



## Preferential spin canting in nanosize zinc ferrite

Brajesh Pandey<sup>a,b,\*</sup>, F.J. Litterst<sup>b,c</sup>, E.M. Baggio-Saitovitch<sup>b</sup>

<sup>a</sup> Department of Applied Science, Symbiosis Institute of Technology, SIU, Lavale, Pune 411112, India

<sup>b</sup> Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud 150, 22290-180 Rio de Janeiro, Brazil

<sup>c</sup> Institut für Physik der Kondensierten Materie, Technische Universität Braunschweig, Mendelssohnstr. 3, 38106 Braunschweig, Germany



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### ABSTRACT

Zinc ferrite nanoparticles powder with average size of  $10.0 \pm 0.5$  nm was synthesized by the citrate precursor route. We studied the structural and magnetic properties using X-ray diffraction, vibrating sample magnetometry and Mössbauer spectroscopy. X-ray diffraction patterns show that the synthesized zinc ferrite possesses good spinel structure. Both Mössbauer and magnetization data indicate superparamagnetic ferrimagnetic particles at room temperature. The magnetic behavior is determined by a considerable degree of cation inversion with Fe<sup>III</sup> in tetrahedral A-sites. Mössbauer spectroscopy at low temperature and in high applied magnetic field reveals that A-site spins are aligned antiparallel to the applied field with some possible angular scatter whereas practically all octahedral B-site spins are canted contrasting some earlier reported partial B-site spin canting in nanosize zinc ferrite. Deviations from the antiferromagnetic arrangement of B-site spins are supposed to be caused by magnetic frustration effects.

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### 1. Introduction

During the last four decades technological importance of ferromagnetic ferrite materials has increased significantly. Progress in synthesis techniques has initiated a new surge of interest in ferrites in order to improve their physical properties and expand their applications. In general, soft ferrites have a cubic (spinel) structure and have the general formula  $MFe_2O_4$ , where M represents one or several of the divalent transition metals such as manganese (Mn), zinc (Zn), nickel (Ni), cobalt (Co), copper (Cu), iron (Fe) or magnesium (Mg). Zinc ferrite ( $ZnFe_2O_4$ ) belongs to the class of normal spinels, which contains two different cationic sites, eight tetrahedral A-sites and sixteen octahedral B-sites. While zinc ions exclusively occupy the tetrahedral A-sites, iron ions are only at the octahedral B-sites.

The magnetic properties of spinel ferrites strongly depend on the distribution of cations. Magnetic coupling in spinel ferrite occurs via superexchange interactions. Superexchange between two metal cations can occur via intermediate oxygen ions in the spinel structure as a result of A–O–A, B–O–B and A–O–B coupling. Pure bulk  $ZnFe_2O_4$  has only B–O–B interaction because all the A-sites are occupied by zinc atoms which have no magnetic

moment. This makes zinc ferrite a strongly paramagnetic substance with antiferromagnetic coupling only occurring below about 10 K [1]. However, when particle size is reduced to nanoscale, it has been found that some of the iron ions go to tetrahedral sites (so-called inversion) leading to A–O–B coupling and thus enhancing the magnetic interaction. Partially inverted ferrite can be described as  $(M_{1-c}Fe_c)[M_cFe_{2-c}]O_4$ , where round and square brackets denote the A- and B-sites, respectively, and c is the inversion parameter.

Spin canting is one of the important aspects to understand the magnetism in ferrites. In 1952, Yafet and Kittel [2] developed a model of *uniform* spin canting relative to the average magnetization and in 1966, Geller [3] proposed a model of *localized* spin canting where the canting angle of magnetic ion spin depends on the local magnetic environment. Dormann and Nogues have discussed issues related to magnetization and spin canting in their review [4].

