Synthesis and characterization of nanosized $ZnFe_2O_4$ powders obtained by sonochemistry

OUTLINE

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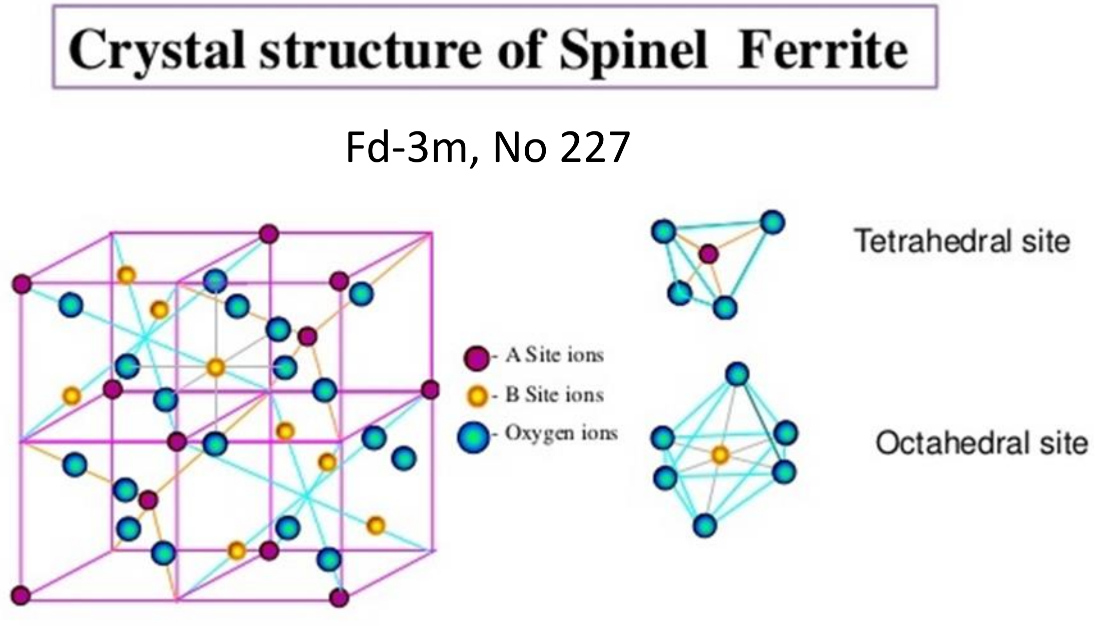
- Characterization
- Researchers
- Final remarks

Introduction

- Prepared in bulk form, $ZnFe_2O_4$ crystallizes in a *normal spinel* structure with Zn^{2+} incorporated almost exclusively at the tetrahedral lattice sites and Fe^{3+} at the octahedral sites ($(Zn)[Fe_2]O_4$). The composition is closely defined at $Zn^{2+}/Fe^{3+} \cong 0.5$.
- Prepared as nanoparticles (NPs), a significant proportion of Zn can enter the structure at the octahedral sites leading to $Zn_xFe_{3-x}O_4$, or $[Zn_x^{+2}Fe_{1-x}^{+3}]_A[Fe_{1+y}^{+3}Fe_{1-y}^{+2}]_BO_{4-\delta}$, wherein few of Fe^{+3} ions at octahedral sites reduced into Fe^{+2} ions, giving metallic character of $ZnFe_2O_4$ films.
- Zink ferrites are widely studied due to their applications in many fields: anode materials for lithium-ion batteries, gas sensors, magnetic materials, catalysts, antibacterial agents in waters, etc.



Brockhouse BN, Corliss LM, Hastings JM *Multiple scattering of slow neutrons by flat specimen and magnetic scattering by zinc ferrite*. Phys Rev **98** (1955) 1721–1727.

Kremenović A.,∗, Antić B. et al, *ZnFe2O4 antiferromagnetic structure redetermination* **426** (2017) 264–266.

Preparation of nanostructured zinc ferrite as powder material

- Sonochemistry assisted co-precipitaion

Generally, the sonochemistry preparation route takes place due to acoustic cavitation phenomenon consisting in the formation, growth and implosive collapse of bubbles generated at a temperature of 5 000 K and a pressure of 800 atm, in liquid medium under the action of ultrasonic waves which enhances the reaction rate, the mass transport and the heat effects.

