e-Fe2O3 nanoparticles synthesized in atmospheric-pressure microwave torch

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The article reports on e-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, e-Fe2O3 phase (d_{XRD}=25 nm, 32 wt%) together with α-Fe2O3 and γ-Fe2O3 phases was found. The characteristic e-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 e-Fe2O3 nanoparticles, atmospheric-pressure microwave torch discharge appears as a new synthesis route for obtaining e-Fe2O3 nanoparticles.

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1. Introduction

Presently, e-Fe2O3 polymorph of ferric oxide generates a high interest due to its significant magnetic property: e-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 e-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 e-Fe2O3 nanoparticles could be obtained as a nanopowder directly by a one-step gas phase or plasma method.

In this article, we show that e-Fe2O3 nanoparticles can be easily synthesized by a plasma-enhanced chemical vapor deposition (PECVD) 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 e-Fe2O3 nanoparticles) 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...
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 $\varepsilon_Q$, quadrupole splitting $\Delta E_Q$, isomer shift $\delta_{IS}$ (against $\alpha$-Fe), and relative spectrum area.

3. Results and discussion

The presence of $\varepsilon$-Fe$_2$O$_3$ 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 $\gamma$-Fe$_2$O$_3$ (ICSD #87119), tetragonal maghemite-Q $\gamma$-Fe$_2$O$_3$ (ICSD #87121), rhombohedral hematite $\alpha$-Fe$_2$O$_3$ (ICSD #82137), and orthorhombic $\varepsilon$-Fe$_2$O$_3$ (ICSD #415250) [20]. Rietveld refinement procedure (ending with $R_{wp} = 2.93$ GOF = 7.61) provided the values for the mentioned phases: maghemite-C phase ($a = 0.8349$ nm, $d_{XRD} = 7$ nm, $F = 24$ wt%), maghemite-Q phase ($a = 0.8350$ nm, $c = 2.4977$ nm, $d_{XRD} = 33$ nm, $F = 23$ wt%), $\varepsilon$-Fe$_2$O$_3$ phase ($a = 0.5087$ nm, $b = 0.8795$ nm, $c = 0.9479$ nm, $d_{XRD} = 25$ nm, $F = 32$ wt%), and $\alpha$-Fe$_2$O$_3$ phase ($a = 0.5035$ nm, $b = 0.5035$ nm, $c = 1.3748$ nm, $d_{XRD} = 51$ nm, $F = 21$ wt%). Maghemite-C/Q phases differ only in the degree of vacancy ordering [1].

The definitive evidence for the presence of $\varepsilon$-Fe$_2$O$_3$ in the nanopowder provided Mössbauer spectrometry. In the Mössbauer spectrum of the sample measured at 293 K, $\varepsilon$-Fe$_2$O$_3$ components were clearly distinguishable from those of $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$ (Fig. 2).

The sextets corresponding to four different Fe sites in the crystalline structure of $\varepsilon$-Fe$_2$O$_3$ were clearly identified (site Fe$_{1+2}$: $B_{HF} = 45.6$ T, $\varepsilon_Q = -0.21$ mm/s, $\delta = 0.40$ mm/s, $A = 0.18$; site Fe$_3$: $B_{HF} = 40.1$ T, $\varepsilon_Q = 0.04$ mm/s, $\delta = 0.37$ mm/s, $A = 0.09$; site Fe$_4$: $B_{HF} = 26.4$ T, $\varepsilon_Q = -0.16$ 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 $\varepsilon$-Fe$_2$O$_3$ sextets are well known from the literature [6]. Some other spectral components, could be assigned to concrete phases, namely $\alpha$-Fe$_2$O$_3$ ($B_{HF} = 51.2$ T, $\varepsilon_Q = -0.09$ mm/s, $\delta = 0.39$ mm/s, $A = 0.34$) and $\gamma$-Fe$_2$O$_3$ (FeB sextet: $B_{HF} = 49.5$ T, $\varepsilon_Q = 0.07$ mm/s, $\delta = 0.42$ mm/s, $A = 0.08$; FeA sextet: $B_{HF} = 49.0$ T, $\varepsilon_Q = 0.01$ 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), 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 $\alpha$-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$ and $\varepsilon$-Fe$_2$O$_3$ phases only. Hematite, $\alpha$-Fe$_2$O$_3$, which is antiferromagnetic below the Morin transition temperature of 250 K, was fitted with one sextet ($B_{HF} = 54.3$ T, $\varepsilon_Q = 0.18$ mm/s, $\delta = 0.49$ mm/s, $A = 0.22$). Ferrimagnetic $\gamma$-Fe$_2$O$_3$ was again fitted with two sextets (FeB sextet: $B_{HF} = 52.0$ T,
$\varepsilon$-Fe$_2$O$_3$ 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 Fe$_{1.2}$: $B_{HF} = 51.6$ T, $\varepsilon = 0.06$ mm/s, $\delta = 0.71$ mm/s, $A = 0.13$; site Fe$_2$: $B_{HF} = 49.7$ T, $\varepsilon = -0.26$ mm/s, $\delta = 0.34$ mm/s, $A = 0.06$; site Fe$_4$: $B_{HF} = 45.7$ T, $\varepsilon = -0.04$ 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 $\varepsilon$-Fe$_2$O$_3$ nanoparticles the HR-TEM was employed (Fig. 4) and the rod-shaped particle in Fig. 4a was confirmed to be $\varepsilon$-Fe$_2$O$_3$. 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 O$_2$ atmosphere in 1963, $\varepsilon$-Fe$_2$O$_3$ has not been synthesized by any other plasma method. Our work evidences the possibility of obtaining $\varepsilon$-Fe$_2$O$_3$ nanoparticles by a very simple and effective method of atmospheric-pressure microwave 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 (e.g., 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 $\varepsilon$-Fe$_2$O$_3$ nanoparticles from $\alpha/\gamma$-Fe$_2$O$_3$ 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 $\gamma$-Fe$_2$O$_3$ [17]).

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