

MAGNETIC $\gamma\text{-Fe}_2\text{O}_3$ NANOPARTICLES OBTAINED BY SOL - GEL SYNTHESIS

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Abstract

$\gamma\text{-Fe}_2\text{O}_3$ nanoparticles embedded in a silica matrix were obtained by sol-gel method and thermal treatment at high temperatures. The effect of the thermal treatment temperature over the phase composition was followed by X-ray diffraction, Mössbauer spectroscopy. XRD analysis indicated that $\gamma\text{-Fe}_2\text{O}_3$ is present as crystalline phase in the nanocomposites annealed at temperatures higher than 900 °C. Based on resulting TEM and XRD data, it can be concluded that synthesized materials possess uniformly distributed spherical nanoparticles with average size around 12 nm at 1100 °C. Mössbauer spectra recorded at 4.2 K show that the magnetic ordered phase is virtually pure $\gamma\text{-Fe}_2\text{O}_3$.

Introduction

Magnetic particles with sizes in the nanometer scale are now of interest because of their many technological applications and unique magnetic properties which differ considerably from those of bulk materials.

Below a critical size, magnetic particles become single domains in contrast with the usual multidomain structure of the bulk magnetic materials exhibiting unique phenomena such as superparamagnetism [1] and quantum tunneling of the magnetization [2]. Magnetic nanoparticles with superparamagnetic behavior, i.e. they display little or no remanence and coercivity while keeping a very high saturation magnetization, have potential applications in medical diagnostic, magnetic drug delivery and cell-sorting systems [3-4] or in magnetic refrigeration technology [5].

In the last decade many studies on the formation of ferric oxide nanoparticles in silica matrix by sol-gel method were developed [6-9]. They showed that iron oxide nanoparticles precipitate in the pores of the matrix, the growth of particles being limited by diameter of the nanopores. However, the iron oxide phase formed in the system is different in many cases, as a result of the sensitivity of the process to the precursors preparation conditions, thermal treatments and the atmosphere employed.

According to X-ray diffraction data, a single phase $\gamma\text{-Fe}_2\text{O}_3$ can be obtained, as magnetic nanoparticles dispersed in a silica matrix, when the content of iron oxide is as small as 13 wt.% [10]. However, additional measurements are required to confirm X-ray diffraction results.

The aim of this work is to obtain and characterise the $\gamma\text{-Fe}_2\text{O}_3$ phase at a certain content in the silica matrix (13 wt. %), following a procedure previously described [10]. Fe and Si precursors solutions were transformed through hydrolysis-condensation reactions into gels at room temperature and then subjected to drying and thermal treatments in 200-1100°C range.

Experimental

Synthesis. A hydroethanolic solution of tetraethoxysilane (Aldrich 98%) and iron (III) nitrate (Riedel de Haen, 96%) were mixed together by stirring at room temperature. The resulted sols (pH~0.9) were kept in covered vessels. Gelation occurs after 15 days. Wet gels were dried at 60-80 °C for 14 h. The dried xerogels with brownish glassy appearance were rather hard. Samples were crushed in an agate mortar, and the resulting powders were subjected to thermal treatments up to 1100 °C in air, in steps of 3 h annealing at every 100 °C, and then the samples were slowly cooled to room temperature. The samples containing 13 wt. % iron oxide and thermally treated at 1000 °C and 1100 °C were labeled F13 1000 and F13 1100, respectively.

Characterisation. The identification of formed crystalline phases was realized by X-ray diffractometry (XRD) using a Siemens D5005 powder diffractometer, with diffracted beam monochromator and Cu K radiation $\lambda = 1.5406 \text{ \AA}$. Diffraction patterns were recorded from 10° to 90° with a step size of 0.1° and a scanning rate of 15 s per step. Transmission electron microscopy (TEM) investigations were carried out using a Hitachi H800MT microscope operating at 200 kV. Mössbauer spectra (MS) were acquired in the temperature range 5-300 K, using a conventional Mössbauer spectrometer with a ⁵⁷Co/Rh source.

Results and Discussion

For samples annealed at temperatures below 1000 °C, XRD data are not relevant for phase identification, because either the particles are too small, or are in amorphous state. X-ray powder diffraction patterns of the samples treated at 1000 °C and 1100 °C, respectively were recorded in order to determine the crystalline phase(s) formed in the nanocomposites (Figure 1). The baseline presents a broad maximum around 22-24° corresponding to the amorphous silica matrix. The epsilon phase of ferric oxide diffraction lines appear in both patterns. The indexing was done using the pattern proposed by Tronc et al. [11] for $\gamma\text{-Fe}_2\text{O}_3$ phase and the JCPDS 16-0653 file [12]. The mean diameter of crystallites of ~ 11 nm was determined by the Scherrer formula ($K = 0.89$) [13], from X-ray diffraction broadening of



(122) line of γ - Fe_2O_3 . Rietveld refinement was done in the case of F13 1100 sample, which seems to contain iron oxide only in the crystalline form of epsilon phase. The resulted cell parameters ($a = 5.0210$, $b = 8.8672$, $c = 9.4565$) are close to that ones reported by Tronc et al. [11] for γ - Fe_2O_3 .

