Experimental report

10/06/2022

Proposal: **5-23-742** **Council:** 10/2019

Title: Zn distribution and magnetic orderin Zn x Fe 3-x O 4 ferrite nanoparticles for biomedical applications as a function of Zn content

Research area: Physics

This proposal is a new proposal

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Samples: $Zn_xFe_{3-x}O_4$

Instrument	Requested days	Allocated days	From	To
D1B	3	3	12/09/2020	14/09/2020
			25/05/2021	26/05/2021

Abstract:

In this work, zinc ferrite nanoparticles (NPs) for application in magnetic fluid hyperthermia will be studied by neutron powder diffraction. The objective of the work is to determine the effects on the structural details and magnetic order, of Zn substitution in the spinel, as well as of the production process (crystallinity, stress). These fundamental aspects have direct consequences on the performance of the NPs in the biomedical application, as they control the heat dissipation, the catalytic activity and the magnetic response. The correlation is, however, still poorly understood. We apply for 3 days at D1B diffractometer, using a cryostat sample environment to study the magnetic order at low temperature. Six samples will be measured to study the Zn-content effects, the production method and the parent bulk compound. We estimate around 1.5 hs per diffractogram, and extra time for calibration measurements, setup, temperature control and sample changes.

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Zn distribution and magnetic order in $Zn_xFe_{3-x}O_4$ ferrite nanoparticles for biomedical applications as a function of Zn content

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Magnetic nanoparticles (NPs) are frequently designed for their use in biomedical applications, in particular for magnetic hyperthermia, where ferrites are the most required. The magnetic anisotropy, diameter and magnetic saturation of Nps play different roles to improve the heating effect in different systems. In particular, in $Zn_xFe_{3-x}O_4$ ferrites, the site distribution of Zn^{2+} affects the magnetic saturation of the NPs. Such distribution is controlled by the synthesis method used. In this experiment, we analysed the effect of the synthesis method, by collecting data for 3 samples obtained by thermal decomposition (JT01, JT02 and JT03), one sample prepared by a co-precipitation method (CP) and one sample where the co-precipitation was followed by ball-milling (CPBM). In addition, a $ZnFe_2O_4$ bulk sample was synthetized by solid state reaction (bulk).

Particle Induced X-ray Emission (PIXE) measurements were carried out at Centro Atómico Bariloche, Argentina, to determine the Zn content in each sample, as presented in Table 1.

Table 1. $Zn_xFe_{3-x}O_4$ composition calculated from analysis of Particle Induced X-ray Emission (PIXE).

sample	x
JT01	0.11
JT02	0.09
JT03	0.03
CP	0.39
CPBM	0.40

Neutron power diffraction data were collected at D1B for two wavelengths: 1.28 Å and 2.52 Å. Rietveld refinements were carried out using Fullprof suite [1]. The nuclear structure was refined under the cubic space group *Fd-3m*.

A comparison between a sample prepared by thermal decomposition (JT03) and by ball milling (CPBM) is presented in Figure 1. It is possible to observe differences in the width of the reflections between both samples, indicating that the CPBM has a smaller crystallite size than JT03, as expected from the preparation method.

Crystallite diameters of 30 nm and 7 nm were obtained for JT03 and CPBM, respectively, from the refinements using Scherrer equation.

The PIXE result were used to fix the Zn composition in the refinements and explore site preference of Zn^{2+}. The refinements indicate that Zn^{2+} ions are sitting at the **tetrahedral site** corresponding to Wyckoff position (1/8,1/8,1/8) in both samples. Fe_2O_3 and NaCl minority phases were found in the CPBM sample, and included in the refinement.

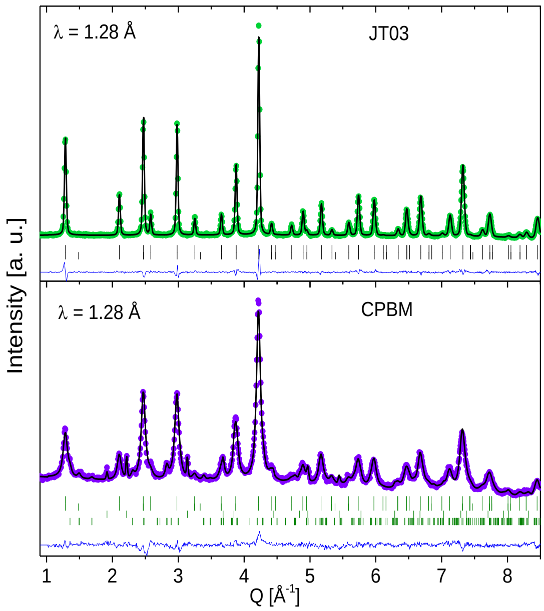

Figure 1. Neutron diffraction data collected at room temperature for nanoparticles synthesized by thermal decomposition (JT03) and nanoparticles synthetized by ball milling (CPBM).

