



ϵ -Fe₂O₃ nanoparticles synthesized in atmospheric-pressure microwave torch

Bohumil David^{a,*}, Naděžda Pizúrová^a, Petr Synek^b, Vít Kudrle^c,
Ondřej Jašek^{b,c}, Oldřich Schneeweiss^a

^a CEITEC IPM, Institute of Physics of Materials, ASCR, v.v.i., Žitkova 22, CZ-61662 Brno, Czech Republic

^b CEITEC MU, Central European Institute of Technology, Masaryk University, Kamenice 753/5, CZ-62500 Brno, Czech Republic

^c Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, CZ-61137 Brno, Czech Republic

ARTICLE INFO

Article history:

Received 24 June 2013

Accepted 15 November 2013

Available online 23 November 2013

Keywords:

ϵ -Fe₂O₃

Nanoparticles

Microwave plasma

Mössbauer spectroscopy

ABSTRACT

The article reports on ϵ -Fe₂O₃ nanoparticles synthesized in a single step by atmospheric-pressure microwave torch discharge using gaseous precursors only. Morphology and composition of the as-synthesized nanopowder were studied by HR-TEM, XRD, and Mössbauer spectroscopy. In the studied nanopowder, ϵ -Fe₂O₃ phase ($d_{\text{XRD}}=25$ nm, 32 wt%) together with α -Fe₂O₃ and γ -Fe₂O₃ phases was found. The characteristic ϵ -Fe₂O₃ and α/γ -Fe₂O₃ sextets in the Mössbauer spectra measured at 293 and 5 K confirmed the phase composition of the powder. Compared with the methods currently used for the synthesis of ϵ -Fe₂O₃ nanoparticles, atmospheric-pressure microwave torch discharge appears as a new synthesis route for obtaining ϵ -Fe₂O₃ nanoparticles.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Presently, ϵ -Fe₂O₃ polymorph of ferric oxide generates a high interest due to its significant magnetic property: ϵ -Fe₂O₃ rod-shaped nanoparticles have the giant coercivity of ~ 1.6 MA/m at room temperature [1–4], which is expected to have large applicability.

In past years, the methods used for its synthesis were sol–gel [4–8], sol–gel combined with reverse-micelle [2,3], solid state [9–12], co-precipitation [13], solid-phase decomposition under exposure to γ -rays [14], and laser-assisted pyrolysis of a gas mixture [15]. As ϵ -Fe₂O₃ is structurally an intermediate polymorph between γ -Fe₂O₃ and α -Fe₂O₃ [16], it is often observed in synthesized samples together with α -Fe₂O₃, γ -Fe₂O₃ or β -Fe₂O₃ [10]. Hence, it would be of a great advantage if ϵ -Fe₂O₃ nanoparticles could be obtained as a nanopowder directly by a one step gas phase or plasma method.

In this article, we show that ϵ -Fe₂O₃ nanoparticles can be easily synthesized by a plasma-enhanced chemical vapor deposition (PE-CVD) method at atmospheric pressure.

2. Experimental

For the synthesis of Fe-based nanoparticles microwave torch discharge at atmospheric pressure was used. The apparatus was the

same as it was used in our previous works [17,18]. It consisted of a microwave generator working at the frequency of 2.45 GHz and a standard rectangular waveguide transmitting microwave power to a hollow nozzle electrode over which the 2–3 cm long plasma torch (1 mm over the electrode) developed. The plasma torch was enclosed by a quartz tube (length 200 mm, diameter 80 mm) with a duralumin shielding net wrapped around it. The discharge was ignited in argon, which flowed through the central gas flow channel, and the reactive mixture of H₂/O₂ gas and vapors of Fe(CO)₅ (Alfa Aesar, purity 99.5) was added through the outer channel. The synthesis parameters for the further analyzed sample (chosen from 15 samples each of them contained ϵ -Fe₂O₃ particles) were 420 sccm of Ar through the central nozzle, 140 sccm of Ar through the Fe(CO)₅ bubbler, 500 sccm of O₂, the power of 230 W, and the deposition time was 60 min. The synthesized nanopowder resided on the inner wall of the quartz tube from which it was collected and without any post-processing stored in air.