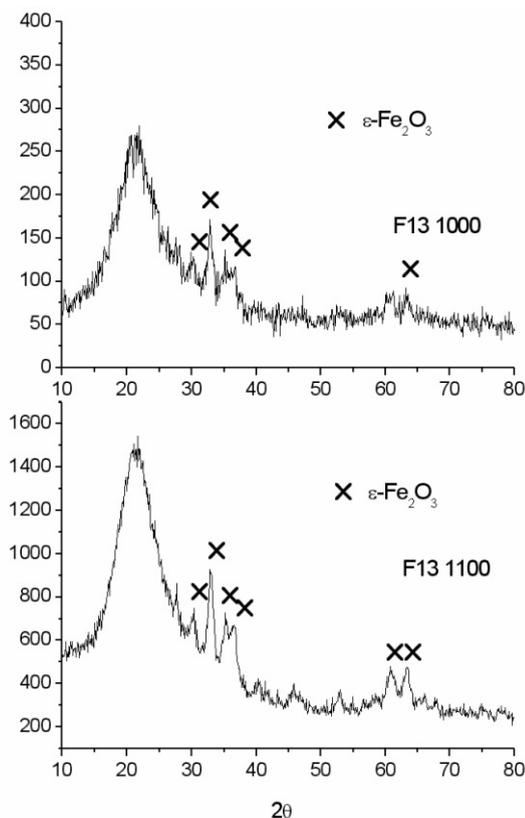


Fig. 1. XRD pattern of F13 1000 and F13 1100 nanocomposites.

The transmission electron microscopy (TEM) image of F13 1100 sample (Figure 2) was thoroughly examined. The shape of the particles is nearly spherical and an average particle size of 11.6 ± 1.6 nm was obtained.

SAED image, (Figure 3) reveals diffraction rings corresponding to γ - Fe_2O_3 phase.

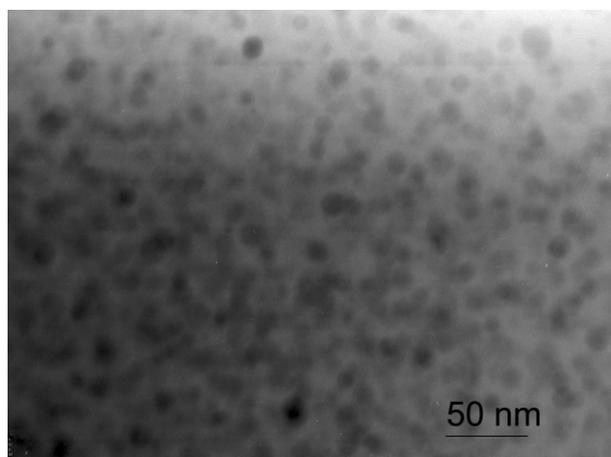


Fig. 2. TEM and SAED of F13 1100 sample.

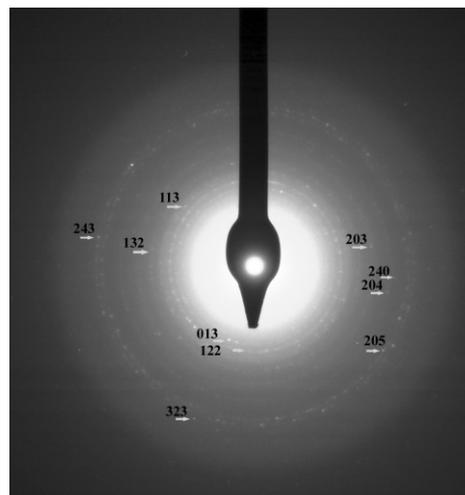


Fig. 3. SAED micrograph of F13 1100 sample.

Table 1 presents the d-spacings resulting from the measurement of the diffraction-ring diameters and the corresponding hkl Miller indices. All d-spacings correspond to γ - Fe_2O_3 pattern [11].

