have been prepared by the sol-gel method. The particles were characterized using nitrogen adsorption-desorption isotherms and SEM techniques. The properties of the magnetic nanopowders were characterized by ^{57}Fe Mössbauer absorption spectrometry and magnetization measurements.

Key words: *sol-gel; magnetic particles; ferromagnetic, superparamagnetic*

1. Introduction

The development of polymer and hybrid particles composed of polymeric and magnetic materials is of great interest due to their e.g. biological applications. For such purposes it is necessary that the materials – especially the surfaces of the particles – are biocompatible and non-toxic [1]. Studies of magnetic nanoparticles combine a broad range of synthetic and investigative techniques from physics, chemistry, and materials science [2]. In this paper, we report preliminary results of the structural and magnetic properties of silica powders doped with magnetic particles prepared by the sol-gel method. One of the most interesting aspects of this approach is the possibility of producing uniform silica spheres of submicron size. It needs to be stressed that these syntheses are carried out at room temperature in water solutions of the precursors.

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Magnetic nanoparticles exhibit new phenomena such as superparamagnetism, high field irreversibility, high saturation field, extra anisotropy contributions, or shifted loops after field cooling. These phenomena arise from finite sizes and surface effects that dominate the magnetic behaviour of individual nanoparticles [3].

2. Experimental

Silica nanopowders were prepared by hydrolysis and polycondensation of tetraethyl orthosilicate in the systems $Si(C_2H_5O)_4/NH_3/C_2H_5OH$. The sol–gel synthesis of spherical silica particles with a narrow size distribution is based on the Stöber method [4]. The final particle sizes depend on the silicon alkoxide precursors and the alcohol used. Sols were usually mixed for 2 h in an ultrasonic bath at room temperature. After gelation, the wet gels were dried slowly, starting from room temperature up to 80 °C (for 2, 3 days). The magnetic dopant solutions (FF6.2 dissolved in hexane) were added to the hydrolizates. Batches of the magnetic powders were obtained by adding 0,8 cm^3 of the dopant solutions to 56 cm^3 of the hydrolizates. The magnetic dopant FF6.2 is a molecular magnet containing particles of Fe^{2+} and Fe^{3+} belonging to a new group of EMC compounds (EMC – electromagnetic compatibility) capable of absorbing electromagnetic energy. FF6.2 was prepared by Kolodziej et. al. [5].

3. Results and discussion

Magnetic powders were obtained by encapsulating magnetic nanoparticles in SiO_2 spherical submicron grains (Fig. 1). The sizes and morphologies of the non-doped and dye-doped silica microspheres were determined from photographs obtained by scanning electron microscopy (JEOL JMS-5800LV I S-180 Cambridge).

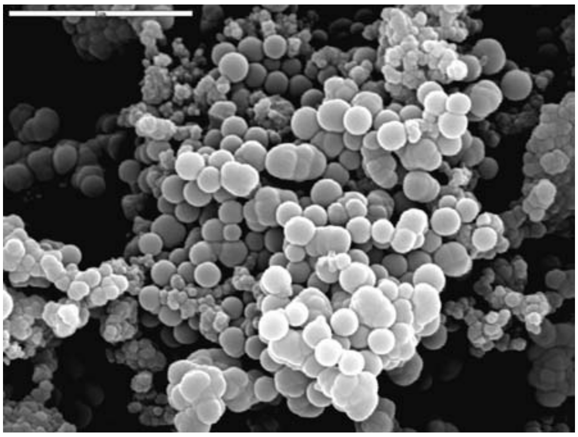

Fig. 1. A SEM photograph of SiO_2 powders doped with magnetic nanoparticles; magnification 8500×

The silica particles are biocompatible and non-toxic. Magnetic nanoparticles did not occur on the surfaces of the grains; they were entrapped in the grain bulk. XPS was performed using a SPES ESCA system equipped with a Phoibos 100 analyser and a Speclab software.

Measurements of the specific BET surface areas (and pore size distributions) were performed with a BET Surface Analyser (Coulter SA 3100) after the samples were outgassed (15 minutes) at 1200 °C. BET isotherms of the SiO_2 powders doped with the magnetic material have the form typical of the isotherm Type II for non-porous absorbents (Fig. 2). The BET surface area of this powder was 6,33 m^2/g.