The data of Dickof et al. [5] and Oliver et al. [6] supported localized spin canting in their zinc ferrite samples prepared by ball milling and aerogel techniques, respectively. Several researchers [6–8] showed from Mössbauer effect measurement that the spins corresponding to iron ions in both A- and B-sites are canted while Shim et al. [9] with the help of nuclear magnetic resonance (NMR) showed that spins in the B-site are canted. In this paper we are reporting our observations on nanosize zinc ferrite prepared via the citrate precursor route and discussing our results in the light of spin canting at different iron environments in our sample.

\* Corresponding author at: Department of Applied Science, Symbiosis Institute of Technology, SIU, Lavale, Pune 411 112, India.

E-mail address: [bpandey@gmail.com](mailto:bpandey@gmail.com) (B. Pandey).

## 2. Experimental

Nanosize zinc ferrite with particles of about 10 nm was synthesized by taking aqueous solutions of nitrate salts. The starting materials were ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , mol. wt. 404.0 g/mol), zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , mol. wt. 297.48 g/mol) and citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ , mol. wt. 192.13 g/mol). The chemicals used were from Sigma Aldrich. The iron salt was 99.99% pure while the zinc salt was more than 99% pure.

The amount of nitrate cation was taken in such a way that the molar ratio of zinc to iron was 1:2 while the iron and zinc nitrate solutions with citric acid were taken such that the ratio of cations to citric acid was 1:3. This aqueous solution was maintained for 1 h at 80 °C under constant stirring. The solution was then dried at 95 °C to obtain the precursor. This precursor was calcined in open air at 300 °C for 1 h to obtain zinc ferrite.

X-ray powder diffraction (XRD) with  $\text{Cu-K}\alpha$  radiation (wave length 0.1541 nm) was used to check the crystallographic structure, and the crystallite size of the prepared sample. The XRD spectra were recorded with a SEIFERT ISO DEBYEFLEX 2002. A Versalab-Cryofree vibrating sample magnetometer (VSM) from Quantum Design was used to study the magnetic behavior at room temperature (RT). Mössbauer spectroscopy was used to elucidate the local spin structure and magnetic properties of the samples via the hyperfine interactions.  $^{57}\text{Fe}$  Mössbauer absorption spectra were recorded at room temperature, 8 K and 4.2 K in transmission geometry using a conventional spectrometer employing a 50 mCi  $^{57}\text{Co}/\text{Rh}$  source. The sample absorber had a thickness corresponding to about 0.2 mg  $^{57}\text{Fe}/\text{cm}^2$ . External magnetic fields parallel to incident gamma ray direction were applied at the absorbers up to 6 T. The spectra were analyzed assuming Lorentzian line shapes allowing for some Gaussian broadening (Voigt profile).

## 3. Results and discussion

### 3.1. X-ray diffraction

Fig. 1 shows the XRD patterns of the zinc ferrite powder. All the diffraction peaks correspond to the spinel structure and are matching well with bulk zinc ferrite. The peaks are quite broad with respect to bulk counterpart. We used the broadening of the most intense XRD peaks to estimate average particle size using the Scherrer formula. The calculated average particle size was

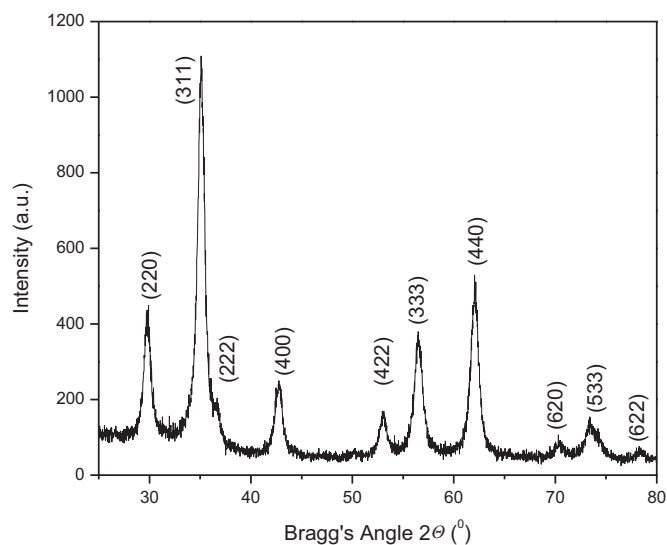


Fig. 1. X-ray diffraction pattern of 10 nm particles of  $\text{ZnFe}_2\text{O}_4$ .