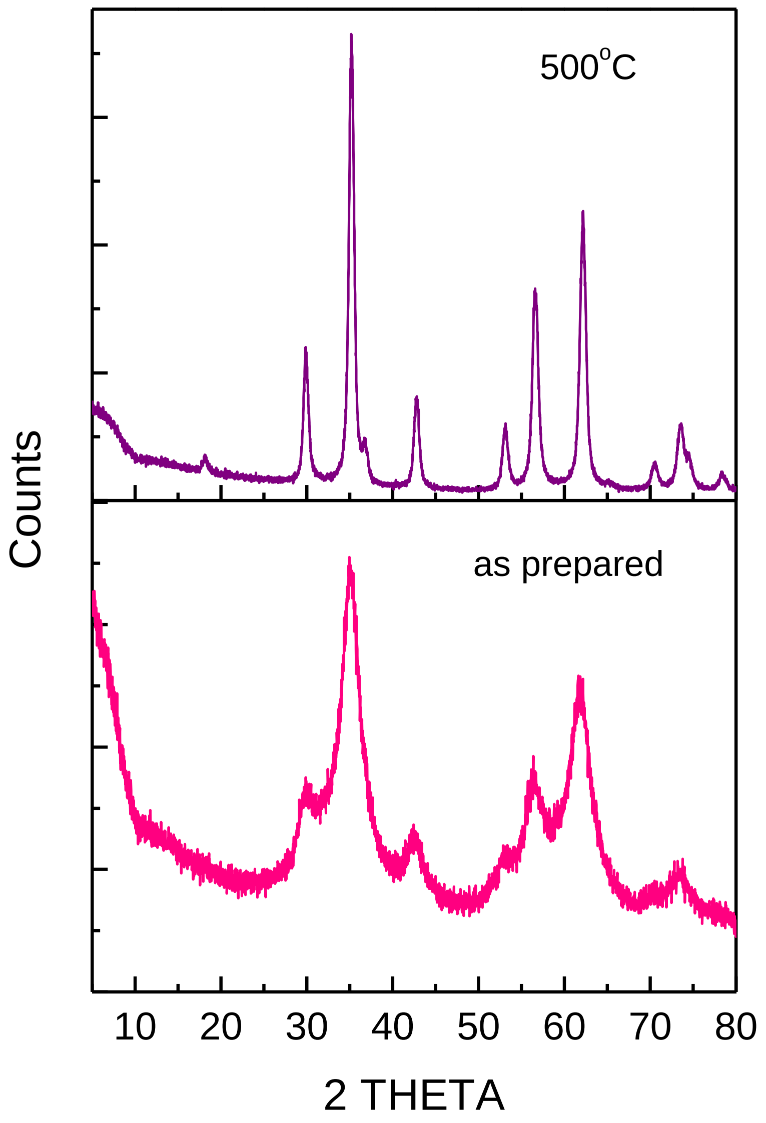
The preparation procedure we followed was as follows:

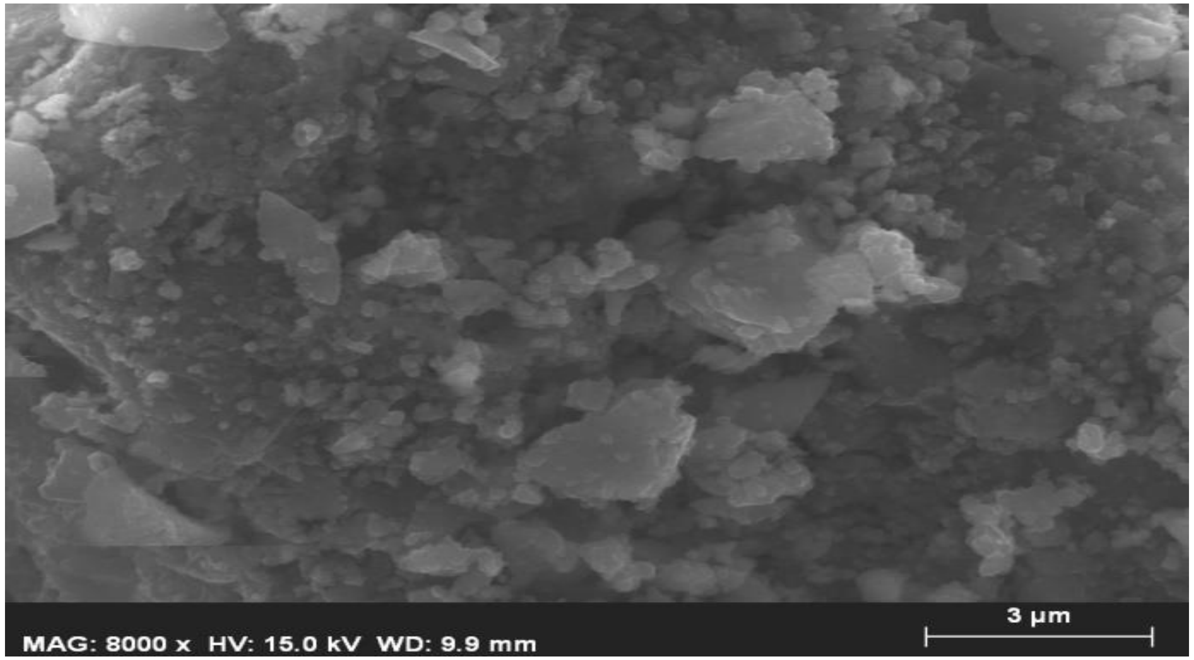
- The Zn^{2+} and Fe^{3+}cations in metal nitrates co-precipitated by solution of NaOH at pH=12 under the applied ultrasonic waves (*Sonics ultrasonic processor*, 750 W) for 15 min: *pulse on*: 0.2 s, *pulse off*: 0.2 s, amplitude 40%.
- The obtained precipitate was annealed at 500ºC for 6 hours.
- Both the as-prepared and the heated substance were identified as zinc ferrite materials.

Characterization

- X-Ray Diffraction (Brucker D8 Advance; 40 kV, 30 mA) in Bragg-Brentano reflection geometry. The Topas-4.2 software was used to analyze the XRD patterns collected with Cu Kα radiation (λ= 1.5418 Å) and LynxEye PSD detector at 20 ^{o}C within the angular range from 10^{o} to 120^{o} 2θ
- Scanning electron microscopy (Philips ESEM XL30 FEG);
- Transmission Electron Microscopy (JEM 200 CX, JEOL Japan)
- Mösbauer spectroscopy (conventional spectrometer) in transmission mode with a ^{57}Co/Rh source; optimized sample thickness. The isomer shifts (IS) of the spectra are referred to the centroid of an α-fe foil (6 µm) reference spectrum at room temperature (RT)
- **SQUID magnetometry** (PPMS, Quantum Design)

