ELSEVIER

Journal of Magnetism and Magnetic Materials 252 (2002) 375–377

journal of magnetism and magnetic materials

www.elsevier.com/locate/jmmm

Rare earth doped maghemite EDL-MF: a perspective for nanoradiotherapy?

J. Depeyrot[a,b,*], E.C. Sousa[a], R. Aquino[b], F.A. Tourinho[b], E. Dubois[c], J.-C. Bacri[d,e], R. Perzynski[d]

[a] *Complex Fluids Group, Instituto de Física, Universidade de Brasília, Caixa Postal 04455, 70919-970 Brasília (DF), Brazil*
[b] *Complex Fluids Group, Instituto de Química, Universidade de Brasília, Caixa Postal 04478, 70919-970 Brasília (DF), Brazil*
[c] *Laboratoire des Liquides Ioniques et Interfaces Chargées, Université Pierre et Marie Curie (Paris 6), Bâtiment F, Case 63, 4 place Jussieu, 75252 Paris Cedex 05, France*
[d] *Laboratoire des Milieux Désordonnés et Hétérogènes, Université Pierre et Marie Curie (Paris 6), Tour 13, Case 78, 4 place Jussieu, 75252 Paris Cedex 05, France*
[e] *UFR de Physique, Université Denis Diderot (Paris 7), 2 place Jussieu, 75251 Paris Cedex 05, France*

Abstract

We report on electric double layered magnetic fluids based on samarium-doped maghemite nanoparticles. The nanostructures chemical composition is carefully checked and X-ray diffraction patterns provide both their mean size and a structural characterization. Magnetization results are presented. Since these particles can become radioactive after neutron activation, they could therefore represent a new perspective for biomedical applications.

Keywords: Ferrofluid; Rare earth; Biomedical applications

1. Introduction

Ferrite magnetic nanoparticles are successfully employed in biomedical applications by chemisorption coating of their surface, with small intermediary molecules that ensure availability for complementary attachment to functional biomolecules and sol stabilization (Biocompatible Magnetic Fluid) [1]. This promising technology includes cell separation, drug delivery, magnetic resonance imaging (MRI) techniques as well as advanced clinical applications in cancer diagnosis and treatment.

To develop a new kind of "nanoradiotherapy", it would be interesting [2] to coat maghemite nanoparticles by iodine (for example) in order to make them radioactive after a neutron activation. Another possibility would be to include the active atoms inside the nanoparticle structure. In Ref. [3], the preparation of polycrystalline rare earth orthoferrite and garnets via hydroxide coprecipitation has been presented. In this context we report hereon a first attempt to elaborate an electric double layered magnetic fluids (EDL-MF) based on samarium-doped maghemite nanoparticles. This could represent a new perspective for biomedical applications in diagnosis as well as in therapy [4]. We present structural investigations performed by X-ray diffraction, associated to chemical titration and density measurements in order to characterize the synthesized nanoparticles. Room temperature magnetization measurements are also presented and discussed.

2. Experimental

The samarium-doped iron ferrite nanoparticles are prepared by using an hydrothermal coprecipitating of aqueous solutions of $FeCl_3$ and $Sm(NO_3)_3$ in alkaline

*Corresponding author. Complex Fluids Group, Instituto de Química, Universidade de Brasília, Caixa Postal 04478, 70919-970 Brasília (DF), Brazil. Fax: +55-61-307-23-63.
E-mail address: depeyrot@fis.unb.br (J. Depeyrot).

0304-8853/02/$ - see front matter
PII: S0304-8853(02)00623-6

medium. Then, after the usual chemical surface treatment [5], the particles were peptized in a colloidal sol. The sample composition is checked by chemical analysis: the iron titration is done by dichromatometry and the samarium concentration is determined by inductively coupled plasma atomic emission spectroscopy (ICPAES) using an FVME spectroflame. Measurements of the magnetic solution density are obtained using a PAAR DMA 38 densitymeter. X-rays diffraction are recorded from the powder samples, obtained by evaporation of the liquid carrier, by using a diffractometer installed in a conventional Rigaku–Denki generator operating at 40 kV/20 mA and the CuKα radiation ($\lambda = 1.54$ Å). The magnetization is measured at room temperature in the dilute regime where the solution behaves as a non-interacting system. The initial susceptibility is measured with a Foner device and higher field magnetization (up to a magnetic field of about 5×10^3 kA m^{-1}) are obtained with a superconducting quantum interference device (SQUID).

