Faraday rotation in magnetic γ-Fe_2O_3/SiO_2 nanocomposites

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Faraday rotation spectrum has been measured at room temperature in a magnetic nanocomposite of γ-Fe_2O_3/SiO_2. The material consists of isolated γ-Fe_2O_3 nanoparticles dispersed in a silica matrix, and it was prepared through a sol-gel method. The composite contains 18% of γ-Fe_2O_3 in weight with an average particle size of 20 nm. It has a coercitivity of 30 Oe and an M_S of 6 emu/g. The specific Faraday rotation spectrum exhibits a narrow peak centered around 765 nm, reaching a value of 110°/cm and an absorption coefficient of 64 cm^{-1}. Faraday rotation versus applied field has also been measured, and a cycle similar to the one described by the magnetization has been found. © *1997 American Institute of Physics.* [S0003-6951(97)02444-3]

Materials containing crystallites or particles of nanometer dimensions have shown interesting properties related to its extremely small size. Some of their optical, magnetic, electronic, mechanical, and chemical properties are different from those exhibited by the same composition in bulk material.[1–3] In particular, magnetic particles[4] have become a subject of growing interest and intense research is being carried out. In the nanometric scale, the contribution of the particle surface plays an important role in the magnetic behavior of the whole material.

Among the most attractive properties of the magnetic transparent compounds are those related to the magneto-optical effects and their scientific and industrial applications in such areas as: optical fiber sensors,[5] optical isolators,[6,7] information storage,[8] etc. As regards to the latter, there are several works related to sub-micron particles and Faraday effect or Kerr effect characterizations (for example Ref. 9). In fact, the actual limit of 1 GBit/sq. in. for mass storage media demands magnetic particles smaller than 0.1 μm.

With the aim of obtaining magnetic compounds which will be transparent at room temperature, a dispersion of nanometric iron oxide particles (γ-Fe_2O_3) has been synthesized in a polymer organic matrix and interesting optical and magnetic properties have been achieved.[10] In this line, some efforts have been made to replace the polymer organic matrix by a glass-based matrix, which improves the nanocomposite physical and chemical properties. This has been achieved through sol-gel methods, which have been found to be quite effective for preparing small particles dispersed in different matrices. Several authors have reported the synthesis and characterization of γ-Fe_2O_3 or Fe/SiO_2 magnetic nanocomposites by sol-gel methods.[4,11–13] Besides, some magneto-optical properties (Kerr effect) have been measured in nanoparticle dispersions of γ-Fe_2O_3/SiO_2.[14]

The purpose of this work is to report what is, to our knowledge, the first observation of Faraday rotation in dispersions of nanoparticles synthesized by sol-gel and, in particular, of γ-Fe_2O_3/SiO_2 nanocomposites. This material has been named gamma-ferrite Faraday rotator (GFFR) due to its interesting properties related to the Faraday effect.

The GFFR was obtained through the sol-gel method as has been widely described in a recent work.[13] The porous nature of the sol-gel matrix provides adequate chemical conditions in the sites for nucleation of the iron oxide particles, minimizes their tendency to magnetic aggregation, and imposes an upper limit to their size. The initial solution consisted of a mixture of iron nitrate and tetraethyl orthosilicate (TEOS). The medium was acidified with ClH in ethanol. Then, a thermal treatment at 45 °C was performed for several days during the gelation process. Finally, the wet gel was heated in air at 400 °C during several hours, thus obtaining γ-Fe_2O_3 particles inside the dried silica cage. For our magneto-optical measurements we have used a sample containing 0.18 Fe_2O_3/SiO_2 molar ratio due to its excellent optical properties.

The GFFR sample was characterized magnetically, by x-ray diffraction, and by Mössbauer.[13] The γ-Fe_2O_3 was identified as the only component. The lattice parameter obtained from the x-ray diffraction diagram gives a value of 8.33 ± 0.01 Å in agreement with the presence of pure

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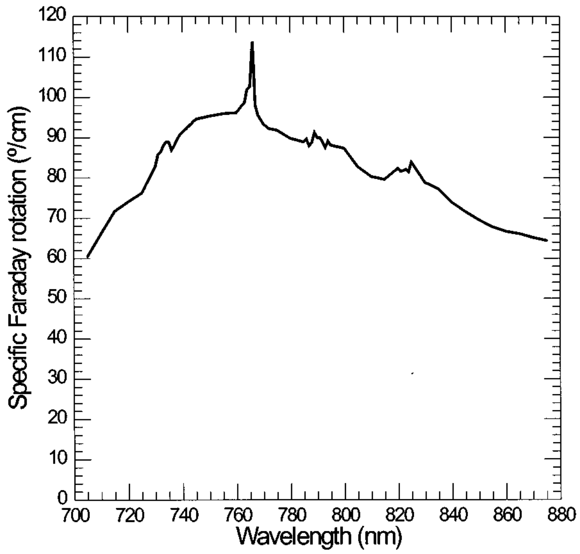

FIG. 1. Specific Faraday rotation versus wavelength for GFFR in the range from 705 to 875 nm. The data presented in this curve were measured with an average error of 1.9% and a maximum error less than 2.7%.