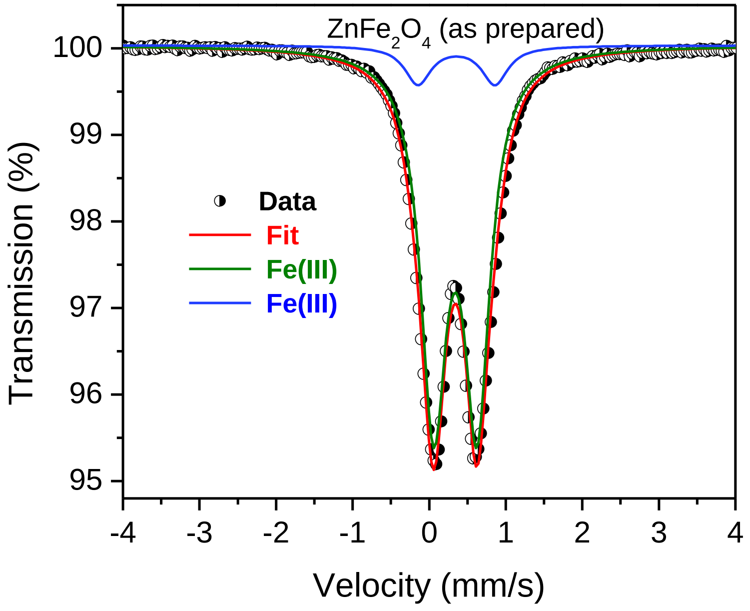
XRD and Electron microscopy



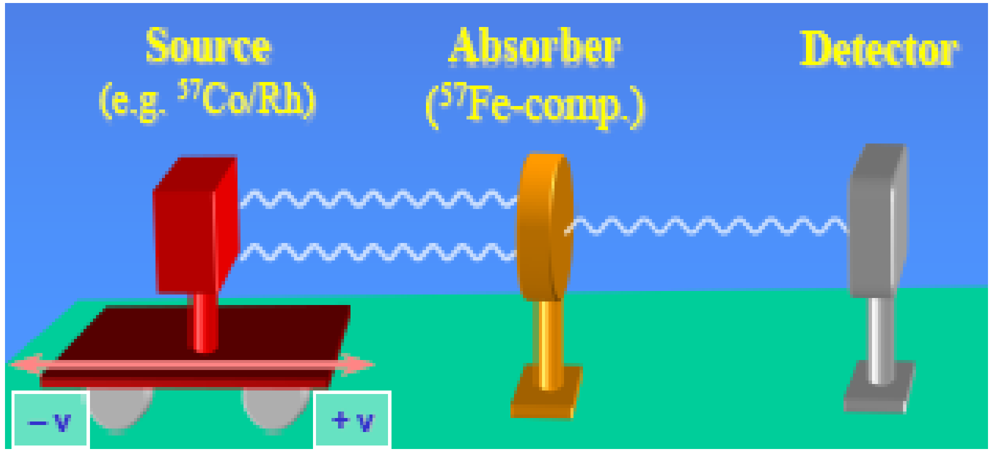


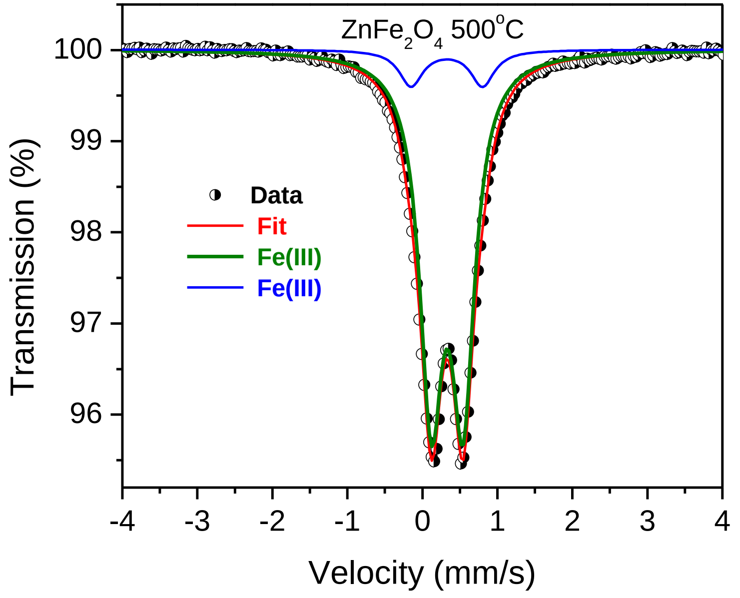
The XRD patterns of the as-prepared samples reveal the presence of both an amorphous and a crystalline $ZnFe_2O_4$ phase.

The peaks In the pattern of the material annealed at 500 ^{o}C are considerably narrower and of higher intensity, proving the sample's higher degree of crystallinity.



