

Microwave and magneto-optic properties of ϵ -Fe₂O₃ nanoparticles arising in borate glasses doped with Fe and Gd

Oxana Ivanova^{1,2,*}, Janis Kliava³, Irina Edelman¹, Ruslan Ivantsov¹ and Eleonora Petrakovskaja¹

¹Kirensky Institute of Physics, FRC KSC RAS, Krasnoyarsk, 660036, Russia

²Siberian Federal University, Krasnoyarsk, 660036, Russia

³LOMA, UMR 5798 Université Bordeaux 1-CNRS, Talence cedex, 33405, France

Abstract. The ϵ -Fe₂O₃ nanoparticles in borate glasses co-doped with low concentrations of Fe₂O₃ and Gd₂O₃ were investigated with two experimental techniques – visible magnetic circular dichroism (MCD) and electron spin resonance (ESR). The most prominent features of the MCD spectra are: non-linear dependence of the spectral maxima intensities on the Gd concentration and strong increase with the temperature decrease. The ESR spectra of these glasses exhibit two features with $g = 4.3$ due to the diluted Fe³⁺ ions and 2.0 associated both with Fe³⁺ ions and with nanoparticles. The integrated spectra intensities do not follow the T^{-1} Curie law suggesting a considerable contribution from the magnetically ordered nanoparticles to ESR. Analysis of the MCD and ESR concentration dependences allow suggestion on the Gd ions incorporation into nanoparticles.

1 Introduction

Iron oxides are among the most used metal oxides with various applications in different scientific and industrial fields. Several stoichiometric phases of iron oxides are under intense study nowadays. The Fe₃O₄, γ -Fe₂O₃, and α -Fe₂O₃ phases have been found in nature as minerals magnetite, maghemite, and hematite, correspondingly. Despite the fact that they are known and serve humanity since ancient times, synthesis of these compounds in the form of nanoparticles, in particular as core-shell structures, allows to discover new properties and develop a lot of new practical applications on their basis. Two other phases β -Fe₂O₃ and ϵ -Fe₂O₃ are not found in nature and have been synthesized recently [1, 2] as nanoparticles. Structure and physical properties of the nanoparticles were shown to depend critically on the technology which creates difficulties in the identification of the particular iron oxide phase. This is especially important in the case of ϵ -Fe₂O₃ nanoparticles (e.g., [3-7]).

In the processes of iron oxide transformations under an action of the heat treatment ϵ -Fe₂O₃ is considered as an intermediate polymorph between γ -Fe₂O₃ and α -Fe₂O₃ [6]. The transformation temperature of ϵ -Fe₂O₃ to α -Fe₂O₃ is within the range of 500-750 °C in dependence on method of preparation. The particles ϵ -Fe₂O₃ size prepared by various methods varies within the range of 10-80 nm.

Recently, we have observed the formation of unusual magnetic nanoparticles in borate glasses co-doped with low concentrations of Fe₂O₃ and Gd₂O₃ [8] which were identified as ϵ -Fe₂O₃ nanoparticles. At that,

only part of the observed properties of nanoparticles corresponded well to the properties of ϵ -Fe₂O₃ nanoparticles presented in literature. Besides, the role of Gd in the formation of nanoparticles and its localization in the glass remained unclear. To elucidate these questions, we have undertaken a study of these glasses with two experimental techniques – visible magnetic circular dichroism (MCD) and electron spin resonance (ESR). The MCD and the ESR are closely related to each other by the underlying physical phenomenon, viz., splitting of electronic energy levels due to breaking the degeneracy in an applied magnetic field. However, the electronic transitions involved in the MCD and the ESR are quite different. MCD, as a rule, is due to electrical dipole transitions between different orbital states, and it usually occurs in the optical wavelength range. ESR is associated with magnetic dipole transitions between different Zeeman sublevels of one and the same orbital state, and it usually occurs in the microwave frequency range. Besides, MCD is associated, mainly, with magnetically ordered phases while ESR includes a contribution of diluted paramagnetic ions, as well. So, these methods are expected to provide consistent and complementary data.

