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Magnetic Properties of γ -Fe₂O₃ Nanopowder Synthesized by Atmospheric Microwave Torch Discharge

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A nanopowder containing γ -Fe₂O₃ particles was synthesized by adding a gas mixture of H₂/Fe(CO)₅ into a microwave torch discharge at 1 bar. The presence of γ -Fe₂O₃ phase was confirmed by powder X-ray diffraction (mean crystallite size $d_{\text{XRD}} = 24$ nm). The dominating characteristic sextets of γ -Fe₂O₃ were identified in the Mössbauer spectrum taken at 5 K. The presence of pure Fe₃O₄ in the nanopowder was excluded. The Mössbauer spectrum taken at 5 K exhibited six times larger total spectrum area than the Mössbauer spectrum taken at 293 K. Zero field cooled/field cooled curves measured down to 4 K in the magnetic field of 7.9 kA/m are reported.

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1. Introduction

Over the past years, a lot of work has been done on the synthesis of γ -Fe₂O₃ (maghemite) particles because of their potential applications for ferrofluid, magnetic refrigeration, bioprocessing, information storage and gas sensitive materials [1]. Maghemite has spinel structure with two magnetically nonequivalent interpenetrating sublattices and exhibits ferrimagnetic behavior [2]. Its structural formula is $[\text{Fe}^{3+}]_{\text{A}}[\text{Fe}_{5/3}^{3+}\square_{1/3}]_{\text{B}}\text{O}_4$ and it differs from Fe₃O₄ (magnetite) by the presence of cationic vacancies \square within octahedral B sites.

Nanoparticles can be also synthesised in a wide range of plasma processes, which can be classified e.g. by gas temperature and pressure. At atmospheric pressure, maghemite particles have been synthesized using the vaporized Fe(CO)₅ carried by argon gas and pyrolyzed either in the oxygen plasma generated by microwave plasma jet [3] or in the argon plasma generated by microwave torch discharge [4].

In the present paper we report on the magnetic properties of a γ -Fe₂O₃ nanopowder synthesized by the plasma method used in Ref. [5].

2. Experimental

The apparatus consisted of a microwave generator working at 2.45 GHz powering a double-walled nozzle electrode (via a broadband transition to a coaxial line by means of a ridge waveguide) over which a discharge was ignited [4, 5]. Argon (700 sccm) flowed through the central nozzle and the mixture of H₂ (250 sccm) and Fe(CO)₅ vapour was added into the Ar discharge through the outer concentric nozzle. Vapours of liquid Fe(CO)₅

were entrained into the discharge by Ar (280 sccm) flowing over its surface. The power used at the experiment was 140 W. The nanopowder was collected on reactor walls and labelled T96.

Transmission electron microscopy (TEM) was performed on a Philips microscope CM12 (W cathode, 120 kV electron beam). Phase composition was studied by X-ray diffraction (XRD) with a PANalytical X'Pert Pro MPD device (Co K_{α}). XRD pattern fitting was done using commercial software and database and it yielded mean crystallite size d_{XRD} for a studied phase [6].

⁵⁷Fe Mössbauer spectra (MS) were obtained at standard transmission geometry with ⁵⁷Co in Rh matrix source. As a result of the fitting procedure performed with CONFIT [7] we obtained the value of the relative spectrum area A for a given phase and spectral component parameters: hyperfine magnetic induction B_{HF} , quadrupole shift ε_Q , quadrupole splitting ΔE_Q and isomer shift δ (against α -Fe). A CCS-800 Mössbauer closed cycle refrigerator system from Janis was used for low-temperature measurements.

A physical properties measurement system PPMS 9 from Quantum Design was employed for low-temperature magnetic measurements (ACMS option). High-temperature magnetic measurements were done on a vibrating sample magnetometer (VSM) EG&G PARC.

3. Results and discussion

The XRD pattern of the T96 sample was fitted with cubic maghemite-C with partially ordered vacancies (ICSD #87119, unit cell $a = 0.8345$ nm, space group $P4_332$) with the result: $a = 0.8358$ nm, $d_{\text{XRD}} = 24$ nm. Compared to Fe₃O₄ (ICSD #75627, unit cell $a = 0.8397$ nm, space group $Fd-3mZ$) γ -Fe₂O₃ has distinctive lines at $2\theta = 17.5^\circ, 27.8^\circ, 30.5^\circ, 58.9^\circ, 85.4^\circ$ which are not present in the Fe₃O₄ pattern. Because the lines of Fe₃O₄ are a subset of the lines of γ -Fe₂O₃, the presence of Fe₃O₄ could not be excluded. A very low-intensity peak at

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$2\theta = 52.5^\circ$ was assigned to the main diffraction line of α -Fe (ICSD #53451). The other peaks typical of α -Fe were not present.