Mössbauer spectra at room temperature



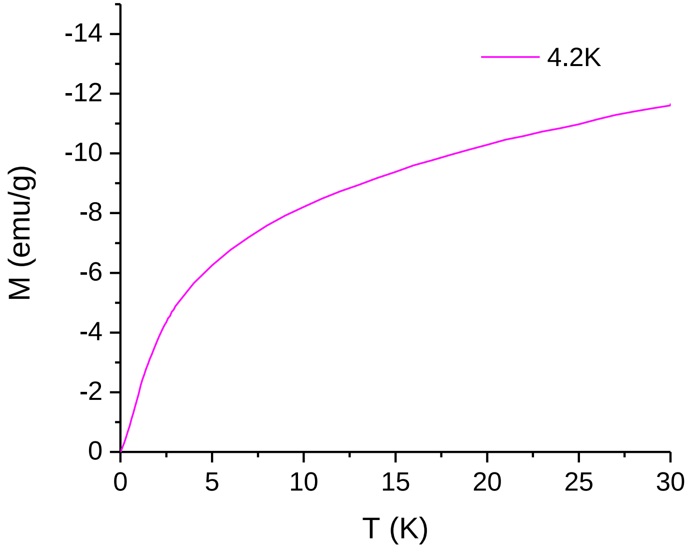


	Iron sites	δ (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})	Area (%)
$ZnFe_2O_4$ as prepared	a-Fe(III)	0.34 (2)	0.57 (1)	0.41 (3)	90 (1)
	b-Fe(III)	0.36 (1)	1.00 (2)	0.42 (1)	10 (1)
$ZnFe_2O_4$ annealed at 500ºC	a-Fe(III)	0.33 (1)	0.42 (1)	0.37 (2)	90 (1)
	b-Fe(III)	0.33 (2)	0.95 (2)	0.38 (1)	10 (1)

Δ - Isomer shift
Δ - quadrupole splitting
Γ - line width
B_{hf} - hyperfine field