In order to explore possible magnetic transitions, data were collected at different temperatures for sample JT01. The thermal evolution does not show signatures of any other magnetic order different to the observed at room temperature. Figure 2(a) presents the refinement at T = 2 K, for a wavelength of 2.52 Å using the collinear ferrimagnetic model proposed for a Fe_3O_4 with an easy axis in the <111> direction [2] and the octahedral sites antiparallel to the tetrahedral sites, as shown in Figure 2 (b). This result indicates that the addition of around 10% Zn does not affect the magnetic order of the sample.

(a) (b)

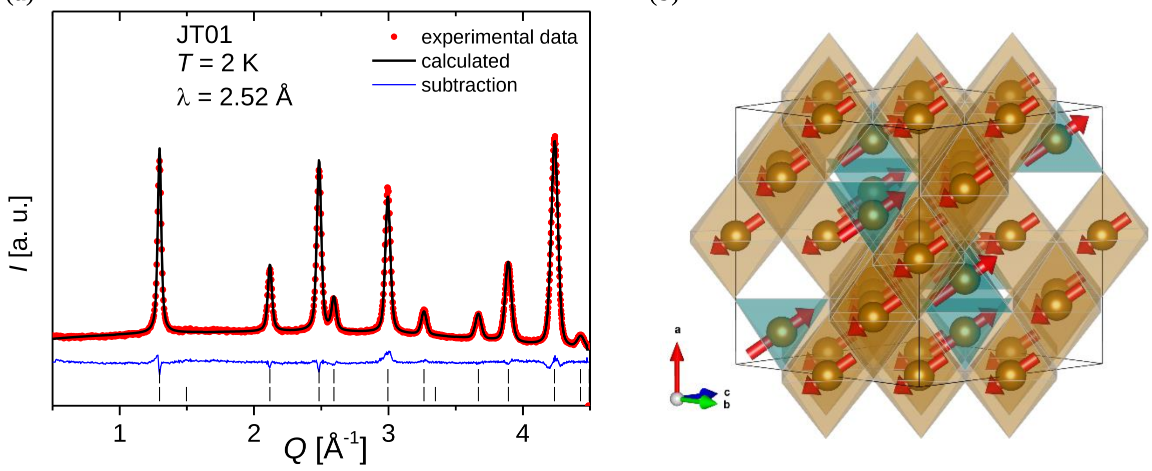

Figure 2. a) Rietveld refinement for neutron data from nanoparticles JT01 ($Zn_{0.11}Fe_{2.89}O_4$) collected at T = 2 K. b) Illustration of the magnetic model used in refinement.

A bulk sample of $ZnFe_2O_4$ was investigated for reference. We confirmed from the refinements that Zn is sitting at the tetrahedral site, as expected [2]. Figure 3 shows data collected at temperatures between 2 K < T < 32 K. Experimental data at 32 K are compatible with a nuclear structure described in the *Fd-3m* space group, as the NPs.

Below this temperature, a wide reflection is observed. For $ZnFe_2O_4$, a long-range antiferromagnetic order is reported below T_N = 10.5 K [3] with a sharp a magnetic reflection expected at Q = 0.77 Å^{-1} corresponding to the propagation vector **k** = (0,0, ½). In our case, instead, a wide peak consistent with short-range order is observed. Figure 3 b) shows the integrated intensity for 0.35 Å^{-1} < Q < 1.07 Å^{-1} calculated to estimate the onset temperature for short-range order (T_{SR}=32 K).

(a) (b)