The phase composition was studied by X-ray diffraction (XRD) on a PANalytical X'Pert Pro MPD device. XRD pattern fitting procedure yielded lattice constants a , b , c , mean crystallite size d_{XRD} , and weight fraction F [19,20].

High-resolution transmission electron (HR-TEM) observations were carried out on a JEM-3010 JEOL microscope (LaB₆ cathode, 300 kV electron beam). Copper grids coated with a carbon support film were used to prepare the sample. TEM images were processed with the help of a commercial database and software [20,21].

⁵⁷Fe Mössbauer spectra were obtained at standard transmission geometry with ⁵⁷Co in Rh matrix using a CCS-800 Janis Mössbauer

* Corresponding author. Tel.: +420 532290436; fax: +420 541218657.

E-mail addresses: david@ipm.cz, bohumildavid@seznam.cz (B. David).

closed-cycle refrigerator system. As a result of the fitting procedure performed with CONFIT [22], we obtained spectral component parameters: hyperfine magnetic induction B_{HF} , quadrupole shift ε_{Q} , quadrupole splitting ΔE_{Q} , isomer shift δ_{IS} (against α -Fe), and relative spectrum area.

3. Results and discussion

The presence of ε - Fe_2O_3 phase in the as-synthesized nanopowder was firstly observed in its XRD pattern (Fig. 1) whereby the following reference patterns were used by its fitting: cubic maghemite-C γ - Fe_2O_3 (ICSD #87119), tetragonal maghemite-Q γ - Fe_2O_3 (ICSD #87121), rhombohedral hematite α - Fe_2O_3 (ICSD #82137), and orthorhombic ε - Fe_2O_3 (ICSD #415250) [20]. Rietveld refinement procedure (ending with $R_{\text{wp}}=2.93$ $\text{GOF}=7.61$) provided the values for the mentioned phases: maghemite-C phase ($a=0.8349$ nm, $d_{\text{XRD}}=7$ nm, $F=24$ wt%), maghemite-Q phase ($a=0.8350$ nm, $c=2.4977$ nm, $d_{\text{XRD}}=33$ nm, $F=23$ wt%), ε - Fe_2O_3 phase ($a=0.5087$ nm, $b=0.8795$ nm, $c=0.9479$ nm, $d_{\text{XRD}}=25$ nm, $F=32$ wt%), and α - Fe_2O_3 phase ($a=0.5035$ nm, $b=0.5035$ nm, $c=1.3748$ nm, $d_{\text{XRD}}=51$ nm, $F=21$ wt%). Maghemite-C/Q phases differ only in the degree of vacancy ordering [1].

The definitive evidence for the presence of ε - Fe_2O_3 in the nanopowder provided Mössbauer spectrometry. In the Mössbauer spectrum of the sample measured at 293 K, ε - Fe_2O_3 components were clearly distinguishable from those of α - Fe_2O_3 and γ - Fe_2O_3 (Fig. 2).

The sextets corresponding to four different Fe sites in the crystalline structure of ε - Fe_2O_3 were clearly identified (site Fe_{1+2} : $B_{\text{HF}}=45.6$ T, $\varepsilon_{\text{Q}}=-0.21$ mm/s, $\delta=0.40$ mm/s, $A=0.18$; site Fe_3 : $B_{\text{HF}}=40.1$ T, $\varepsilon_{\text{Q}}=0.04$ mm/s, $\delta=0.37$ mm/s, $A=0.09$; site Fe_4 : $B_{\text{HF}}=26.4$ T, $\varepsilon_{\text{Q}}=-0.16$ mm/s, $\delta=0.23$ mm/s, $A=0.09$). The sextets for the Fe_1 and Fe_2 sites had the same parameters and were handled as one sextet. Such ε - Fe_2O_3 sextets are well known from the literature [6]. Some other spectral components, could be assigned to concrete phases, namely α - Fe_2O_3 ($B_{\text{HF}}=51.2$ T, $\varepsilon_{\text{Q}}=-0.09$ mm/s, $\delta=0.39$ mm/s, $A=0.34$) and γ - Fe_2O_3 (Fe_B sextet: $B_{\text{HF}}=49.5$ T, $\varepsilon_{\text{Q}}=0.07$ mm/s, $\delta=0.42$ mm/s, $A=0.08$; Fe_A sextet: $B_{\text{HF}}=49.0$ T, $\varepsilon_{\text{Q}}=0.01$ mm/s, $\delta=0.25$ mm/s, $A=0.11$) phases [23]. However, because of the presence of superparamagnetic particles, remaining three sextets and two doublets (not shown in Fig. 2),

