Experimental report

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Proposal: CRG-2710 **Council:** 10/2019

Title: Effect of inversion degree on the magnetic properties of spinel zinc ferrite

Research area:

This proposal is a new proposal

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Samples: ZnFeO4

Instrument	Requested days	Allocated days	From	To
D1B	3	2	03/02/2020	05/02/2020

Abstract:

Proposal CRG-2710: "Effect of inversion degree on the magnetic properties of spinel zinc ferrite"

1. **Objectives**:

This proposal is aimed to understand the relation between microstructure and magnetic properties of the stoichiometric spinel zinc ferrite using the D1B diffractometer to characterize 4 samples with different level of structural disorder.

2. **Samples analyzed:**

3 samples of stoichiometric $ZnFe_2O_4$ particles synthetized by the conventional ceramic method with different values of the inversion parameter introduced by means of a mechanical milling process during 0, 2 and 50h.

3. **Measurements performed:**

The following measurements have been performed on the different samples:

a) SC 0h: According to the Rietveld refinement of the X ray diffraction (XRD) patterns recorded at room temperature (RT) this sample corresponds to an almost ideal spinel with Zn^{2+} and Fe^{3+} ions occupying only tetrahedral and octahedral sites. After taken reference diffraction patterns at 300K during 30 min with a wavelength of 2.52 and 1.28 Å, the sample was cooled down to 1.5K in 2h. This cooling process was monotorized by recording a ND pattern every 2 min using a wavelength of 2.52Å (in total 60 frames were obtained). After stabilizing the temperature a 1.5K, reference diffraction patterns were recorded during 30 min with both wavelengths. Finally, the sample was heated to 300K at a rate of 0.5K/min taking a pattern with a wavelength of 2.52Å every 2 min.

b) SC 50h: According to the Rietveld refinement of the XRD pattern taken at RT, this sample should correspond to a fully disordered zinc ferrite characterized by an inversion degree close to 2/3. This sample was cooled down to 1.5K in 2h, taking a pattern with a wavelength of 2.52Å every 2 min. After stabilizing the temperature at 1.5K, a diffraction pattern was recorded for 30 min for each of the 2 available wavelengths (2.52 and 1.28 Å). Then, the sample was heated to 300K at a rate of 0.8 K/min taking a pattern with a wavelength of 2.52Å every 2 min. Finally, reference diffraction patterns at 300K were taken during 30 min with the 2 available wavelengths. As according to magnetic measurement this sample is ferrimagnetic at room temperature, the transition to the paramagnetic state was fallowed using a heating cycle up to 540K taking a ND pattern every 2 min, and diffraction patterns were recorded at this temperature during 30 min with the 2 available wavelengths.

c) SC 2h: According to the Rietveld refinement of the XRD pattern taken at RT, this sample should be partially disordered. The sample was cooled down to 1.5K in 2h, taking a pattern with a wavelength of 2.52Å every 2 min. After stabilizing the temperature a 1.5K, diffraction patterns were recorded during 30 min with a wavelength of 2.52A and 1.28 Å. Then, the sample was heated to 300K at a rate of 1 K/min taking a pattern with a wavelength of 2.52Å every 2 min. Finally, reference diffraction patterns were recorded at 300K during 30 min with a wavelength of 2.52 and 1.28 A.

d) These measurements indicated were complemented with the measurement at room temperature of standards of Si and Na2Ca3Al2F14 for the 2 wavelength used to determine the precise wavelength value and to parameterize empirically the instrument functions from their profile shape analysis, respectively.

4. Results appreciated in-situ in ILL from the evolution of recorded diffractograms:

a) SC 0h: From the preliminary analysis of the Bragg peak intensities observed in the ND patterns during the cooling and heating process, we have verified the paramagnetic state at RT and the transition to an antiferromagnetic state below 10K by the appearance of an additional highly asymmetric shaped broad and diffuse peak at 2θ between 10 and 20º in the patterns recorded with 2.52Å.

b) SC 2h: Diffraction patterns obtained at 300K and their evolution during cooling and heating is quite similar to that observed in the previous sample. The major difference with the previous ND patters was a decrease of the intensity of broad peak associated to the antiferromagnetic ordering below 10K.

c) SC 50h: All the diffraction peaks recorded between 540 and 1.5K may be indexed in the Fd-3 m space group. However, the analysis of the evolution of the intensities of the Bragg peaks with temperature showed the occurrence of an additional contribution in intensity of the peaks located at the lower 2 theta positions that increases with decreasing temperature. As this extra contribution rapidly falls off for high reflection angles, it was associated to the presence of a ferromagnetic like ordering due to the high inversion degree present.

5. Conclusions and future work.

a) The analysis of the ND patterns confirms the presence of different magnetically ordered states depending on the inversion parameter and temperature. The patterns recorded with the samples SC0 and SC2 at temperatures below 10K show a broad peak at low angles associated to short range antiferromagnetic interaction. On the other hand, the sample SC50 shows a ferromagnetic like ordering, whose contribution to the ND pattern increases with decreasing the temperature.

b) As the high correlation between the contribution associated to cation occupancies and magnetic moments may lead to unsatisfactory fits, ND and XRD patterns were refined simultaneously by the Rietveld method.

c) For the samples showing ferromagnetic long range order at the diffraction temperature, the nuclear and magnetic contributions were calculated separately using a two-phases model in the refinement. Thus, the spinel structure with the Fd-3m symmetry was used to account the nuclear structure and their ferrimagnetic structure was modelled with a rhombohedral cell with the Shubnikov BNS space-group R-3m′ (166.101) with the scale factor linked to the parent spinel to account for the different cell volumes.

d) As the inversion parameters increases, the fractional coordinate of the oxygen atom also increases. Thus, the angles Fe^{3+}-O-Fe^{3+} associated to the A-B and B-B interaction are 124.1 and 91.6º in the sample with δ = 0.55. As those values are very close to the theoretical values 125º and 90º, it was concluded that Fe cations are ferromagnetically coupled on octahedral sites but antiferromagnetically coupled between the tetrahedral and octahedral sites. However, as the angle associated to the B-B interaction increases to a value of 94.8º in the sample with δ = 0.10, it makes possible that coupling between Fe^{3+} cations on octahedral sites can varies from ferromagnetic to antiferromagnetic.

e) The refinement ND data showed that the 3 samples studied present a net magnetic moment at 2K, but at room temperature only the samples SC2 and SC50. The values of magnetic moments at 300 and 2K obtained by the Rietveld refinement agree quite well with the saturation magnetization derived from the magnetization curves recoded up to maximum applied field of 5T at 5 and 300K.

A new proposal has been raised to further clarify the effect of cation distribution on the magnetic behavior of spinel zinc ferrite by additional measurements on 4 samples with similar values of both, crystallite size and lattice constant but with different level of structural disorder. These samples have been prepared from the commercial zinc ferrite by a milling process of 50h followed by an annealing treatment of 1h up to 600ºC