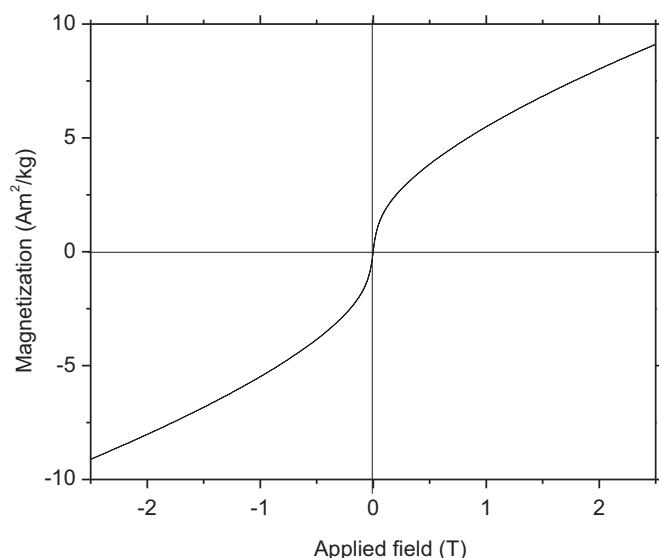


Fig. 2. Magnetization vs. applied field for 10 nm particles of  $\text{ZnFe}_2\text{O}_4$ .

$10.0 \pm 0.5$  nm. From an analysis using the Rietveld method we found that the strain in the sample was negligible. Our XRD data show that the nitrate method used in the present study is capable of producing nanosize  $\text{ZnFe}_2\text{O}_4$  particles in pure phase and is less time consuming as compared to previously used citrate precursor method, where citrate salt solution of cations was refluxed for 24 h as described earlier [10].

### 3.2. Magnetization measurement

Bulk magnetization obtained from the measurements in the VSM at room temperature is shown in Fig. 2. The data were recorded up to an external magnetic field 2.5 T in a full cycle to see any hysteresis behavior. The unsaturated magnetization behavior observed in our nanocrystalline zinc ferrite is typical for superparamagnetic and single domain zinc ferrite powders [8]. Coercive field and remanent magnetization are negligibly small. The magnetization rises sharply as the applied field increases from zero in either direction but still does not reach saturation due to magnetic anisotropy. The maximum magnetization obtained at 2.5 T is  $9.1 \text{ A m}^2/\text{kg}$ , which is quite high for a paramagnetic system. This shows that the magnetic order within our 10 nm size zinc ferrite particles is ferrimagnetic at room temperature though superparamagnetic in its magnetic behavior. Hofmann et al. [11] have also found ferrimagnetic structure for zinc ferrite of this particle size.

It is worth to mention here the maximum magnetization reported in  $\text{ZnFe}_2\text{O}_4$  nanopowders prepared via different preparation routes. For example, Kundu et al. [12] prepared  $\text{ZnFe}_2\text{O}_4$  of size 13 nm with a relatively less common co-precipitation technique, using urea hydrolysis for few minutes and reported magnetization of about  $21 \text{ A m}^2/\text{kg}$  at an external applied field of 1.07 T. Shenoy et al. [13] prepared  $\text{ZnFe}_2\text{O}_4$  nanosize particles using co-precipitation followed by ball milling, and found saturation magnetization around  $7.5 \text{ A m}^2/\text{kg}$  for 9 nm particles. Chinnasamy et al. [8] prepared nanosize  $\text{ZnFe}_2\text{O}_4$  particles of different sizes using high energy ball milling and reported saturation magnetization around  $11 \text{ A m}^2/\text{kg}$  for particles of 11 nm size. This shows that our preparation of  $\text{ZnFe}_2\text{O}_4$  nanosize particles reveals magnetization values comparable to the earlier reported.

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