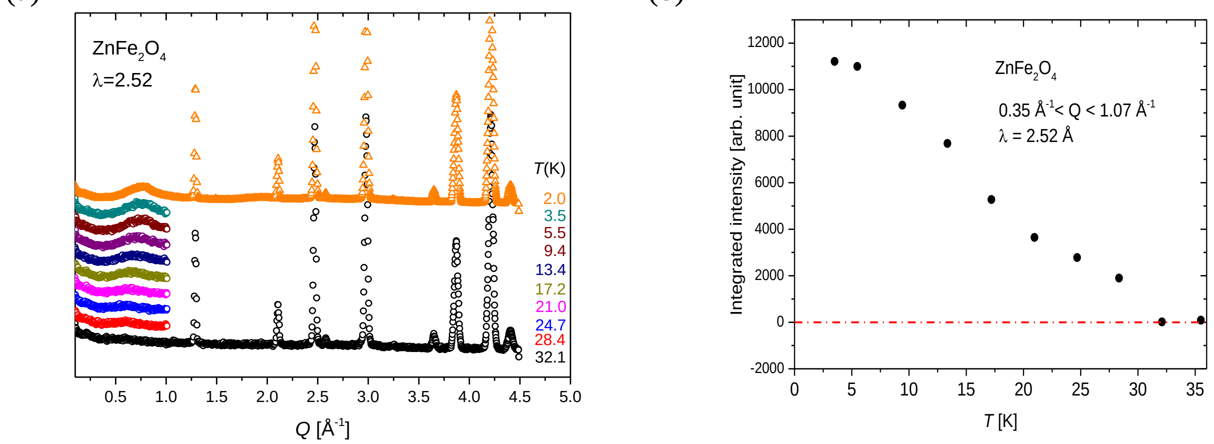

Figure 3. a) Neutron diffraction data for a bulk sample of $ZnFe_2O_4$ collected at different temperatures. b) Integrated intensity of the region between 0.35 Å^{-1} < Q < 1.07 Å^{-1}.

Figure 4 shows the cell parameter (a) for the six samples studied. The cell parameter increases with temperature, as expected.

At room temperature, the lattice parameter of the ball-milled sample is higher than in the CP sample, indicating the ball milling process induces a change in cell parameter.

An increase in the cubic cell parameter with Zn content is reported for bulk samples [4]. The same trend in the NPs is difficult to observe due to the very slight difference in composition (JT samples).

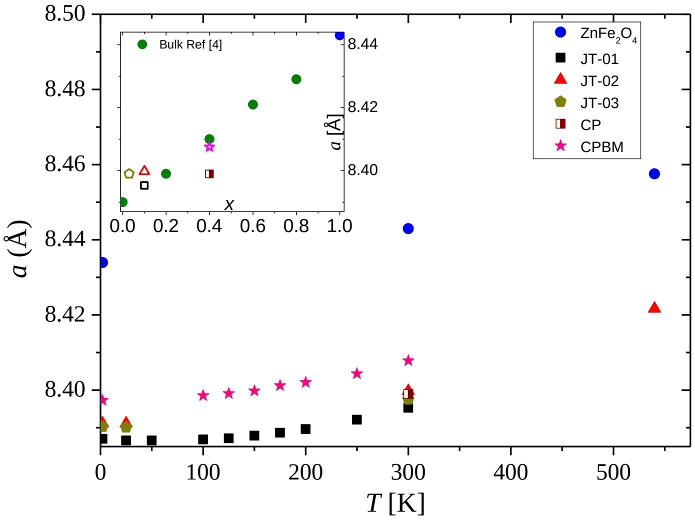

Figure 4. Cubic cell parameter of nanoparticle synthesised by thermal decomposition (JT01, JT02, JT03), co precipitated (CP), ball milling (CPBM) and $ZnFe_2O_4$ bulk sample. Inset, room temperature cell parameter as composition function ($Zn_xFe_{3-x}O_4$), hole symbols are nanoparticle data and solid symbols are bulk data, also data from ref [4] is showed.

To sum up, we found that Zn^{2+} is sitting exclusively in the tetrahedral site of the spinel structure. The magnetic order in NP produced by thermal decomposition is the same as that reported for bulk magnetite in all the temperature range studied. We also found that the ball milling process reduces the crystallite size to 7mm and produces an increase in the cubic cell parameter.

These results are now under analysis under the light of complementary magnetic saturation and magnetic hyperthermia experiments, that have been carried out at Centro Atómico Bariloche, to be prepared for publication.

The team acknowledges ILL and its staff, in particular Dr. Inés Puente Orench and Dr. Gabriel Cuello, who run this experiment during the COVID-19 pandemics with the remote assistance of the proposers.

References

[1] Rodríguez-Carvajal, J. (1993). Recent advances in magnetic structure determination by neutron powder diffraction. Physica B: Condensed Matter, 192(1-2), 55-69.

[2] Introduction to Magnetic Materials, Second Edition. By B. D. Cullity and C. D. Graham. 2009. the Institute of Electrical and Electronics Engineers, Inc. ISBN 978-0-471-47741-9. Page 180.

[3] Schiessl, W., Potzel, W., Karzel, H., Steiner, M., Kalvius, G. M., Martin, A., ... & Wäppling, R. (1996). Magnetic properties of the $ZnFe_2O_4$ spinel. Physical Review B, 53(14), 9143.

[4] Srivastava, C. M., Shringi, S. N., Srivastava, R. G., & Nanadikar, N. G. (1976). Magnetic ordering and domain-wall relaxation in zinc-ferrous ferrites. Physical Review B, 14(5), 2032.