Effect of processing synthesis route on the magnetic and structural properties of Zn ferrite

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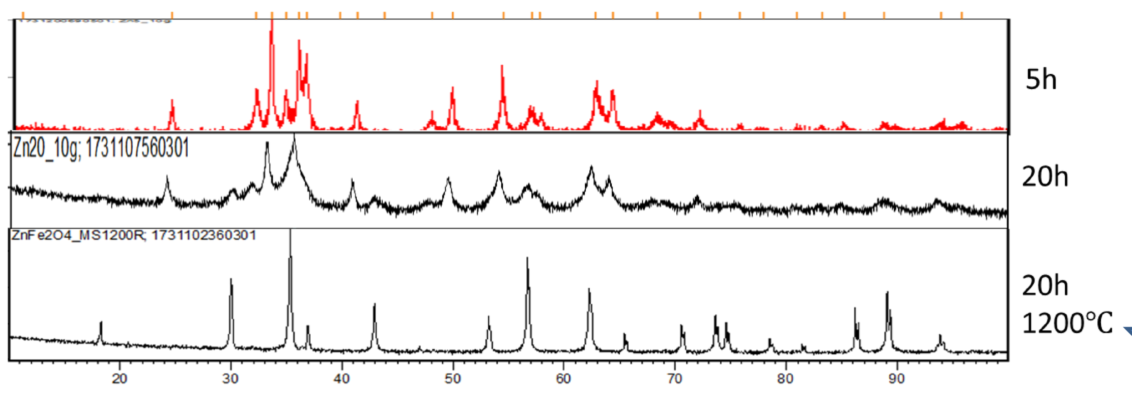
Abstract: Paramagnetic Zn ferrite stabilizes in normal spinel structure with Zn in tetrahedral A sites and Fe in octahedral B ones at room temperature. When Zn and Fe atoms exchange sites, superparamagnetic or even ferromagnetic behaviour can be observed. Two different processing routes have been carried out to obtain Zn ferrite by high energy mechanical milling, leading to different magnetic behaviours.

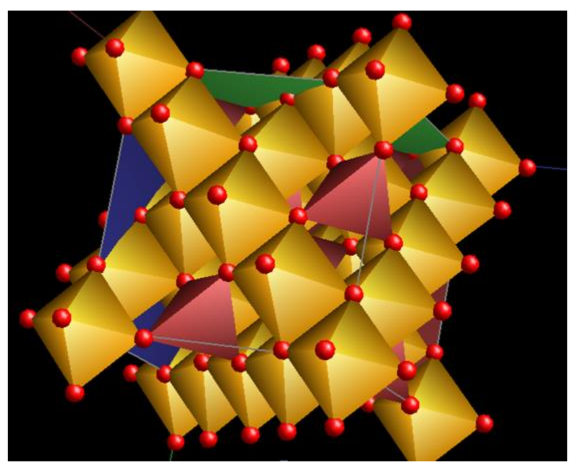
High energy ball milling was performed in a planetary mill using stainless steel vessels and balls

Powder of pure hematite and zincite to give 10 gr of $ZnFe_2O_4$ were mixed together with 1cm diameter balls in a mass ratio 1:10. The milling process was performed in air without any process controlling agent (PCA).

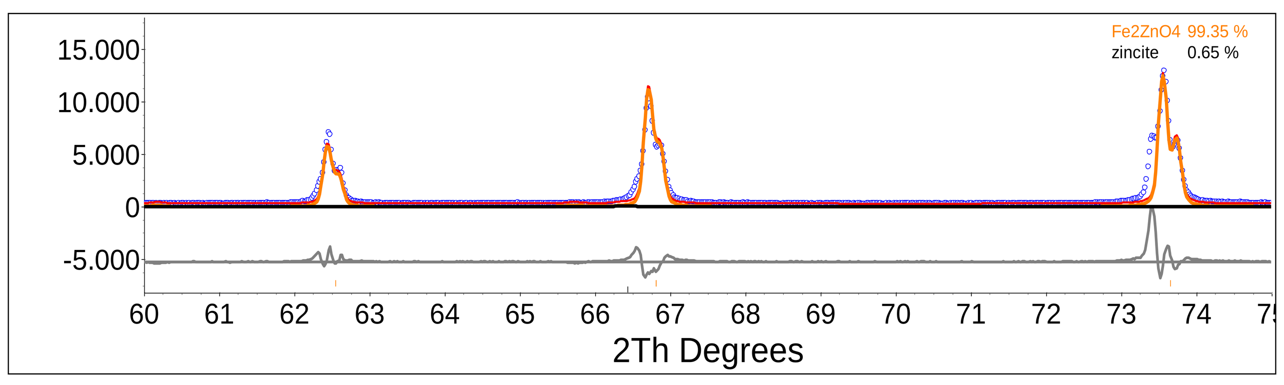
Short Mechanical milling and calcination route:

1. XRD and Rietveld analyses of as-milled powder and after calcination





Graphic representation of tetrahedral and octahedral places on spinel ferrite

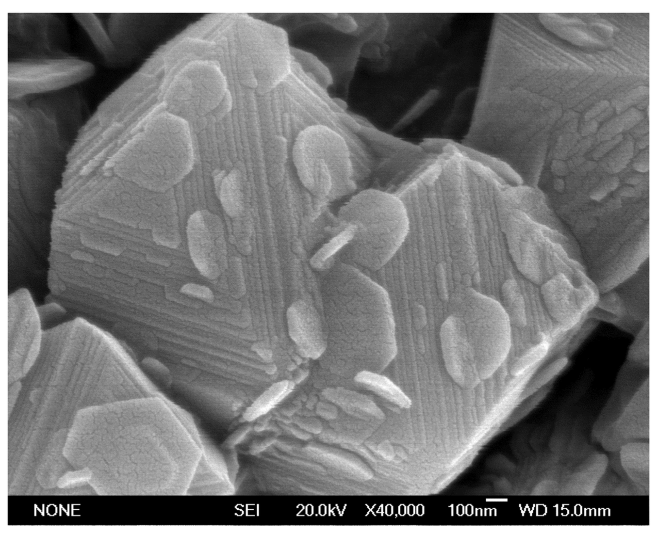


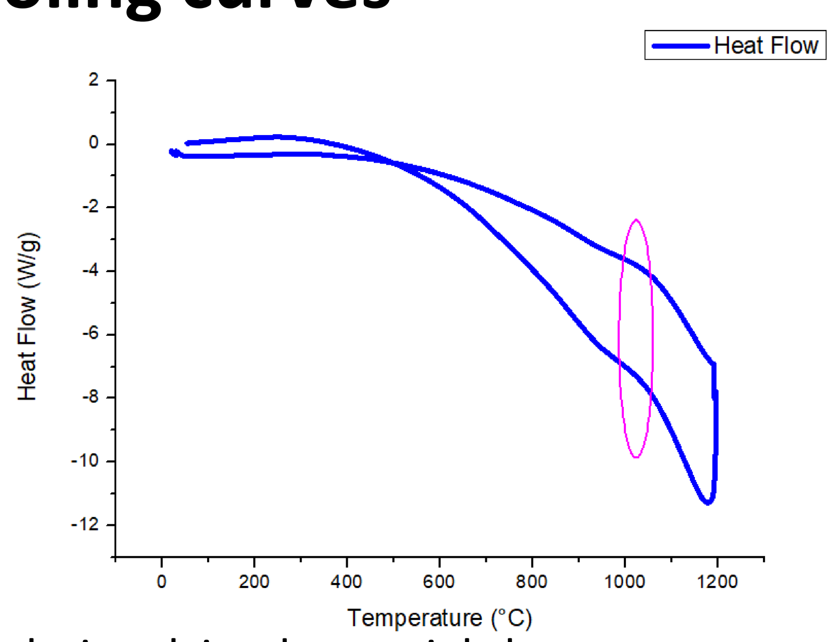
Rietveld refinement of 20h milled and 1200C calcinated sample

SINTESIS	% FASES
Zn20_1200C48hER (1)	86% (I)
	14% (D)
Zn_2,5_1200C 2,5hEL	70% (I)
	30% (D)
(1) + 1000C-3h	72% (I)
	28% (D)
(1) + 850C-3h	65% (I)
	35% (D)
(1) + 700C-5h	55% (I)
	45% (D)

XRD patterns were fitted using two phases with a close lattice parameter (e.g. two spinel like structures with different degree of ion exchange between Zn^{++} and Fe^{+++}). Diffraction peaks show asymmetric broadening that can not be associated only to cell size and microstrain effect.