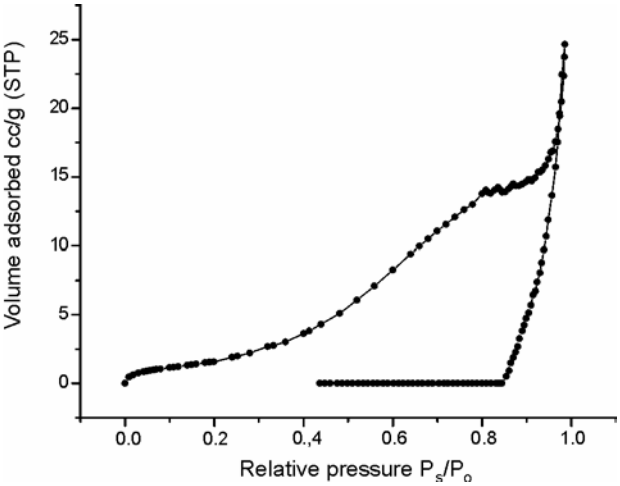

Fig. 2. BET isotherm of SiO_2 powder doped with magnetic nanoparticles

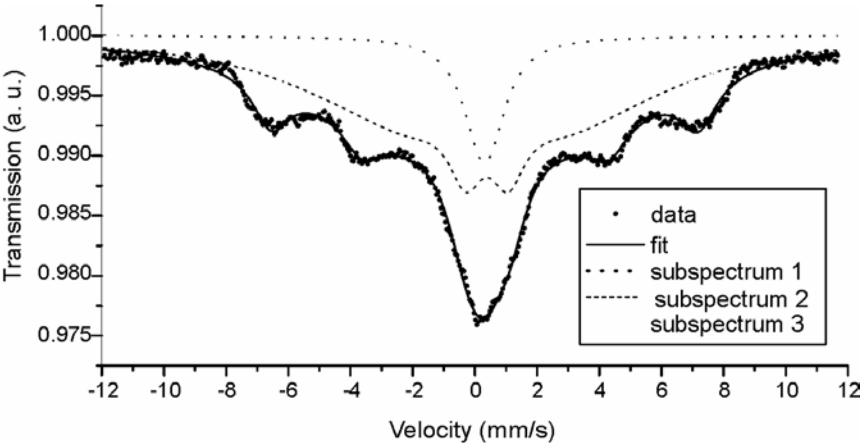

Fig. 3. Mössbauer spectra of magnetic particles in silica powders

Mössbauer spectra were obtained at room temperature (Fig. 3). Measurements were done in the transmission mode with ^{57}Co diffused into a Cr matrix as the source, moving with a constant acceleration. The spectrometer was calibrated using a standard Fe foil and the isomer shift was expressed with respect to this standard at 293 K. The fitting of the spectra was performed with the help of the NORMOS program.

Table 1. The results of Mössbauer measurements of magnetic particles in silica powders

Parameter	Subspectrum 1	Subspectrum 2	Subspectrum 3
Isomer shift δ	0.31 mm/s	0.39 mm/s	0.32 mm/s
Quadrupole splitting ΔE_Q	0.00 mm/s	–0.01 mm/s	0.00 mm/s
Hyperfine field B_{Hf}	X	28.4 T	42.7 T
Full line width at the half height of the BHf distribution	1.9 mm/s	44 T	1.44 mm/s

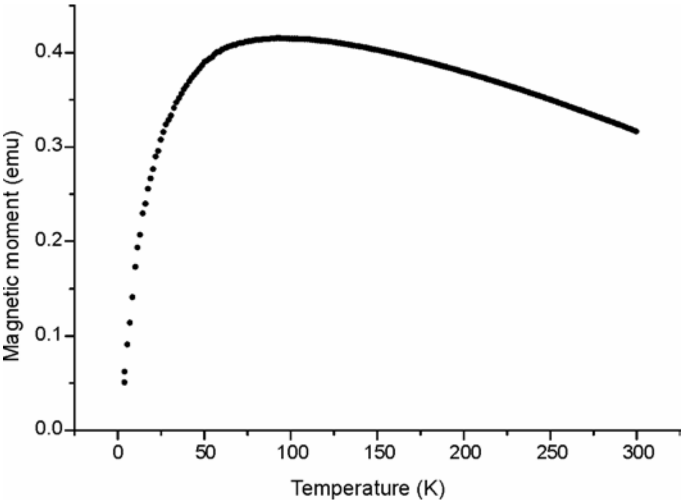

Fig. 4. The ZFC curve. Temperature dependence of the magnetic moment of doped powders