3. Results and discussion

A typical powder diffractogram is displayed in Fig. 1. Using the Bragg Law, several lines can be indexed, and correspond to the interplanar spacing [2 2 0], [3 1 1], [4 2 2], [5 1 1], [4 4 0] and [5 3 3]. Table 1 compares the measured peak intensities with the American Society for Testing and Materials (ASTM) values for γ-Fe_3O_4 [6] and also gives the cubic lattice cell deduced from the peak position with an average value of 0.839 nm to be compared to the ASTM one equal to 0.835 nm. Moreover, as the broadening of the diffracted beam is only due to the finite dimension of the crystal (polycrystalline samples), the nanoparticle size is related to the width of the diffractogram peaks according to the Scherrer equation [7]. Using the [3 1 1] most intense diffracted line it leads to a mean diameter equal to 3.5 nm. The inset of Fig. 1 displays the variation of magnetic material yield as a function of the Sm molar fraction. The experimental procedure used to determine the best value in Sm molar fraction is an adaptation of the method of continuous variation or "Job's method" and has been described elsewhere [5]. The maximum yield approximately corresponds to $X_{Sm} = 0.5$.

Table 1
Crystallographic analysis of Fig. 1: experimental peak intensities I_{exp}^{Xr} are compared to the ASTM ones for maghemite

hkl	d_{hkl}	*a* (nm)	I_{exp}^{Xr}	$I_{ASTM}^{\gamma\text{-}Fe_3O_4}$
220	2.926	0.828	43	34
311	2.546	0.844	100	100
422	1.710	0.838	15	12
511	1.626	0.845	22	33
440	1.487	0.841	52	53
533	1.275	0.836	13	11

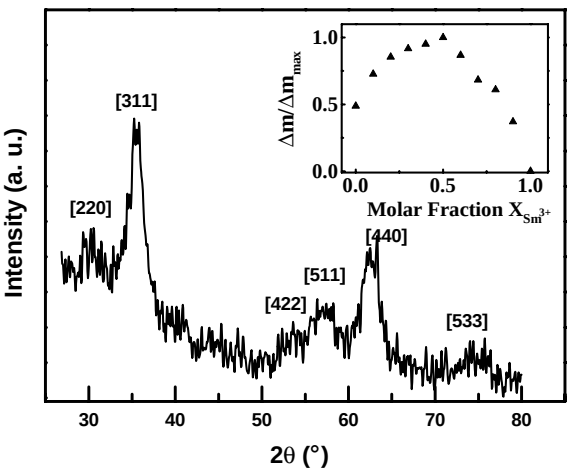

Fig. 1. X-ray powder patterns of the synthesized nanoparticles. The labeled lines correspond to the characteristic interplanar spacing of the spinel structure. The inset displays the normalized mass variation or magnetic material yield as a function of the Sm molar fraction X_{Sm}^{3+}.

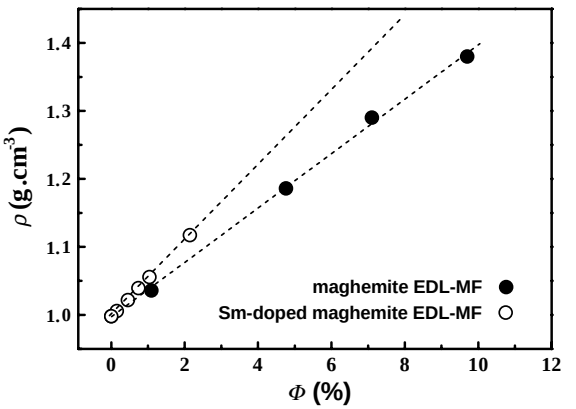

Fig. 2. Density ρ of our EDL-MF samples and of pure maghemite ferrofluid as a function of the volume fraction in magnetic material Φ.

However, the chemical analysis performed with the precursor ferrofluid sample indicates the presence of Sm in our nanoparticles ($[Fe^{3+}] = 1.45_0 \pm 0.01$ mol l^{-1} and $[Sm^{3+}] = 7.5_0 \times 10^{-3}$ mol l^{-1}). In Fig. 2 the density ρ_{MF} of our samples and of pure maghemite ferrofluid is plotted as a function of the volume fraction ϕ of magnetic material (with the hypothesis of a spinel structure). Such measurements allow to determine the nanoparticles material density ρ_{part}, using the following