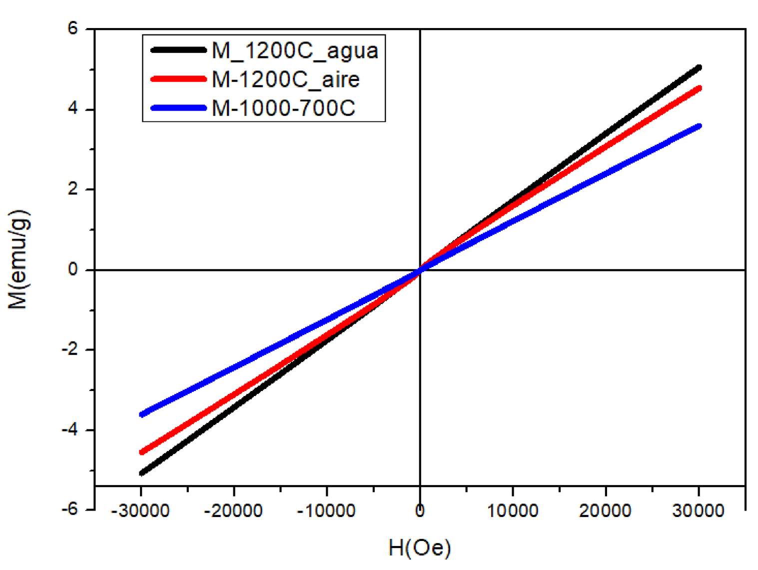
2. SEM & DSC heating and cooling curves





SEM 1200C 24h quenching sample and DSC analysis calcined material shows an inflection at around 1000°C on both, heating and cooling curves

3. Magnetic properties

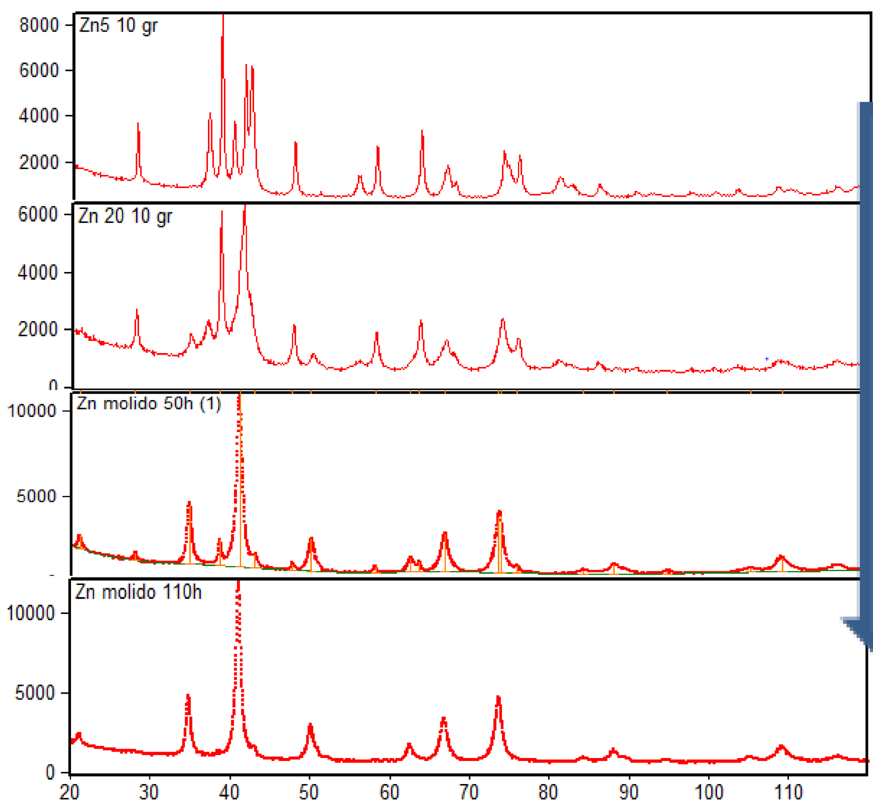


Compuesto	χ (emu/cm³·Oe) 300K	Fases / distribución catiónica
Zn2,5-1200C-24h-ERagua	$8,99 \times 10^{-4}$	86% I / 14% D
Zn20-1200C_48h_ERaire	7.44×10^{-4}	80% I / 20% D
Zn2,5-1200C_24hEL_furnace	6.60×10^{-4}	70% I / 30% D
Zn20-1200C_48h_Eraire + 1000C-3h	6.5×10^{-4}	72% I / 28% D
Zn20-1200C_48h_Eraire + 850C-3h	6.46×10^{-4}	65% I / 35% D
Zn20-1200C_48h_Eraire + 700C-5h	6.36×10^{-4}	55% I / 45% D