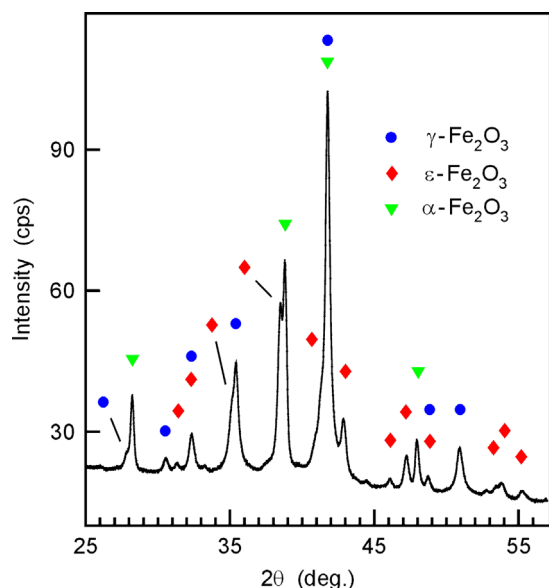


Fig. 1. The XRD pattern (Co K_{α}) for the nanopowder.

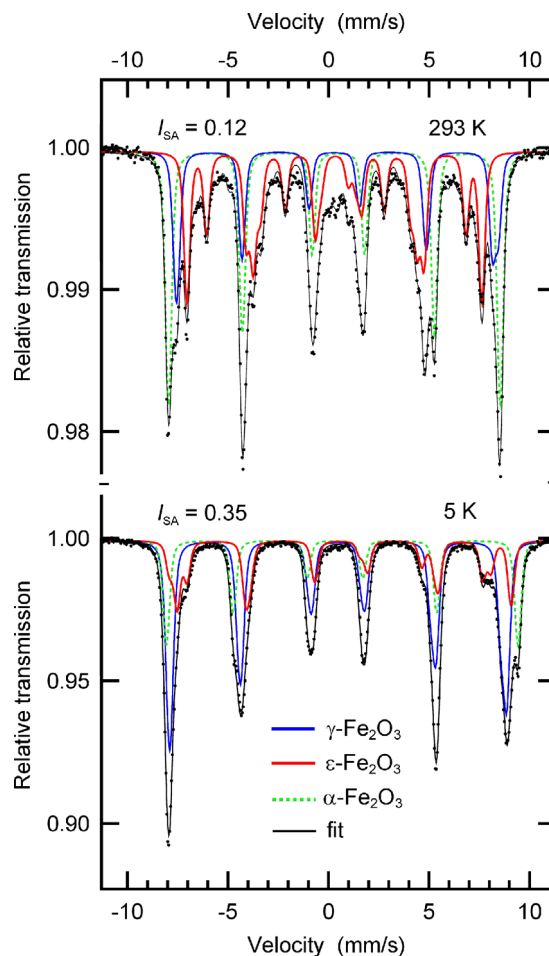


Fig. 2. The transmission ^{57}Fe Mössbauer spectra for the nanopowder measured at the indicated temperatures. Only the components not influenced by superparamagnetic relaxation are shown in the spectrum measured at 293 K.

