Journal of Siberian Federal University. Mathematics & Physics 2016, 9(4), 459–462

УДК 537.632.3

A Comparative Study of γ-Fe_2O_3 and ϵ-Fe_2O_3 Nanoparticles Arising in Borate Glasses Doped with Fe and Gd

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Received 25.08.2016, received in revised form 10.10.2016, accepted 10.11.2016

Formation and properties of the iron oxides γ-Fe_2O_3 *and* ϵ-Fe_2O_3 *nanoparticles arising in glasses of basic compositions* Ge_2O-K_2O-Al_2O_3-B_2O_3 *and* K_2O-Al_2O_3-B_2O_3 *doped with different concentrations of* Fe_2O_3 *and* Gd_2O_3 *and subjected to the additional thermal treatment are studied. The X-ray diffraction, TEM microscopy, magnetooptical effects, and electron spin resonance study allow elucidating the matrix and Gd role in determining the nanoparticle properties.*

Keywords: magnetic nanoparticles, magnetic circular dichroism, magnetic measurements.
DOI: 10.17516/1997-1397-2016-9-4-459-462.

Maghemite, γ-Fe_2O_3, belongs to the most intensively studied magnetic materials due to its properties that can be exploited in a variety of applications in magnetic recording media, catalysts, ferrofluids, biomedicine, magnetic seals and inks, etc. Contrary to γ-Fe_2O_3, compound ε-Fe_2O_3 refers to the unstable phase and therefore a long time it remains poorly studied until the possibility was shown to synthesize ε-Fe_2O_3 nanoparticles in some matrices [1–3]. Increased interest to ε-Fe_2O_3 nanoparticles observed in last years is associated mainly with their very high coercivity [4]. Recently, we presented the first study of the ε-Fe_2O_3 nanoparticles synthesized in the oxide glass matrix [5]. The present work is aimed to the elucidation of the technologic conditions providing formation of the specific iron oxides γ-Fe_2O_3 or ε-Fe_2O_3.

Glasses of the basic composition Ge_2O-K_2O-Al_2O_3-B_2O_3 doped with 3.0 wt.% Fe_2O_3 and 1.5 wt.% Gd_2O_3 (sample 1) and K_2O-Al_2O_3-B_2O_3 doped with 1.5 wt.% Fe_2O_3 and 0.1, 0.2, 0.3, 0.4, 0.6, 1.0 wt.% Gd_2O_3 (samples 2.1–2.6, correspondingly) were synthesized using a technique described in [5]. The glasses were subjected to the additional thermal treatment at 560 °C. The XRD analysis was done at the "Structural Materials Science" beamline in the Kurchatov Synchrotron Radiation Centre. The visualization of particles was carried out using electron microscope JEM-2200FS (JEOL Ltd.) operating in the high-resolution (HRTEM), high-angle annular dark-field scanning (STEM-HAADF) transmission modes and energy dispersive X-ray analysis (EDX). Magnetic properties of the samples were studied with a superconducting quantum interference device (SQUID) magnetometer at temperatures 78–300 K in the applied magnetic field up to 2 T. Magnetic circular dichroism (MCD) was measured in the energy interval 2–2.9 eV at temperatures 300 and 90 K.

Nanoparticles of γ-Fe_2O_3 were identified with XRD (Fig. 1a) and TEM in sample 1. In the samples 2.1–2.6 another type of nanoparticles formed which could be referred to ε-Fe_2O_3

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(Fig. 1b). TEM images and EDX elemental mapping revealed some common features for the both types of glasses: Fe ions are localized, practically, inside nanoparticles; Gd ions are detected also in the nanoparticles regions but noticeable Gd quantity is observed in glass regions free of particles. An example is shown in Fig. 2 for sample 2.6.

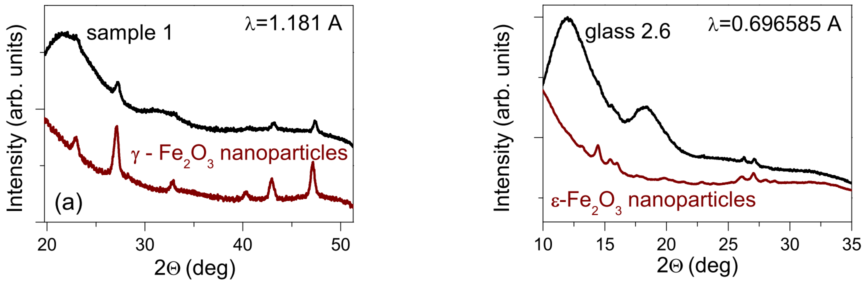

Fig. 1. X-ray diffraction patterns for sample 1 and the referent γ-Fe_2O_3 nanoparticles (a), and for sample 2.6 and the referent ε-Fe_2O_3 nanoparticles [6] (b)

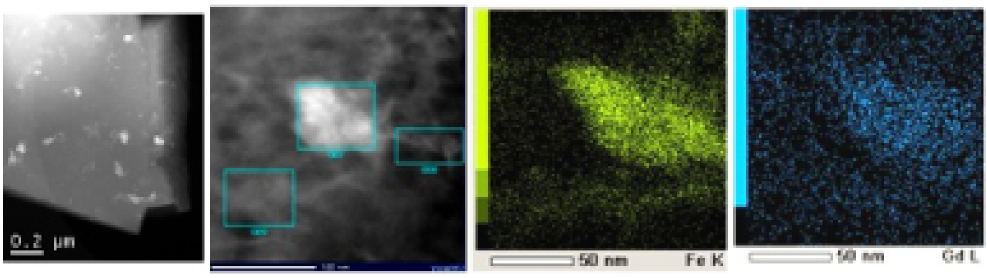

Fig. 2. TEM and HRTEM images, EDX elemental mappings for Fe (green) and Gd (blue) elements in the nanoparticle region for sample 2.6