The sample obtained by heat-treatment at 1100°C was examined by Mössbauer spectroscopy. At 300K the registered spectrum shows a superparamagnetic behaviour and no phase identification is possible in such case (Figure 4). From this reason, supplementary spectra at 80K and 4.2K were recorded. The results of spectra fittings are presented in Table 2. At 80K, an amount of $\sim 22\%$ iron is still in the magnetic disordered state. The rest of the iron is present as a magnetic ordered structure. The hyperfine parameters having values in the range between 26.1 T and 50.0 T correspond to γ - Fe_2O_3 [10]. At 4.2 K we deal with a completely ordered magnetic structure (Figure 5) characterised by values of hyperfine fields situated in the range of 46.2-52.3 T, characteristic to γ - Fe_2O_3 [10].

The four different values are assigned to Fe^{3+} ions. This result from the fact that Fe^{3+} ions is localised in three octahedral sites, two of them characterized by similar values (~ 52 T) of hyperfine field and a third one by smaller hyperfine field (~ 50.3 T). The lowest hyperfine field value of ~ 46 T is due to the fourth type of Fe^{3+} ions having tetrahedral coordination.

Conclusions

Sol-gel chemical synthesis of pure γ - Fe_2O_3 nanoparticles embedded in a silica matrix was investigated. Hyperfine parameters derived from Mössbauer spectrum recorded at 4.2 K confirm the X-ray diffraction and electron diffraction results concerning the presence of a unique iron oxide phase, γ - Fe_2O_3 . Transmission electron microscopy observations reveal that γ - Fe_2O_3 particles are roughly spherical and have sizes of around 12 nm.

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Table 1. Observed d-spacings in F13 1100 sample. Experimental error is 0.002 Å.

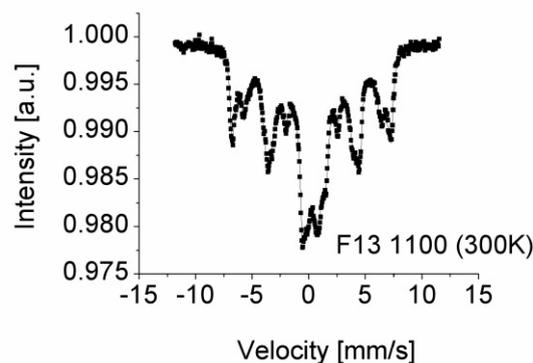
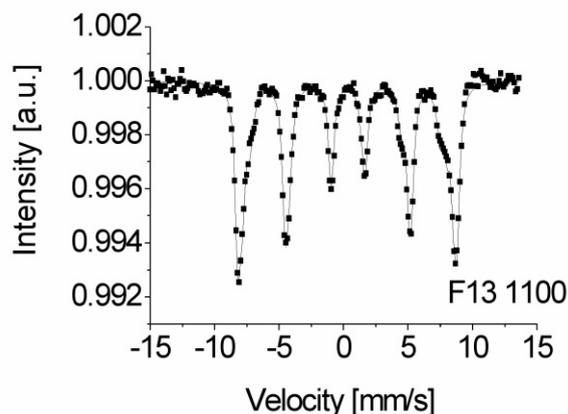
| d-spacings 0.002 [Å] | Ref. [11] | hkl |
|----------------------|-----------|----------|
| 2.965 | 2.962 | 013 |
| 2.718 | 2.718 | 122 |
| 2.565 | 2.561 | 113 |
| 2.455 | 2.451 | 131 |
| 2.283 | 2.285 | 123 |
| 2.238 | 2.237 | 132 |
| 2.020 | 2.018 | 140 |
| 1.985 | 1.980 | 203 |
| 1.730 | 1.732 | 204 |
| 1.532 | 1.534 | 053, 144 |
| 1.522 | 1.518 | 205 |
| 1.473 | 1.469 | 060 |

Table 2. Hyperfine parameters of F13 1100 sample at 80K and 4.2 K.

| No. Sample/ Registering Temperature | Relative area (%) | Isomer shift (mm/s) | Quadrupole splitting | Hyperfine field H_{hf} (T) |
|-------------------------------------|-------------------|---------------------|----------------------|-------------------------------------|
| F13 1100 80 K | 21.2 | 0.42 | -0.13 | 50.0 |
| | 18.5 | 0.40 | -0.09 | 47.5 |
| | 31.8 | 0.32 | -0.10 | 42.0 |
| | 4.8 | 0.40 | 0.25 | 26.1 |
| | 11.3 | 0.39 | - | - |
| | 11.0 | 0.32 | broad component | - |
| F13 1100 4.2 K | 47.9 | 0.35 | -0.10 | 52.3 |
| | 14.7 | 0.64 | 0.04 | 51.9 |
| | 13.1 | 0.29 | -0.23 | 50.3 |
| | 24.3 | 0.27 | -0.07 | 46.2 |

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Fig. 4. The Mössbauer spectrum at 300 K of F13 1100 sample.

Fig. 5. The Mössbauer spectrum at 4.2 K of F13 1100 sample.