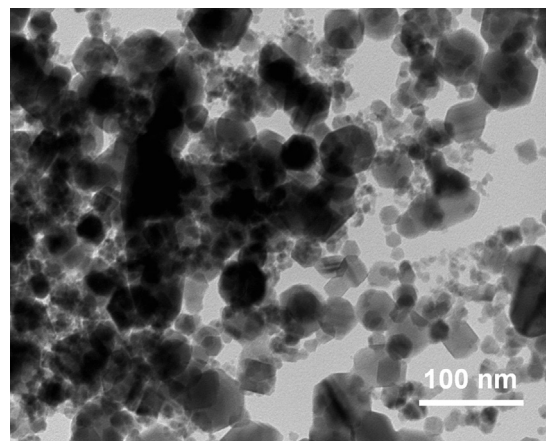


Fig. 3. Lower-resolution TEM image for the portion of the nanopowder.

which were needed to fit the spectrum properly, could not be assigned to specific phases due to their untypical parameters.

No superparamagnetic components were present in the Mössbauer spectrum measured at 5 K (Fig. 2), so it was then easily fitted with α - Fe_2O_3 , γ - Fe_2O_3 and ε - Fe_2O_3 phases only. Hematite, α - Fe_2O_3 , which is antiferromagnetic below the Morin transition temperature of 250 K, was fitted with one sextet ($B_{\text{HF}}=54.3$ T, $\varepsilon_{\text{Q}}=0.18$ mm/s, $\delta=0.49$ mm/s, $A=0.22$). Ferrimagnetic γ - Fe_2O_3 was again fitted with two sextets (Fe_B sextet: $B_{\text{HF}}=52.0$ T,

