



## Influence of the surface treatment on the local structure of magnetic nanoparticles

F. L. O. Paula<sup>(1)</sup>, F. H. Martins<sup>(1)\*</sup>, F. A. Tourinho<sup>(2)</sup>, J. Depeyrot<sup>(1)</sup>, J. A. Gomes<sup>(1)</sup>, and R. Aquino<sup>(3)</sup>

(1) Complex Group Fluids – Physics Institute – University of Brasília – Brasília (DF) - Brazil

(2) Complex Group Fluids – Chemistry Institute – University of Brasília – Brasília (DF) – Brazil

(3) Complex Group Fluids – Faculdade UnB Planaltina – Brasília (DF) - Brazil

\* Corresponding author. [nandofisunb@yahoo.com.br](mailto:nandofisunb@yahoo.com.br)

### Abstract

Nanoparticles prepared by a soft chemistry method are dispersed in acidic medium thanks to a core-shell strategy that prevents the particles from dissolution. In this work, the local structural properties of magnetic nanocrystals of cobalt or manganese ferrite are investigated by chemical titrations, X-ray diffraction and X-ray Absorption Spectroscopy.

Magnetic fluids are colloidal dispersions in a liquid carrier of magnetic nanoparticles based on composites of metal oxides (ferrites). To disperse properly these nanoparticles and obtain chemically stable magnetic nanocolloids, it is necessary during the synthesis process to avoid their dissolution in acidic media. Thus a core-shell strategy has been developed and consists in protecting the ferrite nanocore with a thin coat enriched with iron obtained after a hydrothermal surface treatment with  $\text{Fe}(\text{NO}_3)_3$ . Recently we have studied this composition heterogeneity and proposed a chemical core-shell model with a core of stoichiometric ferrite and a shell of maghemite [1].

In this work, our purpose is to investigate the surface treatment step of the magnetic fluid elaboration based on manganese and cobalt ferrites nanoparticles. We therefore explore the modifications of the local nanocrystal structure induced by the duration of the hydrothermal treatment. All the samples are first tested by chemical titrations of metals content which allow determining the characteristics of our core-shell particles; then, measurements of X-ray absorption spectroscopy (XAS) and X-ray Diffraction, both performed at the Brazilian Synchrotron Light Laboratory (LNLS) allow following the structural changes.

The analysis of the XANES region of the X ray absorption spectra allow to qualitatively characterize the cation distribution at the interstitial sites of the nanocrystals, indicating mixed spinel structures. Moreover, the oxidation state of the metallic cation is deduced from the absorption edge position of the XANES spectra and it shows a different behavior as a function of the surface treatment duration for the two kinds of investigated ferrite. For manganese ferrite nanoparticles, the oxidation state of the Mn ion varies from +2 to +4 as the duration of the surface treatment increases. For cobalt ferrite particles, no variation of the oxidation state of Co ions is observed. X-ray diffraction results also show discrepancies between the two nanomaterials. The structure of both kinds of nanocrystals remains the same during the surface treatment and is characteristic of spinel type. Nevertheless, for manganese ferrite particles, it is observed a significant shift of the diffraction peaks towards larger diffraction angles as the duration of the treatment increases. On the contrary, the Bragg positions remain unchanged for cobalt ferrite particles.

The fitting procedure of EXAFS data includes single and multiple scattering paths determined from *ab-initio* calculations and allows to determine the interatomic distance, the coordination number, the structural disorder and the cation distribution. The nanoparticle core-shell model is confirmed to be due to the surface treatment used during the synthesis procedure. Rietveld refinement of the XRD patterns are also carried out using a core phase of partially inverted spinel type and a shell one made of maghemite. For manganese ferrite particles, the shift of the diffraction peak positions is related to a lower cubic cell in good agreement with the variations of the oxidation state of the manganese ion.

### References

[1] GOMES, J. A.; SOUSA, M. H.; TOURINHO F. A.; AQUINO, R.; SILVA, G. J. da; DEPEYROT, J.; DUBOIS E. and PERZYNSKI R. Synthesis of Core-Shell Ferrite Nanoparticles for Ferrofluids: Chemical and Magnetic Analysis. Journal of Physical Chemistry, v. 112, p. 6220-6227, 2008.