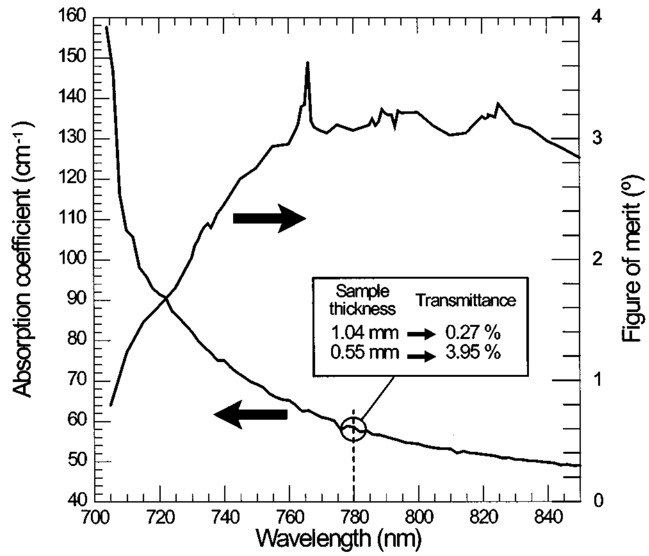

FIG. 2. Absorption coefficient and figure of merit of the GFFR vs wavelength.

maghemite phase in our material (γ-Fe_2O_3). The mean crystallite size, estimated from the (311) reflection, was 20 nm. Direct observation of the sample by means of transmission electron microscope (TEM) photographs evidenced two populations of particles: one of isometric particles of small size (<10 nm), and another with different shapes and sizes, around 20 nm. Further measurements are being undertaken and they will be presented in forthcoming work.

The magneto-optical properties of the γ-Fe_2O_3 nanocomposites were measured by embedding blocks of the material inside an acrylic resin and polishing until obtaining plates with a thickness ranging from 0.2 to 1 mm. The first measurement done was Faraday rotation spectrum. The experimental setup is based on a Xe light source, a monochromator (with a resolution of 1 nm), an optical power-meter, two near infrared (IR) polarizers with their axis at 45°, and an electromagnet with tapered pole pieces filled in with optical fiber bundles.[15] In ferri- and ferromagnetic materials, a useful physical constant, F, to describe the Faraday effect is the Faraday rotation at saturation magnetization M_S per unit path length, that is the specific Faraday rotation. These magnitudes are related by means of the constant of Kundt, K:

$$F = K \cdot M_S. \tag{1}$$

A typical specific Faraday rotation spectrum (from 705 to 875 nm) of the GFFR is shown in Fig. 1. The data were obtained with a plate of thickness $t = 1.04$ mm. The average error for the data represented in the curve is 1.9%, with maximum error being less than 2.7%. The curve exhibits a narrow peak centered around 765 nm, and other secondary maxima being at 734, 789, and 825 nm, with specific rotations of 89°/cm, 91°/cm, and 84°/cm, respectively.

In Fig. 2, the absorption coefficient, α, and the figure of merit, $2F/\alpha$, of the GFFR are displayed. The absorption coefficient has been measured using an optical fiber spectrum analyzer (Spectro 320 of Instrument Systems). The measurement has been taken placing a plate of GFFR between the free ends of the optical fibers of the spectrum analyzer (one of which is connected to a white light source and the other to a monochromator). In this situation, and according to the Beer–Lambert law, the optical intensity transmitted by the system, I, and the optical intensity transmitted when the GFFR has been removed, I_0, are related by means of the expression

$$I = I_0 \cdot e^{-\alpha \cdot t}, \tag{2}$$

where t is the thickness of the plate. We have taken all these measurements for two samples of GFFR with a thickness of 1.04 and 0.55 mm, respectively. The mean absorption coefficient derived from both samples is displayed in Fig. 2. Since we have not taken into account the reflectivity loss due to the refractive index change at the sample interfaces, this curve describes the absorption coefficient spectrum by excess. The absorption coefficient measured for nanoparticles of γ-Fe_2O_3 in organic matrices[10] is about one order of magnitude higher than the one presented in this letter. This is in agreement with the fact that the volume loading fraction of our nanocomposite is 0.12. However, considering that the volume fraction (volume filled in with γ-Fe_2O_3 particles) is of 12%, the ''apparent absorption coefficient'' α measured is nearly the same to the suggested for γ-Fe_2O_3 nanocomposites prepared in organic matrices.[10]

In the spectral region (760–820 nm) the figure of merit values are higher than 3. Compared to other magnetic materials, this one presents similar values.[16] However, the figure of merit for garnets is higher by a factor of 5.