Characteristic powder morphology and particle sizes can be observed in Fig. 1. Although particles smaller than ~ 30 nm prevail, larger particles with diameters up to ~ 100 nm could be found in TEM images. It was also observed that some smaller particles formed chains. The diffraction rings in electron powder diffractograms were undoubtedly assigned to γ -Fe₂O₃/Fe₃O₄.

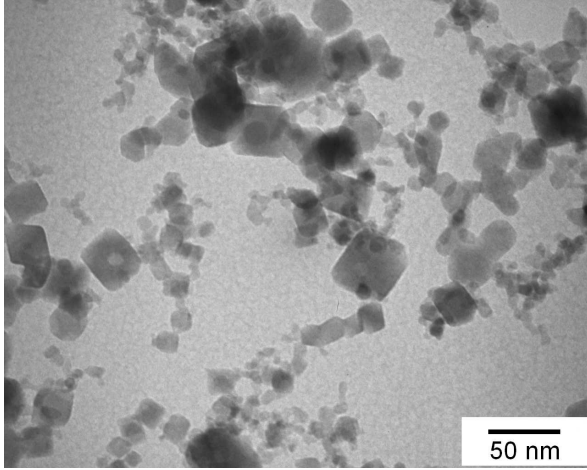


Fig. 1. TEM image for the T96 nanopowder.

The Mössbauer spectrum (MS) of maghemite (spinel structure with two sublattices) consists of two sextets [2]. As can be seen in Fig. 2, the integral spectrum area (I_{SA}) was six times higher at 5 K (measured for 2 days; cryostat was on) than at 293 K (10 days spectrum; cryostat was off). The broader lines observed at 5 K were due to the vibrations of the closed cycle cryostat. The anomalous decrease of the absorption at 293 K is attributed to a large portion of particles, which can thermally move, and the chain-like morphology of interconnected particles, which enables diffusive tilting motions of particles [8]. This way the probability of resonance absorption of γ -radiation on ^{57}Fe nuclei is lowered. It is an anomalous deviation from the recoilless Lamb–Mössbauer factor, which is based on the Debye model of a solid [9]. Similar decrease was observed for a nanopowder synthesized in low-pressure microwave plasma [10].

In the MS measured at 293 K, due to small absorption, a doublet ($\Delta E_Q = 0.40$ mm/s, $\delta = 0.21$ mm/s, dashed line) and a singlet ($\delta = 0.41$ mm/s; full line) were visible. They belonged to Fe impurities in the Al foil in which the nanopowder was wrapped [11]. It was confirmed by the separate MS measurement of the Al foil only. The spectral component characteristic for superparamagnetic γ -Fe₂O₃ particles (doublet with $\Delta E_Q = 0.23$ mm/s, $\delta = 0.33$ mm/s [2]) was surprisingly not present in this spectrum.

The MS measured at 5 K, which was decisive for phase assessment, was fitted with: Fe_A sextet ($B_{\text{HF}} = 51.0$ T,

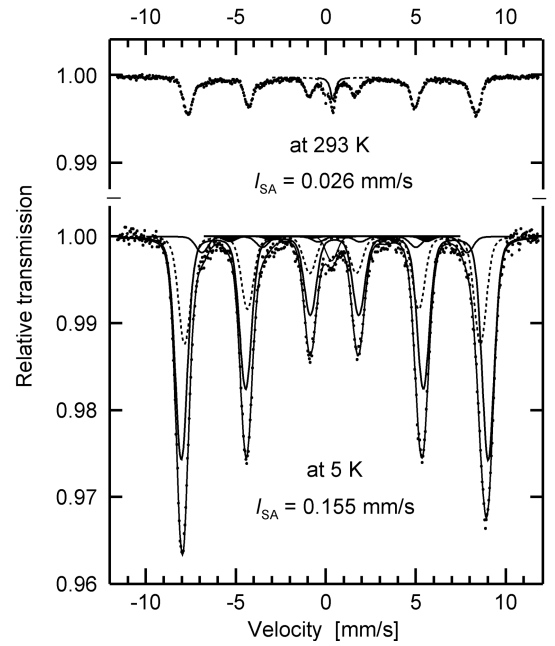


Fig. 2. Mössbauer spectra for the T96 nanopowder.