2. Experimental detail

Glasses of the basic composition K₂O–Al₂O₃–B₂O₃ were synthesized using a conventional glass technique. Prior to the synthesis, 1.5 wt.% Fe₂O₃ were loaded in the charge together with Gd₂O₃ in concentrations of 0.1, 0.2, 0.3, 0.4, 0.6, and 1.0 wt.% (samples 1-6,

* Corresponding author: osi@iph.krasn.ru

correspondingly) with respect to basic glass composition. The mixtures were molten at 1100–1300 °C under oxidizing conditions. The melts were poured onto steel sheets, cooled down in air to 380 °C. Then the glass plates were subjected to additional thermal treatment at 560 °C during 2 h.

The nanoparticles morphology and structure, and the elements distribution in a glass were studied with electron microscope JEM-2200FS, energy dispersive X-ray analysis (EDX), Fast Fourier transform (FFT). The MCD spectral, temperature, and magnetic field dependences were measured using the laboratory made device in the energy range 2-3 eV, at temperatures 90 and 300 K, and in magnetic fields up to 15 kOe. The ESR spectra were recorded in the X band (9.46 GHz) with a Bruker EMX spectrometer equipped with an ER4112HV variable-temperature unit (300 and 120 K).

3. Results and discussion

3.1 TEM

Particle formation in the samples is clearly seen in the TEM images. As an example STEM-HAADF image for sample 6 is shown in Fig. 1. Several meanings of the interplanar distances in the lattice of these particles obtained with the FFT analysis can be related to several modifications of iron oxide. The closest coincidence is observed between the obtained spacing's and the spacing's in disordered ϵ -Fe₂O₃ [5]. Elemental analysis and elemental mapping show the basic matrix elements (Al, K, and B) distribution to be practically homogeneous through sample with visible "holes" in places of the particles. Fe and Gd ions are detected, mainly, in the particle regions and in the trace amounts in the region free of particles.

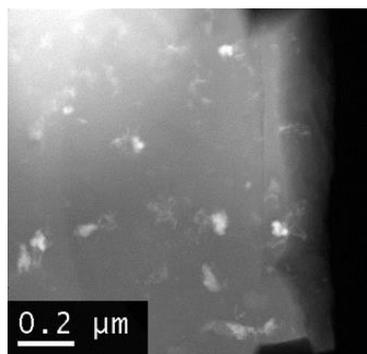


Fig. 1. STEM-HAADF image for samples 6.

Earlier we have already shown that the X-ray diffraction patterns contained several weak reflexes approximately the same for all samples [8]. The positions of the reflexes were closest to those for ϵ -Fe₂O₃ nanoparticles prepared by the wet chemical pore filling impregnation method [9]. Thus, electron microscopic data suggest that the nanoparticles can be referred to the phase ϵ -Fe₂O₃.

3.2 MCD

In Fig.2, there are presented the MCD magnetic field dependences for two samples with 0.6 and 1.0 wt.% concentrations of Gd₂O₃ measured at the light wave energy 2.5 eV close to a maximum in the MCD spectral dependence shown in Fig.3. A hysteresis at T=300 K was observed in all samples with a coercive field, H_c, in range 0.05 – 0.5 kOe. Parameters of the hysteresis loop such as H_c and remnant MCD value increase practically monotonic with the increase of the Gd concentration. At the same time, the MCD value in the maximal magnetic field 13 kOe changes non-monotonously with the Gd concentration increase (Fig.4).

