MAGNETIC AND STRUCTURAL PROPERTIES OF IRON OXYHYDROXYNITRATE NANOPARTICLES

N. J. O. Silva[1], *V. S. Amaral*[2], *L. D. Carlos*[2], *Angel Millán*[1], *Fernando Palacio*[1], *Benito Rodríguez-González*[3], *Luis M. Liz-Marzán*[3], *Thelma Berquó*[4], *F. Fauth*[5], *Verónica de Zea Bermudez*[6]

[1]*Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain.*
[2]*Departamento de Física and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal.*
[3]*Departmento de Quimica Fisica, Universidade de Vigo, 36310 Vigo, Spain.*
[4]*Institute for Rock Magnetism, University of Minnesota, Minneapolis 55455-0128, USA5.*
[5]*Labor. Llum Sincrotró, BM16-CRG,c/o ESRF, 6 rue Jules Horowitz, BP220, 38043 Grenoble, France.*
[6]*Departmento de Química, Universidade de Trás-os-Montes e Alto Douro and CQ-VR, Quinta de Prados,Apartado 1013, 5001-911 Vila Real, Portugal.*
nunojoao@unizar.es

Iron oxyhydroxynitrate, with general formula $FeO(OH)_{1-x}(NO_3)_x$ ($0.2<x<0.3$), is an ordered precursor of 6-line ferrihydrite in the process of hydrolysis of an iron nitrate salt in aqueous solution [1]. The iron(III) oxyhydroxynitrate was obtained for the first time in the form of a powder consisting of aggregated nanoparticles after freeze drying a Fe(III) nitrate water solution [1,2]. Here we report magnetic and structural properties on iron(III) oxyhydroxynitrate nanoparticles with different average sizes grown in a organic-inorganic hybrid matrix and compare them to those of other iron oxides. The use of a matrix to grow iron(III) oxyhydroxynitrate allowed to access the magnetic properties of the isolated nanoparticles. The first step of the nanohybrids preparation involves the synthesis of a cross-linked organic-inorganic hybrid precursor, similar to the one used in the synthesis of an undoped matrix, termed di-ureasil [3]. In the second step, a solution of iron(III) nitrate nonahydrate, water and ethanol was added to the non-hydrolyzed hybrid precursor. The resulting mixture was then stirred in a sealed flask for a few minutes at RT. After this, the solution was cast into a mould and transferred to an oven at ca. 40 ºC during 7 days. Samples were obtained after aging for 3 weeks at ca. 80 ºC. Samples were labelled Ih(x), where x is the iron mass concentration.

The powder XRD patterns of the two most concentrated samples of Ih nanohybrids (Fig. 1a) show that iron(III) oxyhydroxynitrate nanoparticles were efficiently stabilized in the matrix. Differences between patterns of iron(III) oxyhydroxynitrate and ferrihydrite are apparent: in the iron(III) oxyhydroxynitrate nanoparticles XRD patterns the relative intensity of the double peak at 60-65 ºC is the opposite of that of ferrihydrite, and the shoulder appearing at 33 ºC in the ferrihydrite nanoparticles is not present in the Ih nanohybrids. TEM images of the Ih(3.8) and Ih(6.5) nanohybrids show the presence of globular-shaped nanoparticles, with diameters of the order of 3 nm. The nanoparticles have nonfacetted and fuzzy edges and the nanoparticles/matrix contrast is low. SAXS patterns of Ih nanohybrids can be modelled as spherical isotropic and diluted Ih nanoparticles dispersed in a homogeneous matrix using GNOM [4]. With this analysis we conclude that the particles size increases with the iron content. The temperature dependence of the dc susceptibility χ shows that the Ih nanoparticles are superparamagnetic (Fig. 1b). The zero-field-cooled curves present a maximum at $T=T_B$ that increases with the iron content (Fig. 1b, inset). This increase agrees qualitatively with the observed size increase, since the anisotropy energy E_a and therefore T_B are expected to be related to size by a positive power. Below $T \approx T_F$, the $M(H,T)$ curves of the Ih nanocomposites show irreversibility, that depends on the sample temperature and field history. Above $T \approx T_F$, the *M(H,T)* curves of the Ih nanohybrids are reversible, and can be described has having linear and partial saturation components, associated to the antiferromagnetic susceptibility and the uncompensated moment, respectively. For $T > T_B$, a paramagnetic-like doublet in the Mössbauer spectra of the Ih nanohybrids is observed, as expected for unblocked superparamagnetic particles. For temperatures below T_B, the Mössbauer spectrum is magnetically split in a sextet. As observed in the susceptibility, T_B identified with Mössbauer increases with the iron content. In sample Ih(6.5), the magnetic hyperfine field B_{hf} at 4.2 K is similar to that previously found for iron(III) oxyhydroxynitrate powders B_{hf} =450-460 kOe [2]), being lower than that of 6-line ferrihydrite. At the same time, the isome shift *QS* shows some differences when compared to that usually found in 6-line ferrihydrite (-0.06 mm/s), approaching for that fitted for schwertmannite (*QS*=-0.37 mm/s at 4.2 K).

References:

[1] U. Schwertmann, J. Friedl, and H. Stanjek, J. Coll. Interface Sci., **209** (1999) 215.
[2] U. Schwertmann, J. Friedl, and G. Pfab, J. Sol. State Chem., **126** (1996) 336.
[3] V. de Zea Bermudez, L. D. Carlos, and L. Alccer, Chem. Mater., **11** (1999) 569.
[4] D. Svergun, J. Appl. Cryst., **25** (1992) 495.

Figures:

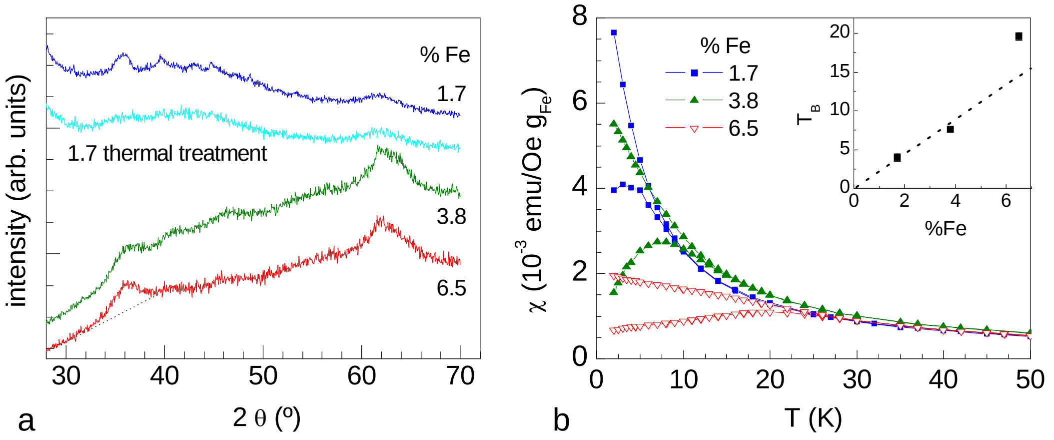

Fig 1. a. X-ray diffraction (XRD) patterns of Ih(x) nanohybrids and sample Ih(1.7) after a thermal treatment; b. dc susceptibility χ of Ih nanohybrids as a function of temperature. Inset shows the dependence of T_B with the iron content.