Experimental report

07/09/2021

Proposal: 5-31-2742 **Council:** 10/2019

Title: Effect of microstructural featuresand defects introduced by mechanical milling and thermal treatments on the magnetic order of spinel zinc

Research area: Materials

This proposal is a new proposal

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Samples: ZnFe2O4

Instrument	Requested days	Allocated days	From	To
D1B	3	0		
D2B	3	2	07/09/2020	09/09/2020

Abstract:

A wide range of different microstructures has been developed in ZnFe2O4 by combining a non-equilibrium processing route that introduces a significant amount of structural and microstructural defects, and thermal treatments. Previous results using XRD and SQUID magnetometry showed that the overall increase in magnetization with milling time is related with distribution of Zn+2 and Fe+3 cations and microstructural parameters like crystallite size and microstrain. However, the influence of other relevant structural parameter, like occupancy factor and special distribution of oxygen and the symmetry of the magnetic moments were not taken in account. We want to investigated the correct distributions of anions and cations and the magnetic and nuclear behaviour of 3 samples (as milled for 50h, and after annealing at 400 and 600ºC) at RT, 200,150, 100, 75, 50, 25 and 5K with the D2B high resolution diffractometer, and combining this study with the complete thermal variation of the diffraction patterns (1.5 - 300 K) obtained in the high intensity D1B diffractometer with 4 samples at a different level of structural disorder, i.e., after different milling times.

Proposal 5-31-2742: "Effect of microstructural features and defects introduced by mechanical milling and thermal treatments on the magnetic order of spinel zinc"

1. Objectives:

This proposal is aimed to clarify the effect of cation distribution between A- and B-site on the magnetic order present of spinel zinc ferrite. For this goal, the use of a high-resolution powder diffractometers is essential to refine a crystal structure, and for determining low differences in lattice parameters.

2. Samples analyzed:

Stoichiometric ZnFe2O4 particles with a low value of the inversion degree were obtained by the conventional ceramic synthesis (sample SC0 old) or annealing a commercial high purity zinc ferrite supplied by Alpha Aesar at 1100 ºC for 2h (sample SC0 new). Finally, samples with higher degree of inversion were prepared by mechanical milling of particles synthetized by the conventional ceramic method during 2, 10 and 50h (samples SC 2h, SC 10h and SC 50) or annealing for 1h at 400 and 500 commercial powder milled for 50h (samples COM 50-400 and COM 50-500). In total 7 samples.

3. Measurements performed:

The following measurements have been performed on the different samples:

a) SC0 old and SC0 new samples: After taken reference NPD patterns at RT, the samples were cooled down to 80, 20 and 2K to evaluate the phase transition from paramagnetic to antiferromagnetic order.

b) SC 50h: NPD patters were recorded at 540, 300, 80 and 2K to determine the magnetic contribution to the fitted model under the assumption that the cation distribution in the magnetic structure at these temperatures is the same.

c) SC 2h, SC 10h, COM 50-400 and COM 50-500: NPD patters at RT were recorded to compare the experimental saturation magnetization associated with the ferrimagnetic contribution with the magnetics moments obtained in the Rietveld refinement of the magnetic structure.

d) Standards of Si and Na2Ca3Al2F14 were also recorded 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 0 old and SC0 new samples: A paramagnetic state at RT and the transition to an antiferromagnetic state at 2K characterized by the appearance of an additional highly asymmetric shaped broad and diffuse peak at 2θ between 8.5 and 13.5º have been observed for both samples.

b) SC 50: Diffraction peaks recorded at 540, 300, 80 and 2K may be indexed in the Fd-3 m space group. The evolution of the intensities of the Bragg peaks with temperature showed an additional contribution in intensity of the peaks located at the lower 2 theta positions that increases with decreasing temperature, which was associated to the presence of a ferromagnetic like ordering.

c) SC 2h, SC 10h, COM 50-400 and COM 50-500: Diffraction patterns of these samples obtained at 300K are quite similar. The major difference between them is that the intensity of the Braggs peak at the lower 2 theta positions increases with increasing the inversion degree.

5. Conclusions.

a) The analysis of the NPD patterns confirms the presence of different magnetically ordered states depending on the inversion parameter and

temperature. The patterns recorded with the samples SC0 at 2K showed a broad peak at low angles associated to short range antiferromagnetic order. On the other hand, the samples SC50, SC 2h, SC 10h, COM 50-400 and COM 50-500 showed a ferromagnetic like ordering, whose contribution to the NPD patterns increased with decreasing the temperature and/or the inversion degree.

b) For the samples showing ferromagnetic long range order at the diffraction temperature, the nuclear and magnetic contributions were calculated separately using a two-phase model in the Rietveld refinement to display only the magnetic scattering. The spinel structure with the Fd-3m symmetry was used to account the nuclear structure together with a separate second phase that contains only the cations contributing to the magnetic reflections. We could have used a description of the magnetic structure in the space group P1. However, in this approach we have to use too many degrees of freedom to adjust the magnetic diffraction, and as the zinc spinel ferrite only exhibits a limited number of magnetic reflections, the obtained magnetic moment can be quite inaccurate. It was selected and tested the Shubnikov BNS space-group R-3m' for the ferromagnetic structure due to the analogy that exists between the structural properties of the zinc spinel with the Fe_3O_4, but considering the different arrangement of Fe cations in each case and fitting the moment components considering their symmetry restrictions in their Wyckoff positions. As result, it was obtained an excellent agreement between the observed pattern and calculated profiles that includes the nuclear and magnetic phases. The values of the structural parameters and their standard deviations obtained from the Rietveld refinement of both XRD and NPD patterns are reported in Table 1.