For glasses with γ-Fe_2O_3 nanoparticles, the strong increase of the coercivity (Hc) is observed with the temperature decrease typical for this compound (Fig. 3a). Though Hc of the second type glasses is more than one order of value higher comparing to glasses with γ-Fe_2O_3, it is noticeable less than Hc reported in the literature for the ε-Fe_2O_3 nanoparticles [4] in other matrices. At the same time, the Hc decrease observed here with the temperature decrease (Fig. 3b) is specific characteristic for ε-Fe_2O_3 nanoparticles.

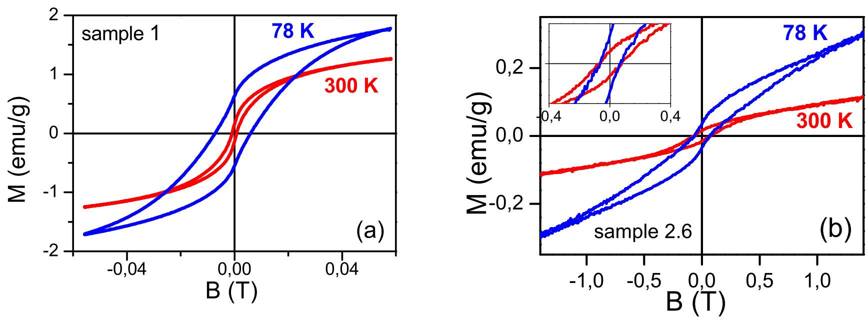

Fig. 3. Hysteresis loops for sample 1 (a) and 2.6 (b) at 300 K and 78 K

Similar to the magnetization, the MCD maxima values are essentially lower in the glasses containing ε-Fe_2O_3 nanoparticles (Fig. 4 b) comparing to the glasses containing γ-Fe2O3 nanoparticles (Fig. 4 a). MCD spectrum for the γ-Fe_2O_3 containing glass consists of two well-resolved maxima. In the case of the ε-Fe_2O_3 containing glass, MCD spectrum seems to consist of two maxima also, but they are wider and situated closer to each other comparing to the first case. One more difference is seen near E=2.75 eV. In the first case, MCD curve crosses the energy axis, while for ε-Fe_2O_3 containing glass MCD at this energy has a definite value associated, probably, with an additional maximum at 2.85 eV. The difference between MCD spectra of two types of the samples can be due to the peculiarities of the Fe^{3+} surroundings in the crystal positions. The Fe^{3+} ions occupy undistorted octahedral and tetrahedral positions in γ-Fe_2O_3 and four types of positions in ε-Fe_2O_3: one undistorted octahedral, two distorted octahedral, and one distorted tetrahedral. The resulting net magnetic moment is due to the octahedral undistorted sublattice in both cases. The peculiarities of the Fe^{3+} surroundings in the crystal positions in γ-Fe_2O_3 and ε-Fe_2O_3 can explain also the difference between details of the ESR spectra of the samples.

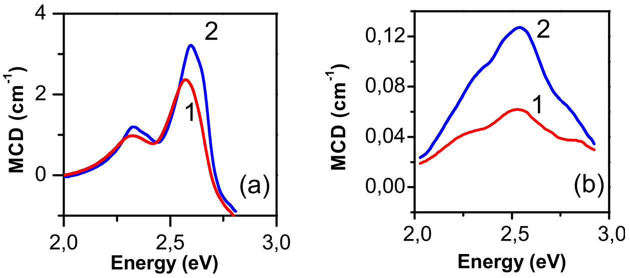

Fig. 4. MCD spectra for sample 1 (a) and sample 2.6 (b) nanoparticles at 300 K (curves 1) and 90 K (curves 2), B=0.25 T

Summarizing the results, one can make a statement that the basic glass composition plays an essential role in the specific Fe oxide nanoparticles formation: γ-Fe_2O_3 or ε-Fe_2O_3. When GeO_2 is introduced in the basic glass composition γ-Fe_2O_3 nanoparticles are typically formed. When only K, Al, and B oxides are the basic glass composition, ε-Fe_2O_3 nanoparticles formed in a glass. Gadolinium oxide in both cases motivates the formation of particles.

The authors thank Yan Zubavichus for the help in the samples synchrotron study.

The work was supported partly by the RFBR, 14-02-01211-a, and by the President of Russia Grant NSh-7559.2016.2.

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Сравнительное изучение γ-Fe_2O_3 и ϵ-Fe_2O_3 наночастиц, формирующихся в стекле, допированном железом и гадолинием

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Изучены свойства наночастиц γ-Fe_2O_3 и ϵ-Fe_2O_3, формирующихся в стеклах основного состава Ge_2O-K_2O-Al_2O_3-B_2O_3 и K_2O-Al_2O_3-B_2O_3, допированных Fe_2O_3 и Gd_2O_3 и подвергнутых дополнительной термической обработке. Результаты исследования рентгеновской дифракции, электронной микроскопии, магнитооптических эффектов и электронного спинового резонанса позволили объяснить роль матрицы и гадолиния в определении свойств наночастиц.

Ключевые слова: магнитные наночастицы, магнитный круговой дихроизм, магнитные измерения.