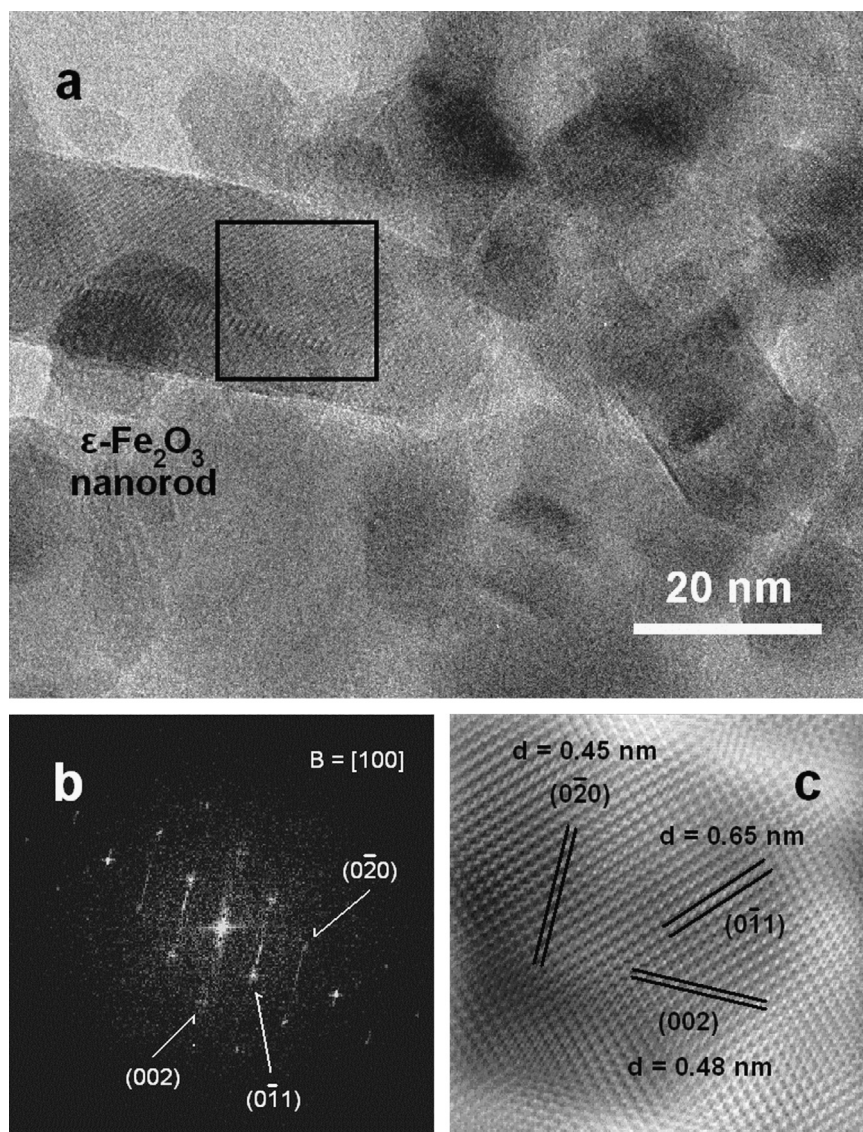


Fig. 4. (a) The HR-TEM image for the nanopowder showing one ϵ -Fe₂O₃ nanoparticle, (b) the Fast Fourier Transformed (FFT) image of the square region depicted in (a), and (c) the inverse Fourier transformation of the filtered FFT image.

$\epsilon_Q = 0.00$ mm/s, $\delta = 0.50$ mm/s, $A = 0.35$; Fe_A sextet: $B_{HF} = 51.4$ T, $\epsilon_Q = 0.00$ mm/s, $\delta = 0.28$ mm/s, $A = 0.17$) [24]. ϵ -Fe₂O₃ compound, whose magnetic ordering below ~ 70 K is supposed to be characterized by a square-wave incommensurate structure [6], was fitted with three sextets (site Fe₁₊₂: $B_{HF} = 51.6$ T, $\epsilon_Q = 0.06$ mm/s, $\delta = 0.71$ mm/s, $A = 0.13$; site Fe₃: $B_{HF} = 49.7$ T, $\epsilon_Q = -0.26$ mm/s, $\delta = 0.34$ mm/s, $A = 0.06$; site Fe₄: $B_{HF} = 45.7$ T, $\epsilon_Q = -0.04$ mm/s, $\delta = 0.34$ mm/s, $A = 0.07$) [6,9].

The TEM image with lower magnification of the portion of the powder (Fig. 3) shows typical morphology of obtained ferric oxide nanoparticles. To check the morphology of ϵ -Fe₂O₃ nanoparticles the HR-TEM was employed (Fig. 4) and the rod-shaped particle in Fig. 4a was confirmed to be ϵ -Fe₂O₃. The interplanar distances measured and shown in Fig. 4c very well correspond to the reference values according to the ICSD #415250 entry, which are $d_{(011)} = 0.640$ nm, $d_{(020)} = 0.439$ nm, and $d_{(002)} = 0.471$ nm.

4. Conclusions

According to our knowledge, except for the single work of Schrader [25], who used direct current arc discharge between iron

electrodes in O₂ atmosphere in 1963, ϵ -Fe₂O₃ has not been synthesized by any other plasma method. Our work evidences the possibility of obtaining ϵ -Fe₂O₃ nanoparticles by a very simple and effective method of atmospheric-pressure microwave torch discharge in continual regime using gaseous precursors only. This synthesis procedure can run continuously with a yield of 1 g powder per hour. This yield is determined by the experimental setup parameters (eg. reactor dimensions, available flow rates and material collecting method) and could be easily scaled up by orders of magnitude for large scale industrial production. Nevertheless, either an appropriate method should be developed for the separation of ϵ -Fe₂O₃ nanoparticles from α/γ -Fe₂O₃ particles (but all three phases exhibit magnetic ordering) or the method should be optimized to provide a single-phase product (which was already reported for γ -Fe₂O₃ [17]).

Acknowledgments

This work was supported by the GA CR (202/08/0178, P205/10/1374, 106/08/1440), the ASCR (AV0Z20410507), the Project R&D Center for Low-Cost Plasma and Nanotechnology Surface Modifications

CZ.1.05/2.1.00/03.0086 and it was realized in CEITEC – Central European Institute of Technology with research infrastructure supported by the project CZ.1.05/1.1.00/02.0068 financed from European Regional Development Fund.