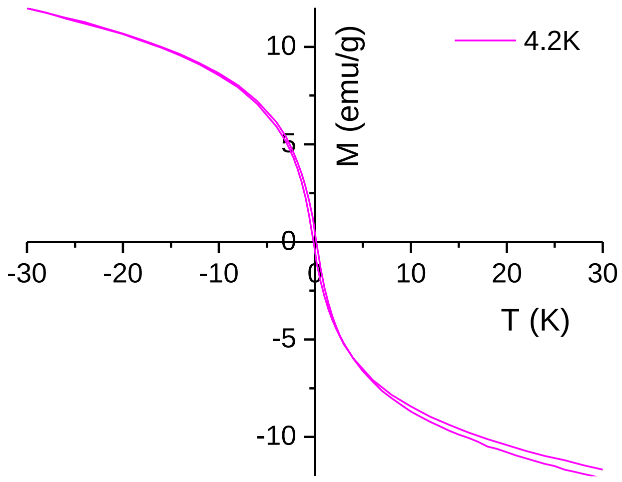
Magnetic Properties

Initial magnetization



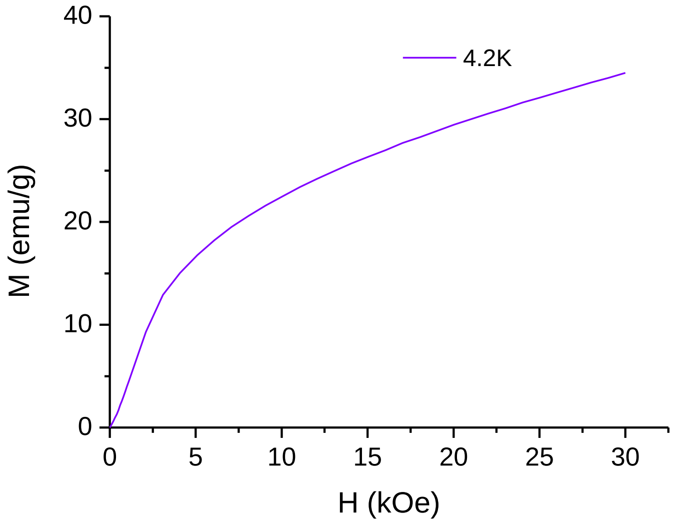
as prepared

Hysteresis curves

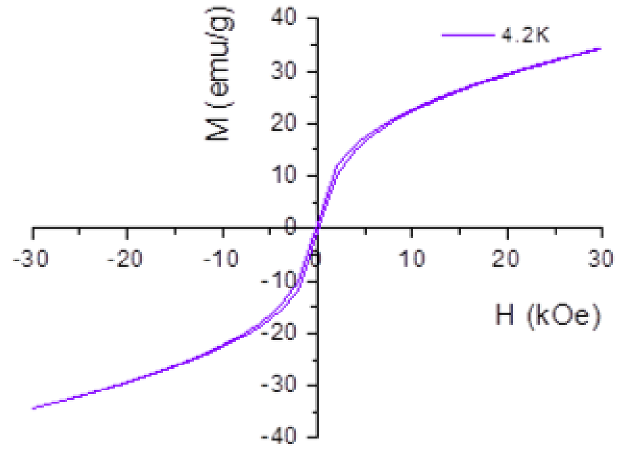


SRMH

Neel, L.. *Ann. Geophys.* **7,** 90 (1951)
Nagata, T. et al *Proc. Jpn. Acad*. **27,** 643–645 (1951)
Jin, H. et al. *JMMM.* **308,** 56–60 (2007)
Yoshikazu, I. & Yasuhiko, S. *.J. Phys. Chem. Solids* **24,** 517–528 (1963)
Ma, J., Chen, K. Sci. Rep. **7** (2017) 42312.