In Fig. 3, the variation of the Faraday rotation with the magnetic field for a GFFR sample of 1.04 mm is presented at 789 nm (crosses) superimposed to its hysteresis magnetic loop. In this figure it is shown the magnetic behavior of the GFFR, with a coercitivity $H_c = 30$ Oe and a saturation magnetization, $M_s = 6$ emu/g. The instantaneous susceptibility of the sample at RT, estimated for 100 Oe, is $\chi_{100} = 0.025$ emu/g Oe. It should be noticed that the agreement between the Faraday rotation values and the magnetization

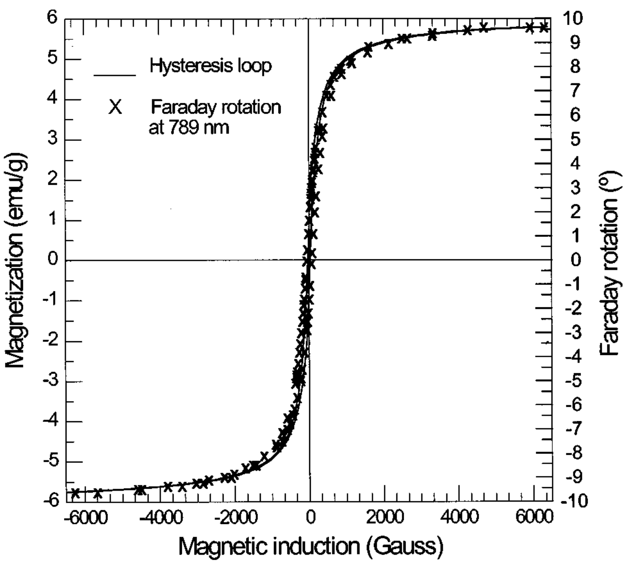

FIG. 3. Faraday rotation (crosses) versus external applied field on GFFR measured at 789 nm. The data are superimposed on the magnetization curve representing the hysteresis cycle.

loop occurs everywhere except in the central region of the curve. This is due to the fact that the Faraday rotation depends on wavelength and there is a different Faraday rotation curve for each wavelength. As the curve slope around 0 G is almost linear (at least in the range from -100 to $+100$ G), we obtain for GFFR a value similar to the Verdet constant, V, as it is calculated for paramagnetic and diamagnetic materials. For these compounds, the Faraday rotation, θ, is related to V by means of:

$$\theta = VBt, \tag{3}$$

where B is the magnetic induction in the direction of light propagation, and t is the thickness of the material. For the GFFR, we can derive a value similar to V of 0.23°/G cm. Although this ''approximation'' is not correct (the GFFR has magnetic hysteresis), the resulting value is useful to predict the magneto-optical behavior of the GFFR in low magnetic field applications.

With respect to the bulk γ-Fe_2O_3, two benefits arise from the properties of γ-Fe_2O_3/SiO_2 nanocomposites: one related to its transparency (as explained before), and the other derived from the magnetic properties of the nanoparticles. Due to the γ-Fe_2O_3 absorption coefficient ($\alpha > 10^4$), from an optical point of view, a practical implementation of γ-Fe_2O_3 as Faraday rotator will be only possible with thickness lower than 1 μm.[17] However, from the magnetic point of view, thin films are not suitable for magneto-optical devices due to the high demagnetizing factor, N, in the normal direction to the plane. As N is nearly 1, it behaves like a shape anisotropy of value $K = -0.5\,\mu_0/M_s$. In the absence of a magnetic field, H, the magnetization lies on the plane of the film, and the walls between the domains are mainly of the 180° walls type. To get the M_s in the normal direction to the plane it is necessary to apply a magnetic field $H = M_s$ (in the case of γ-Fe_2O_3, it is over $M_s > 4600$ Oe).[18] Moreover, the advantages of the nanocomposite become apparent because quasi-spherical particles lack shape anisotropy and reduce the demagnetizing factor ($N \sim 1/3$). Below a critical diameter, they become single-domain particles. As the particle diameter decreases the coercitivity decreases as well. For a given temperature, the sample reaches the superparamagnetic state, with zero coercitivity field.[19] As explained above, we have two distributions of particles of different sizes. The smaller are superparamagnetic at room temperature,[10] and the larger are responsible for the coercitivity field. The combination of both populations produce the final magnetic behavior as displayed in Fig. 3.

In conclusion, for the first time the Faraday effect has been measured on γ-Fe_2O_3/SiO_2 nanocomposites. This material is quite promising for future applications such as optical fiber sensors for measuring low magnetic fields (<1 Oe). Current research on new GFFR composites is already in progress, and it aims at improving their magnetic, optical, and magneto-optical properties.

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