The spectrum contains: a singlet (subspectrum 1, isomer shift 0.31 mm/s) corresponding to the iron in the particles in the superparamagnetic state (the fraction of particles with a blocking temperature below the temperature of measurements), a broad sextet (subspectrum 2, isomer shift 0.39 mm/s, quadrupole splitting 0,01 mm/s, hyperfine field 28.4 T) corresponding to the iron in the particles with a blocking temperature very close to the temperature of measurement, a sextet (subspectrum 3, isomer shift 0.32 mm/s, quadrupole splitting 0.00 mm/s, hyperfine field 42.7 T) probably corresponding to ferrimagnetic magnetite Fe_3O_4. The most probable is maghemite (γ-Fe_2O_3) due to an isomer shift of 0.32 mm/s, which is the characteristic value of three-valent iron.

Magnetization data were obtained with a DC magnetometer (PPMS 9T) in the temperature range of 2–350 K in fields up to 5 T. Low-field temperature scans of zero-field cooled (ZFC) DC magnetization were measured at the field of 0.01 T. The temperature dependence of the magnetic moment of the the samples is shown in Fig. 4.

The “frozen” positions of the magnetic moments of grains in the investigated powders were not random. They were opposite to the direction of the applied external magnetic field (100 Gauss, or 0.01 T). The established blocking temperature (i.e., the point at which the ZFC curve first derivative is zero) $T_B = 96$ K. The magnetization behaviour of the investigated particles above the blocking temperature is identical to that of atomic paramagnets (superparamagnetism) [6]. The dependence of magnetic induction on the external magnetic field obtained at 4 K for doped silica powders is shown in Fig 5. We have observed a weak ferromagnetic character of the samples with a coercive field $H_c = 80$ Oe at this temperature.

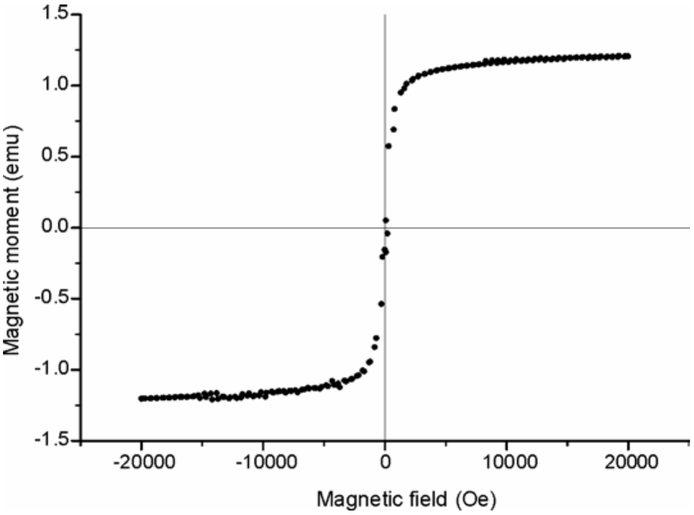

Fig. 5. Magnetic induction vs. external magnetic field dependence at 4 K for doped silica powders. Coercive field *Hc* = 80 Oe

4. Conclusions

SiO_2 powders doped with magnetic nanoparticles (iron crystals of an average grain size of 5 nm) have been prepared via the sol-gel method. The obtained silica particles are bio-inert and non-toxic. The BET surface area of the magnetic powders is 6,33 m^2/g, their adsorption isotherms being of type II, typical of non-porous absorbents. Very broad peaks observed at room temperature in the Mössbauer spectra show that the samples are in the superparamagnetic state. Doped silica powders display a weak ferromagnetic character at 4 K.

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