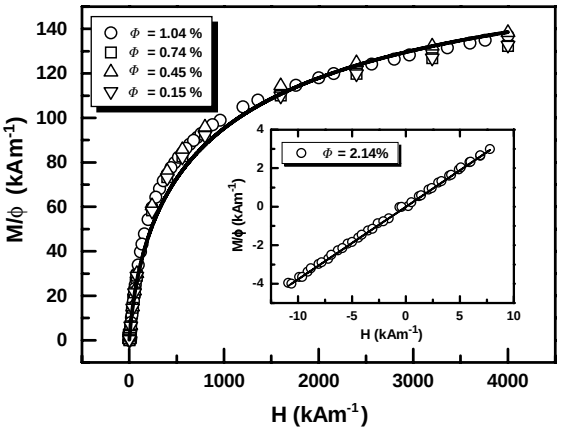

Fig. 3. Magnetization curves and initial susceptibility measurements (inset). The full line is the best fit obtained by using the Langevin formalism coupled with a log-normal size distribution.

equation:

$$\rho_{MF} = \rho_{H_2O} + \phi(\rho_{part} - \rho_{H_2O}), \quad (1)$$

The results are $5.01\,g\,cm^{-3}$ for γ-Fe_2O_3 particles and $6.59\,g\,cm^{-3}$ for our material showing therefore that our particles are not based on pure maghemite.

Fig. 3 shows magnetization curves of dilute samples obtained at 300 K. This magnetic behavior is typically superparamagnetic since at zero field, the magnetization is zero; as the applied field H increases, the magnetization increases too, and no hysteresis is observed in the investigated range of field. The inset of Fig. 3 displays an initial susceptibility measurement showing that, at low field the magnetization M is proportional to the magnetic field. The superposition of the experimental measurements in the reduced representation M/ϕ versus H justifies the use of an independent particle model. Then the magnetic behavior of our Sm-doped EDL-MF can be compared to a Langevin model where the size distribution is taken into account by considering a log-normal volume-weighted superposition of the contributions of all different particles volumes [8,9]. The saturation magnetization of the magnetic particle and the size-distribution parameters as determined by the fit of the magnetization curve are $m_S = 190\,kA\,m^{-1}$, $d_0 = 2.6\,nm$ and $\sigma = 0.6$; to be compared with the low field diameter of 6.2 nm deduced from the linear fit of the initial susceptibility. However, as the particle sizes are here obviously very small, the magnetization is probably strongly influenced in high fields by a surface layer disordered in spins as in Ref. [10]. To enlighten this point complementary investigations at low temperature and magneto-optical probing of the solutions are under process.

In conclusion, it is possible to dope iron oxide nanoparticles with heavy rare earth atoms, that can be rendered radioactive by an activation process, opening the road to nanoradiotherapy. The next steps will be to synthesize larger particles with a larger amount of doping atoms.

Acknowledgements

The authors are greatly indebted to Dr. Itri (USP-São Paulo) for the diffractograms and acknowledge the Brazilian agencies FAP-DF, FAPESP, CAPES and CNPq.

References

[1] U. Häfeli, M. Zborowski, Proceedings of the Third International Conference on Scientific and Clinical Applications of Magnetic Carriers, J. Magn. Magn. Mater. 225 (2001).
[2] J.C. Bacri, Workshop on Magnetic Fluids, Brasilia, Brazil, September 2000.
[3] M. Robbins, G.K. Wertheim, A.R. Storm, D.N.E. Buchanan, Mater. Res. Bull. 7 (1972) 233.
[4] S.F. Ahrabi, J. Heinamaki, S.A. Sande, C. Graffner, Eur. J. Pharm. Sci. 10 (2000) 225.
[5] M.H. Sousa, F.A. Tourinho, J. Depeyrot, G.J. da Silva, M.C.F.L. e Lara, J. Phys. Chem. B 105 (2001) 1168.
[6] ASTM No. 24–81.
[7] C. Hammond, The Basics of Crystallography and Diffraction, Oxford University Press, Oxford, 1997, p. 148.
[8] R.W. Chantrell, J. Popplewell, S.W. Charles, Physica 86 (1977) 1421.
[9] J.-C. Bacri, R. Perzynski, D. Salin, V. Cabuil, R. Massart, J. Magn. Magn. Mater. 62 (1986) 36.
[10] E. Hasmonay, J. Depeyrot, M.H. Sousa, F.A. Tourinho, J.-C. Bacri, R. Perzynski, Yu.L. Raikher, I. Rosenman, J. Appl. Phys. 88 (2000) 6628.