The calcinated samples are paramagnetic, higher the temperature of the treatment, the greater the paramagnetic susceptibility and volume fraction of the spinel having some cationic exchange (ER: quick cooling -quenching-, EL: slow cooling)

Longer Mechanical alloying route:

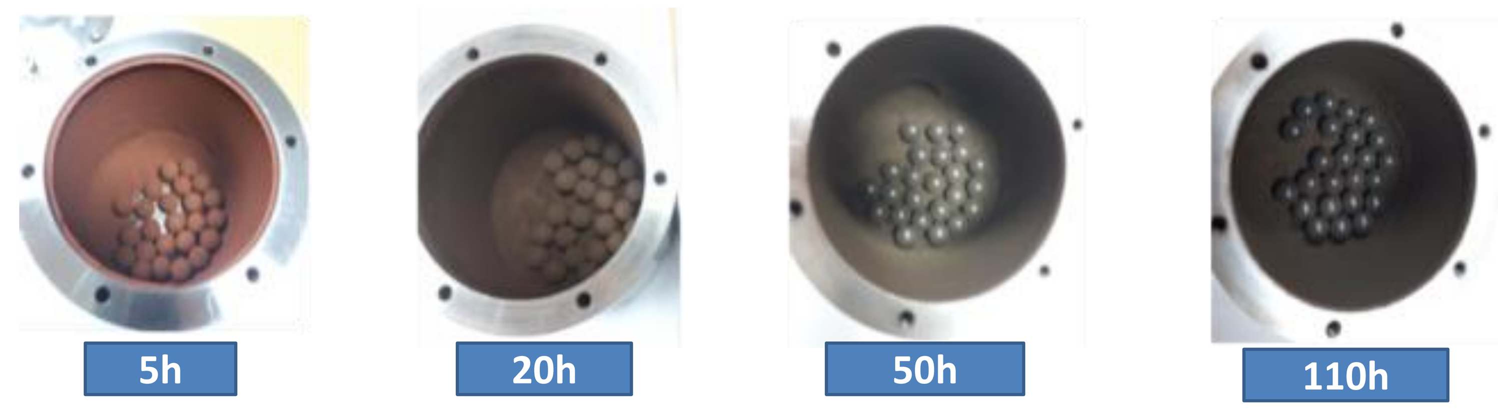
1. XRD evolution and Rietveld analyses as a function of milling time



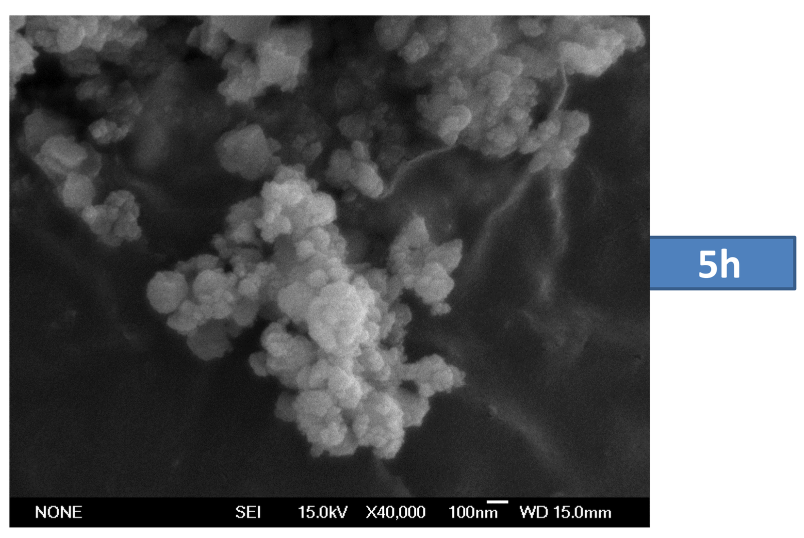
Milling time (h)	Phases	Average	Size(nm)
5	Hematite	65	33
	Zincite	35	58
20	Zn Ferrite	24	10
	Hematite	54	20
	Zincite	22	10
50	Zn Ferrite	81	10
	Hematite	19	40
110	Zn Ferrite	97.5	10
	Hematite	2.5	