References

- [1] Cornell RM, Schwertmann U. The iron oxides: structure, properties, reactions. Occurrence and uses. 2nd ed. Weinheim: Wiley-VCH; 2003.
- [2] Jin J, Ohkoshi S, Hashimoto K. Adv Mater 2004;16:48–51.
- [3] Ohkoshi S, Sakurai S, Jin J, Hashimoto KJ. Appl Phys 2005;97:10K312.
- [4] Sakurai S, Shimoyama J-I, Hashimoto K, Ohkoshi S. Chem Phys Lett 2008;458:333–6.
- [5] Tronc E, Chanéac C, Jolivet JPJ. Solid State Chem 1998;139:93–104.
- [6] Gich M, Frontera C, Roig A, Taboada E, Molins E, Rechenberg HR, Ardisson JD, Macedo WA, Ritter C, Hardy V, Sort J, Skumryev V, Nogués J. Chem Mater 2006;18:3889–97.
- [7] Popovici M, Gich M, Nižňanský D, Roig A, Savii C, Casas L, Molins E, Zaveta K, Enache C, Sort J, De Brion S, Chouteau G, Nogués J. Chem Mater 2004;16:5542–8.
- [8] Brázda P, Nižňanský D, Rehspringer J-L, Poltierová-Vejpravová JJ. Sol-Gel Sci Technol 2009;51:78–83.
- [9] Kurmoo M, Rehspringer JL, Hutlova A, D'Orléans C, Vilminot S, Estournès C, Niznansky D. Chem Mater 2005;17:1106–14.
- [10] Sakurai S, Namai A, Hashimoto K, Ohkoshi S. Am Chem Soc 2009;131:18299–303.
- [11] Tadić M, Spasojević V, Kusigerski V, Marković D, Remškar M. Scr Mater 2008;58:703–6.
- [12] Kelm K, Mader W. Z Anorg Allg Chem 2005;631:2383–9.
- [13] Drbohlavova J, Hrdy R, Adam V, Kizek R, Schneeweiss O, Hubalek J. Sensors 2009;9:2352–62.
- [14] Doroshenko VN, Kaurkovskaya VN, Yakubenko EP, Pobokin DI, Entinon IR, Ogenko VM. High Energy Chem 2002;36:157–62.
- [15] Martelli S, Mancini A, Giorgi R, Alexandrescu R, Cojocaru S, Crunteanu A, Voicu I, Balu M, Morjan I. Appl Surf Sci 2000;154:353–9.
- [16] Tuček J, Zboril R, Namai A, Ohkoshi S. Chem Mater 2010;22:6483–505.
- [17] Synek P, Jašek O, Zajíčková L, David B, Kudrle V, Pizúrová N. Mater Lett 2011;65:982–4.
- [18] David B, Pizúrová N, Schneeweiss O, Kudrle V, Jašek O, Synek P. Jpn J Appl Phys 2011;50:F11.
- [19] X'Pert HighScore Plus 2.0a, PANalytical BV, Lelyweg 1, Almelo, the Netherlands.
- [20] ICSD Inorganic Crystals Structure Database, release 2009/1, FIZ Karlsruhe, Eggenstein-Leopoldshafen, Germany.
- [21] DigitalMicrograph™ v. 1.82.366 software, Gatan GmbH, München, Germany. Stadelmann PA, JEMS v. 3.2 software, CIME-EPFL, Lausanne, Switzerland; 2003.
- [22] Žák T, Jirásková Y. Surf Interface Anal 2006;38:710–4.
- [23] Zboril R, Mashlan M, Petridis D. Chem Mater 2002;14:969–82.
- [24] De Grave E, Vochten R, Quenard O, Van San E, Dessyen H, Rousset A. Nanostruct Mater 1999;11:493–504.
- [25] Schrader R, Büttner G. Z Anorg Allg Chem 1963;320:220–34.