Table 1. Microstructural parameters obtained after Rietveld refinement of the diffraction patterns recorded using laboratory Co X-ray and neutron sources

Sample	Lattice parameter (Å)	Inversion degree (δ)	O-Position (x=y=z)	Crystal. size (nm)	μ-deformation (ε)
SC0 new XRD	8.4489(5)	0.05(1)	0.2416(5)	>150	-
SC0 new ND D2B	8.4498(5)	0.05(1)	0.2397(3)	>150	-
SC0 old XRD	8.4490(5)	0.11(1)	0.2410(5)	>150	-
SC0 old ND D2B	8.4433(5)	0.11(1)	0.2398(3)	>150	-
SC 2h XRD	8.4435(5)	0.27(1)	0.2425(2)	35(3)	0.0010(2)
SC 2h ND D2B	8.4493(4)	0.15(1)	0.2409(3)	30(2)	0.0012(2)
SC 10h XRD	8.4383(5)	0.51(1)	0.2454(3)	13(1)	0.0020(3)
SC 10h ND D2B	8.4412(4)	0.35(1)	0.2424(3)	14(1)	0.0019(2)
SC 50 XRD	8.4305(5)	0.60(1)	0.2463(5)	12(1)	0.0011(2)
SC 50 ND D2B	8.4353(4)	0.40(1)	0.2423(3)	13(1)	0.0010(2)
COM 50-400 XRD	8.4322(5)	0.28(2)	0.2424(5)	15(1)	0.0020(2)
COM 50-400 ND D2B	8.4306(5)	0.21(1)	0.2414(3)	15(1)	0.0014(4)
COM 50-500 XRD	8.4331(5)	0.19(1)	0.2415(5)	16(1)	0.0019(3)
COM 50-500 ND D2B	8.4336(5)	0.15(1)	0.2411(3)	15(1)	0.0012(4)

c) Due to the high quality of both, X-ray and D2B neutron data, the values of lattice parameters, crystallite size and lattice strain determined from their diffraction patterns coincide, as shown in Table 1. The main discrepancies observed in Table 1 are found in the values of the inversion parameter and the O-positions. The contribution to overall XRD scattering intensity by O is significant smaller in the presence of high Z elements like Fe and Zn, but the

neutron scattering length for this element is large (b_O = 5.803 fm). Thus, NPD is a better approach than XRD to determine the positions of oxygen atoms precisely. On the other hand, it is expected that neutron data will provide more reliable inversion parameters since between Zn and Fe there is a more noticeable difference between their neutron scattering lengths than their X-ray scattering factors (greater Zn/Fe contrast).
d) As nuclear and magnetic contributions of the Bragg reflections overlap and new reflections associated with the magnetic lattice do not appear in the NPD pattern, the high correlation between the contribution associated with cation occupancies and magnetic moments can lead to unsatisfactory fits of the data. This problem can be eliminated by the simultaneous Rietveld refinement of both, XRD and NPD patterns. In this refinament, microstructural parameters like lattice parameters, inversion degree, fractional coordinate of the oxygen atom, crystallite size and microstrain were constrained to be the same both for XRD and NPD profiles. Additionally, it was set as a variable both, the sample displacement correction in the XRD pattern and zero shift error in the NPD pattern, to include an extra degree of freedom to the peak positions. Finally, independent magnetic moments were included in the refinement for the NPD data under the assumption that the cation distribution in the magnetic unit cell is the same as in the crystallographic unit cell. The best-fitted microstructural parameters obtained by the combined Rietveld analysis of the XRD and NPD patterns recorded at 300 are given in Table 2

Table 2. Values obtained for the microstructural parameters constrained to the same value in the combined analysis of the patterns recorded at 300 using laboratory Co X-ray and D2B data.

Sample	Inversion degree (δ)	O-Position (x=y=z)	Crystal. size (nm)	μ-defor-mation (ε)	R_{WP}	R_{exp}	GoF
COM 1100	0.05(1)	0.2397(1)	>150	-	4.12	10.15	2.46
SC0	0.10(1)	0.2398(1)	>150	-	2.79	8.27	2.96
SC 2h	0.25(1)	0.2417(1)	40(2)	0.0011(1)	7.02	3.62	1.94
SC 10h	0.49(1)	0.2436(1)	13(1)	0.0020(2)	4.85	3.45	1.41
SC 50	0.56 (1)	0.2442(1)	11(1)	0.0010(1)	4.26	3.11	1.37
COM 50-400	0.18(1)	0.2414(1)	16(1)	0.0019(1)	3.51	2.70	1.30
COM 50-500	0.27(1)	0.2419(1)	14(1)	0.0019(1)	3.27	2.65	1.26

e) NPD patterns together with the observed evolution of the saturation magnetization with the temperature can be explained by the competition between a ferromagnetic like contribution associated with an extended superexchange B-A-B interaction between three neighbors Fe^{3+} ions antiferromagnetically coupled, and an antiferromagnetic B-B interaction. As a result of the competition between these two interactions, it may be originated frustration in the magnetic structure that causes the suppression of the antiferromagnetic long range order (LRO).

All these results have been collected in a manuscript entitled “Coexistence of antiferro- and ferrimagnetism in the spinel ZnFe2O4 with an inversion degree lower than 0.3” authored by M A Cobos, P de la Presa, I. Puente-Orench, I. Llorente, I Morales, A García-Escorial, A. Hernando and J A Jiménez, that has been submitted to Ceramics International.