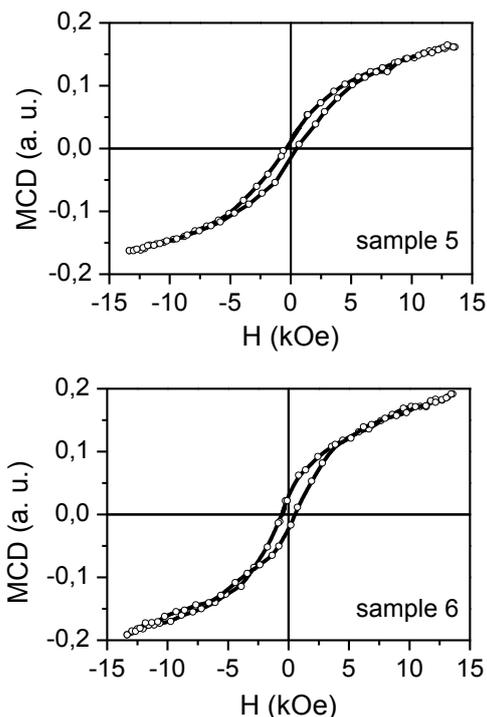


Fig. 2 MCD magnetic field dependences for samples 5 (top) and 6 (bottom) at 300 K (E=2.5 eV).

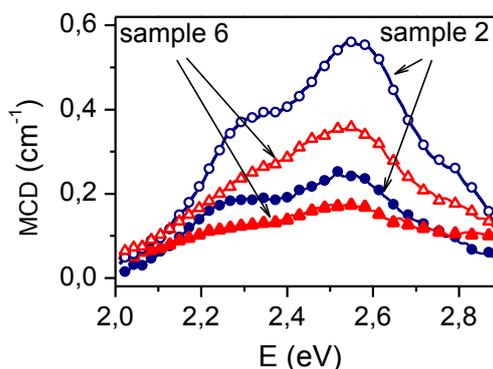


Fig. 3. MCD spectra of samples 2 (circles) and 6 (triangles) at 300 and 90 K (resp., full and empty symbols). H=3.5 kOe.

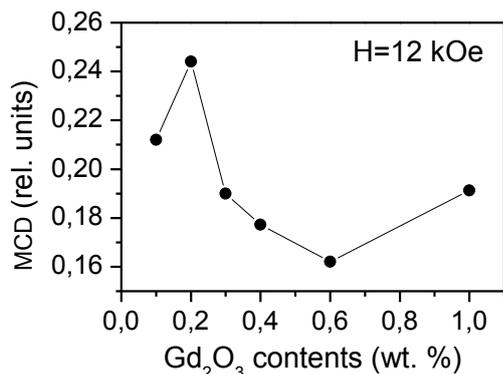


Fig. 4. MCD value in the field 12 kOe for all samples in dependence on the Gd concentration. Here the Gd oxide content in a charge is shown.

The spectral MCD curves are shown in Fig. 3 for samples 2 and 6 at two temperatures. In the region 2.0-3.0 eV, the MCD spectra shape is the same for all samples 1-6 and is close to the shape of the γ -Fe₂O₃ MCD spectrum nanoparticles [10]. However, in the case of ϵ -Fe₂O₃ nanoparticles maxima are noticeable wider and their gravity centres are shifted to lower energies comparing to those of γ -Fe₂O₃. The most prominent difference between ϵ -Fe₂O₃ and γ -Fe₂O₃ nanoparticles is the anomalously strong increase of the MCD maximum amplitudes, by a factor of 2.2 – 2.5, with the temperature decrease.

3.3 ESR

Typical differential and integral forms of the ESR spectra for sample 4 are shown in Figs. 5 and 6 at two temperatures. The differential spectra in all glasses exhibit two features with $g = 4.3$ and 2.0 due to diluted Fe³⁺ ions, and the lowest-field one, with $g = 6.0$, is due to Gd⁵⁺ ions. The line with $g=2$ can be associated also with some contribution of magnetic nanoparticles. Interestingly, with lowering the temperature the $g = 2.0$ feature is broadened whereas the $g = 4.3$ one is narrowed. The integrated spectra intensities do not follow the T^{-1} Curie law suggesting that a considerable contribution to the resonances arises from magnetically ordered nanoparticles.