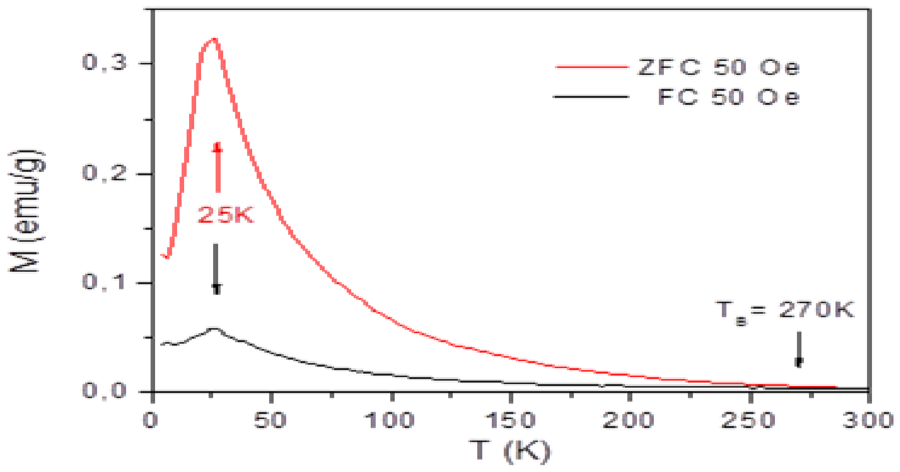


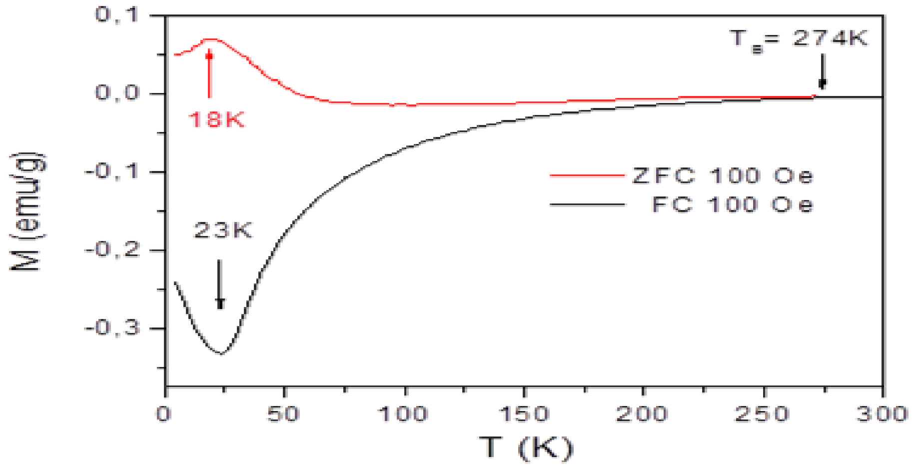
annealed



ZFC- and FC- magnetization

as prepared





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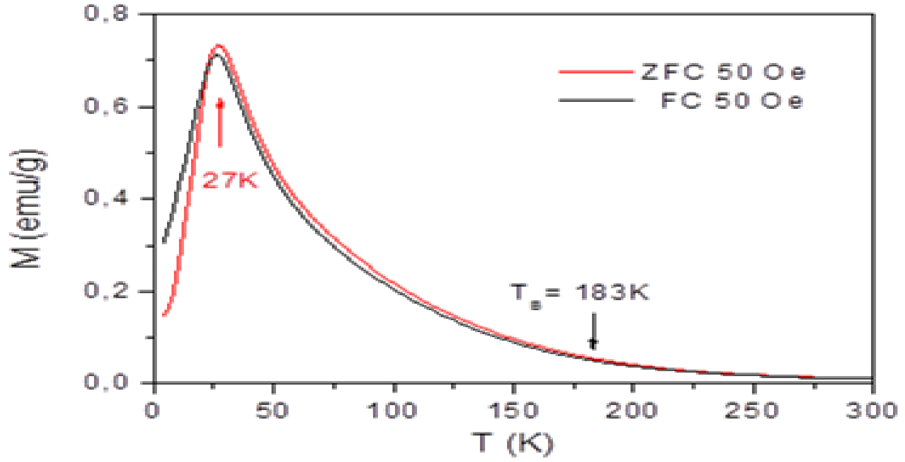

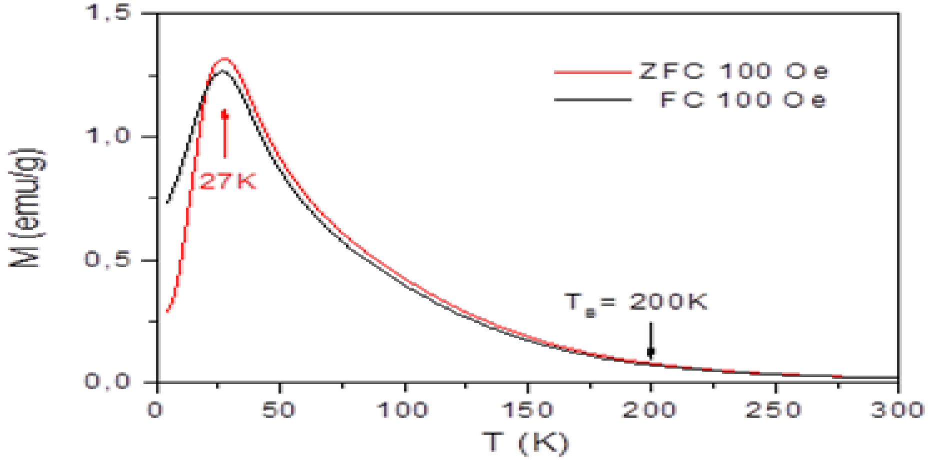

Researchers

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Acknowledgements

Bulgarian National Science Fund, grants KP-06-N48/5 and *KP-06-India-2*
Bulgarian Academy of Science, Joint Research Projects with *Wallonie-Bruxelles International* (**WBI**) , *Belgium* and the *Polish Academy of Sciences, Poland*

Final remarks

A very interesting feature of Zn-ferrite is that at room temperature it exhibits paramagnetic behavior in the bulk, while strong magnetic ordering has been observed at the nanoscale, providing a platform for various spintronic studies and applications in microwave devices.

In recent years, ultrathin spinel ferrite layers have revealed many exciting properties such as electric field-controlled magnetism (and vice versa), interfacial exchange bias, and giant magnetoresistive effects, thanks to the tunable many degrees of freedom of its complex cubic symmetry, see e.g. Bohra, M. , Alman, V. , Arras, R. Nanomaterials 11 (2021) 1286.

We believe that the sonochemistry preparation route is a simple and effective method for synthesizing sufficiently large quantity of materials with clearly expressed self-reversed magnetic hysteresis (SRMH) and may contribute to a better understanding of the mechanism of the phenomenon.