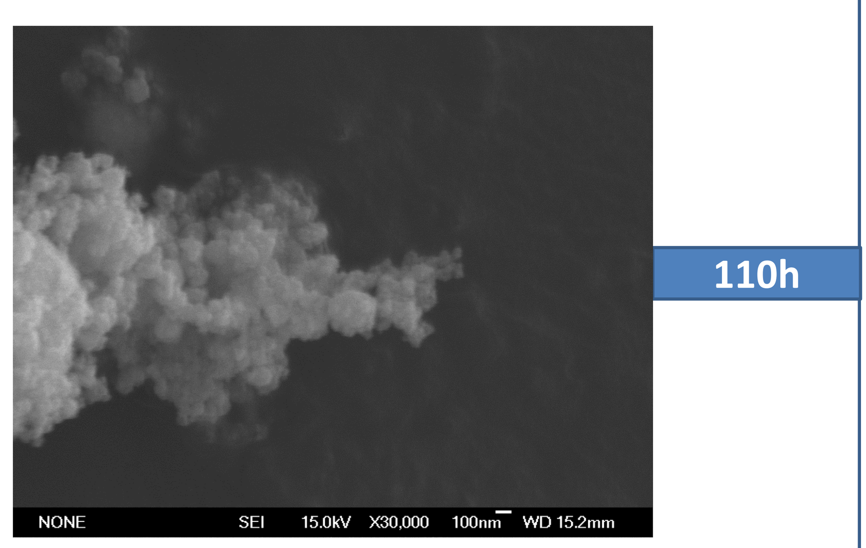
Rietveld refinement shows that after 110h milling the powder contain 97,5 % of nanostructured Zn ferrite

2. Morphology & SEM of milled powder.

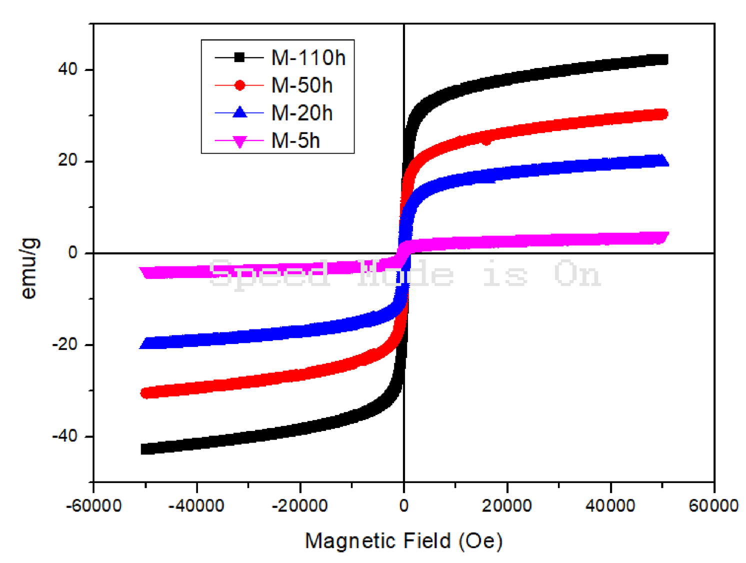


The increase in the amount of Zn ferrite during milling is followed by a change in the color of the milled powder. By SEM is appreciated the size change





3. Magnetic properties:



Mechanical Alloying time (h)	M (emu/g) (5T)
5	3,82
20	19,99
50	30,44
110	42,53

These milled samples are superparamagnetic, increasing M with the volume fraction of nanosized ferrite

Conclusions: Microstructural and magnetic properties depends strongly on the processing route used for synthetizing Zn ferrites. The material milled and calcinated shows a paramagnetic behaviour, with susceptibility χ depending on the heat treatment. These behaviour was associated to an order-disorder transformation at around 1000 ℃ consisting on a ion exchange Zn^{++} and Fe^{+++}. On the other hand, the material milled, the nanosized structure reached by mechanical alloying, lead to a superparamagnetic behaviour.