



## Effect of chromium substitution on the structural and magnetic properties of nanocrystalline zinc ferrite



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### HIGHLIGHTS

- Single-phase Cr doped zinc ferrites nanoparticles have been synthesized.
- The prepared nanoparticles have been characterized using different tools.
- The investigated nanoparticles were tested for their magnetic behavior.

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### ABSTRACT

Single-phase Cr doped zinc ferrites have been synthesized by hydrothermal method. The crystal structure, microstructure, crystallite size and distribution, composition and magnetic properties of the synthesized nanoparticles were determined using X-ray powder diffraction, electron microscopies and vibrating sample magnetometry. Powders are composed of ultrafine spherical nanoparticles with a highly homogeneous elemental composition. The nanoparticles have partially inversed cubic spinel structure with average crystallite size below 10 nm. Superparamagnetic behavior is observed at high temperature while ferrimagnetic ordering and surface spin canting is reported at 5 K. Substitution of Fe with Cr ions controls both structural and magnetic parameters.

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## 1. Introduction

Nanotechnology and nanoscience concern with the synthesis, characterization, exploitation and utilization of nanostructured materials which at least have one dimension in the nanometer range. Such nanostructured systems constitute a bridge between infinite bulk systems and single molecules. Individual nanostructures involve clusters, nanoparticles, nanocrystals, quantum dots, nanotubes and nanowires, while collections of nanostructures

involve arrays, assemblies and super lattices of individual nanostructures [1,2]. The uniqueness of the structural characteristics, energetics, response, dynamics and chemistry of nanostructures constitutes the conceptual background and experimental for the field of nanoscience [3]. Suitable control of properties and response of nanostructures can promise with new devices and technologies.

On this sense, ferrites in nanoscale dimension show unusual and fascinating properties compared to their bulk counterparts, being interesting materials owing to their various applications in modern science and technology [4]. In particular, they have recently attracted considerable research interest on their structural, electrical and magnetic properties such as microwave applications, magnetic sensors and catalytic materials; due to their great magnetic permeability and dielectric constant, low dielectric loss, high

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Curie temperature as well as chemical stability and mechanical strength at low frequencies [5–7]. The properties of ferrite nanoparticles are affected by composition and microstructure. Moreover, the addition of impurities induces changes in the texture and defect structure of the crystal, creating significant modifications in the magnetic and electrical properties of these materials [8].

The spinel ferrite structure is characterized by a cubic unit cell, belonging to space group  $Fd\bar{3}m$ , containing  $8(M)_A(Fe_2)_B O_4$  formula units (with M being a divalent transition metal cation), where the 32 oxygen anions are in cubic close packing corresponding to 32e-Wyckoff position  $(x,x,x)$  which prompt two types of interstitial sites: 64 tetrahedral (A) and 32 octahedral (B). These sites are surrounded by four and six oxygen atoms, respectively [9,10]. In a normal spinel structure 8 tetrahedral A sites and 16 octahedral B sites are occupied by the divalent metal cation and the iron trivalent cation, respectively. On this way, bulk Zn-ferrite is a normal spinel with  $Zn^{2+}$  cations locate in 8b-Wyckoff position  $(3/8,3/8,3/8)$  and  $Fe^{3+}$  cations locate in 16c-Wyckoff position  $(0,0,0)$ . However, when is synthesized at nanoscale a significant proportion of Zn and Fe is redistributed forming a mixed spinel structure that has chemical formula  $(Zn_{1-\delta}Fe_{\delta})_A[Zn_{\delta}Fe_{2-\delta}]_B O_4$ , being  $\delta$  the so-called inversion parameter. Inversion modifies the properties of spinel ferrite, for example, altering the antiferromagnetic coupling below  $T_N = 10$  K between B–B ions reported on bulk  $ZnFe_2O_4$  [11]. Moreover, nanoparticles might be composed of a single magnetic domain below a critical size displaying the superparamagnetic behavior: if the temperature is above a particular temperature, which is called the blocking temperature  $T_B$ , the magnetic moments of each nanoparticle fluctuate around its easy axes of magnetization faster than the change of the magnetic field thus showing no remanence and coercivity [12].

On the other hand, the hydrothermal process among the wet chemical methods seems to be an attractive method for preparing fine well-crystallized ferrite powders [13,14]. It can be easily differentiated from other processes, such as coprecipitation/calcination and sol–gel processes, by the temperatures and pressures used in the synthesis reactions. Hydrothermal method utilizes water under pressure and at temperatures above its normal boiling point in order to speed up the reaction between solids. Thus, the present work reports the synthesis of nano-sized chromium-substituted Zinc ferrites by hydrothermal method and consequent changes on their structural and magnetic properties.