The double-integrated intensities of the experimental ESR spectra recorded at room temperature (Fig.7) tend to decrease with the Gd concentration increase. The similarity of the Gd concentration dependences of the MCD values and the double-integrated intensities of the ESR spectra allows supposition on the Gd incorporating into particles which is supported by the TEM data: Gd was detected in the regions of nanoparticles together with Fe. If it is so, gadolinium ions replace iron ions reducing the total magnetic moment of the iron sub-lattice and causing distortions in the crystal lattice, because of their much larger radius in comparison with the Fe³⁺ ionic radius.

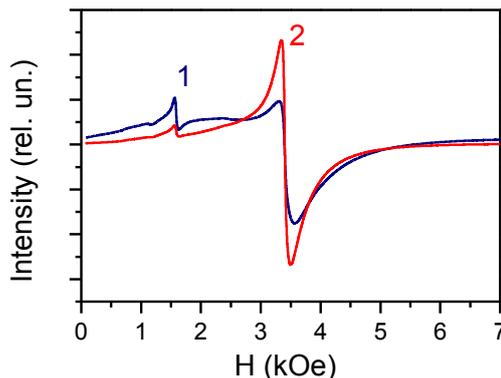


Fig. 5. ESR spectra for sample 3 at 120 (curve 1) and 300 K (curve 2).

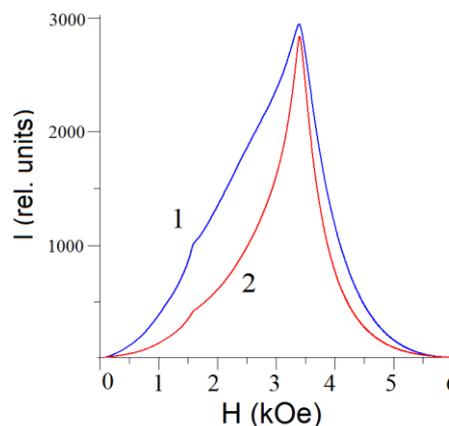


Fig. 6. Integrated experimental ESR spectra for sample 3 at 90 K (curve 1) and 300 K (curve 2).

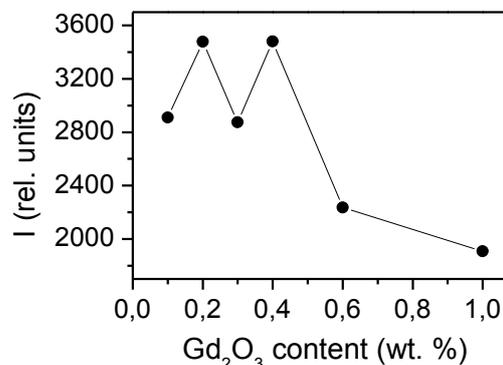


Fig. 7. Double-integrated intensities of the experimental ESR spectra at room temperature.

Distortions of the crystal lattice can lead to an increase in the coercive field and remnant magnetization, which is observed experimentally. The ϵ -Fe₂O₃ magnetic structure remains a subject of discussion up to now. Various authors attribute it to collinear ferrimagnet or a canted antiferromagnets. Besides, magnetic properties and resonance behavior of ϵ -Fe₂O₃ were shown to be modified upon partial Fe substitution by Al [11], Ga [12], or In [13-15]. Gd being the magnetic ion can effect in the ϵ -Fe₂O₃ magnetic properties even in higher extent. The study of the ESR temperature dependences of the ϵ -Fe₂O₃ containing glasses is in progress now.

4. Conclusions

The ϵ -Fe₂O₃ nanoparticles in borate glasses co-doped with low concentrations of Fe₂O₃ and Gd₂O₃ were investigated using transmission electron microscopy methods, visible magnetic circular dichroism, and electron spin resonance. Noticeable decreases of the MCD maximum amplitude and ESR intensity have been revealed at the Gd concentration increase. At the same time, the characteristic features of the MCD hysteresis loops, coercivity and remnant magnetization, increase with an increase of the Gd content. These observations evidence that the Gd ions can be incorporated into nanoparticles.

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