$2\varepsilon_Q = -0.04$ mm/s, $\delta = 0.39$ mm/s, $A = 0.30$, dashed line), Fe_B sextet ($B_{\text{HF}} = 52.9$ T, $2\varepsilon_Q = 0.02$ mm/s, $\delta = 0.49$ mm/s, $A = 0.64$, full line), S1 sextet ($B_{\text{HF}} = 45.8$ T, $2\varepsilon_Q = -0.26$ mm/s, $\delta = 0.61$ mm/s, $A = 0.04$, full line), an insignificant α -Fe sextet ($B_{\text{HF}} = 33.9$ T, $2\varepsilon_Q = 0.00$ mm/s, $\delta = 0.14$ mm/s, $A = 0.01$, black filler), and a low-intensity Fe³⁺ singlet ($\delta = 0.32$ mm/s, $A = 0.01$, thin line). It means that 32% of Fe³⁺ ions in bulk-like γ -Fe₂O₃ occupied tetragonal A sites (according to spectral areas: $A_{\text{FeA}}/(A_{\text{FeA}} + A_{\text{FeB}})$) and the rest, i.e. 68% of Fe³⁺ ions, B sites. The S1 sextet could belong to the surfaces of γ -Fe₂O₃ nanoparticles.

A loose nanopowder was pressed into pellets for magnetic measurements. The parameters of the hysteresis loop (HL) measured on the VSM at 293 K were: $H_C = 12.5$ kA/m, $\sigma_R = 16.1$ Am²/kg, $\sigma_S = 66.6$ Am²/kg (at 795 kA/m) (Fig. 3). The HL measured on the PPMS at 4 K provided the values: $H_C = 42.6$ kA/m, $\sigma_R = 14.3$ Am²/kg, $\sigma_S = 77.0$ Am²/kg (at 795 kA/m). The reference value for bulk-like γ -Fe₂O₃ is $\sigma_S = 82$ Am²/kg [12].

The measured zero field cooled (ZFC) and field cooled (FC) curves (Fig. 4) showed the split between σ_{ZF} (which remained constant) and σ_{FC} curves over the whole measurement range. σ_{ZFC} exhibited no maximum but grew strongly with increasing temperature, i.e. particle magnetic moments tended to align in the direction of H_{ext} . We suppose that particles were strongly magnetically coupled, so superparamagnetic relaxation below 300 K did not take place. No features near 120 K which would mark the Verwey transition expected for Fe₃O₄ phase were present on the curves [13].

It can be summarized that the atmospheric microwave torch discharge method is suitable for the synthesis of

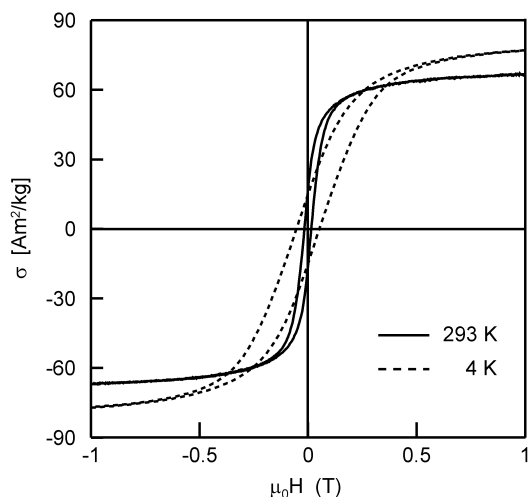


Fig. 3. Hysteresis loops for the T96 nanopowder.

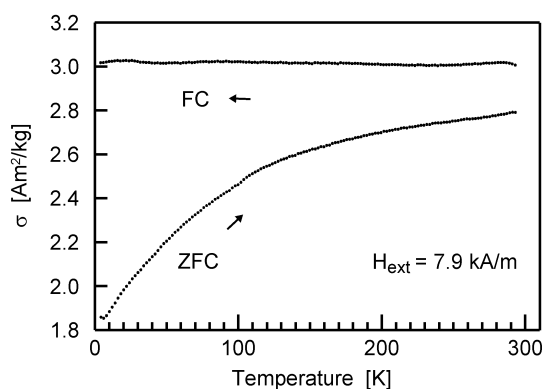


Fig. 4. ZFC/FC curves for the T96 nanopowder.

γ -Fe₂O₃ nanoparticles. The presented analysis supplements the one given in Ref. [4].

Acknowledgments

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