## 2. Experimental

### 2.1. Materials

All reagents used in the investigation were analytical grade and used without further purification.  $Cr(NO_3)_3 \cdot 9H_2O$  (Sigma–Aldrich),  $Zn(NO_3)_2 \cdot 6H_2O$  (Sigma–Aldrich) and  $Fe(NO_3)_3 \cdot 9H_2O$  (Sigma–Aldrich) were the Chromium, Zinc and Iron precursors, while NaOH (pellets, 98%, Alfa Aesar) was the precipitating agent, and Polyethylene glycol 400 (Sigma–Aldrich) was used as a surfactant. All solutions were prepared with distilled water.

### 2.2. Synthesis of the investigated nanoparticles

Cr-doped  $ZnFe_2O_4$  nanoparticles  $ZnCr_xFe_{2-x}O_4$  ( $x = 0, 0.1, 0.2$  and  $0.3$ ) (**Cr0–Cr3**) have been prepared by using stoichiometric molar amounts of chromium nitrate  $Cr(NO_3)_3 \cdot 9H_2O$  (for **Cr1–Cr3**), ferric nitrate  $Fe(NO_3)_3 \cdot 9H_2O$ , and zinc nitrate  $Zn(NO_3)_2 \cdot 6H_2O$  were dissolved in 30 mL and stirred magnetically until the reactants dissolved completely). Later, 20 mL of PEG-400 was added dropwise to the mixture to serve as a surfactant that covers the nanoparticles and prevents agglomeration. The obtained solution was stirred for

an addition 1 h. After that, the pH was adjusted to 12 by adding NaOH (2 M) drop-by-drop. After 2 h under continuous stirring, a homogeneous solution containing hydroxide precipitates was obtained. Finally, the obtained reaction mixture (total volume 75 mL) were sealed in Teflon-lined stainless autoclaves, heated at  $180^\circ C$  for 24 h, and then cooled to room temperature gradually. The obtained products were centrifuged, washed several times with deionized water, acetone and absolute ethanol, and then dried at  $80^\circ C$  for 5 h.

### 2.3. Instruments

A pH-meter (Denver Instrument Co., USA) was used to measure the pH values. X-Ray powder diffraction (XRPD) patterns were recorded using a PANalytical X'Pert PRO diffractometer with  $CuK_{\alpha}$  radiation (1.5418 Å). The samples were gently ground in an agate mortar to minimize the required orientation. All data were collected at room temperature over the angular  $2\theta$  range  $10$ – $80^\circ$  with a step of  $0.05^\circ$  and a counting time of 2.5 s/step. The instrumental resolution was determined using LaB6 standard reference material (SRM 660a) provided by National Institute of Standards and Technology (NIST), which is commonly used for calibrating line position and line shape in powder diffractometers. Rietveld refinement of the structure was performed on the XRPD patterns by Maud software [15].

Scanning electron microscopy (SEM) micrographs and X-ray microanalysis were recorded with a JEOL 6610VL microscope operating at 20 kV equipped with an X-Max Silicon Drift Detector for energy dispersive X-ray spectroscopy (EDS) analysis. Transmission electron microscopy (TEM) studies were performed on a JEOL JEM-2100F microscope operated at an accelerating voltage of 200 kV, equipped with a field emission gun (FEG) and an ultra-high resolution pole-piece that provided a point-resolution better than 0.19 nm. The samples for TEM were dispersed in ethanol, sonified and sprayed on a carbon-coated copper grid and then allowed to air-dry, finally, Gatan SOLARUS 950 was used before observation.

The magnetic properties of the prepared nanoparticles were determinate using a Quantum Design Physical Property Measurement System (PPMS) vibrating sample magnetometer (VSM) option. For magnetic measurements, dried powder specimens were compacted and encapsulated into polypropylene powder holders that snap onto the commercial brass trough for a secure press fit. Then, magnetization (M) as function of temperature (T) was measured under applied magnetic field (H) of 100 Oe between 5 and 300 K. Measurement was carried out in subsequent heating and cooling just after the sample reach 5 K without applied magnetic field (ZFC-FC curve). Afterward, hysteresis loops under a maximum H of 50 kOe were measured at 5 and 300 K.

## 3. Result and discussion

### 3.1. Structural characterization

#### 3.1.1. XRPD analysis

Fig. 1 shows XRPD patterns of the prepared **Cr0–Cr3** samples with nominal composition:  $ZnCr_xFe_{2-x}O_4$  ( $x = 0, 0.1, 0.2$  and  $0.3$ ) respectively. These patterns exhibit only the expected Bragg peaks for the cubic spinel-type structure (space group  $Fd\bar{3}m$ ) being Miller indices of identified reflections depicted. Moreover, Bragg peaks show additional broadening over instrumental resolution due mainly to the nanosize of the crystallites belonging to the pure Cr doped Zn-ferrite samples synthesized.

Rietveld analysis for each pattern (Fig. S1) was carried out refining the cell parameter of cubic spinel-type structure,  $a$ , that fixes angle position of reflections, together with the microstructure

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