

Ferromagnetic Behavior in Zinc Ferrite Nanoparticles Synthesized using Coprecipitation Technique

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Abstract

Zinc ferrite have been produced and used by humans since long time, however understanding of ZnFe₂O₄ as a nano structured materials is very useful in order to be used for technological applications. ZnFe₂O₄ structural, magnetic and electrical properties are different when synthesized using different techniques. Therefore, it would be interesting to investigate the structural and magnetic properties of ZnFe₂O₄ when in nanosize. In the present work nanocrystalline ZnFe₂O₄ was synthesized using coprecipitation technique. The structural and magnetic properties of ZnFe₂O₄ nanopowders were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM), dynamic light scattering (DLS), infrared spectroscopy (FTIR) and vibrating sample magnetometer (VSM). The XRD of ZnFe₂O₄ nanoparticles showed the single phase spinel structure. The average particle size of ZnFe₂O₄ calculated from XRD was observed to be 45 nm. DLS measurements showed the average particle size to be 42 nm. Further, the phase formation of ZnFe₂O₄ was confirmed from the IR measurements. The IR spectra showed the bands corresponding to ZnFe₂O₄. We observed the room temperature ferromagnetic behavior in synthesized ZnFe₂O₄ nanoparticles which may be due to the random distribution of Zn²⁺ and Fe³⁺ at the tetrahedral (A) and octahedral [B] sites. In our future work, we want to investigate the defect induced magnetic properties of ZnFe₂O₄ nanoparticles which is likely to contribute for ferromagnetic behavior in this material.

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INTRODUCTION

Nanoferrites are being extensively investigated due to their potential applications in magnetic refrigeration, drug delivery, high-density information storage, magnetic fluids etc. (Habibi *et al.*, 2013, Choi *et al.*, 2008). Spinel ferrites have been intensively investigated due to their versatile physical and chemical properties and due to their technological applications in magnetic sensors, biosensors, photocatalysts, nanoelectronics, biomedical (Ling *et al.*, 2013, Durka Prasad *et al.*, 2014). Zinc ferrite is one of the most important technological material having applications in radio engineering, radio technology, semiconductors etc. Bulk zinc ferrite have the normal spinel structure with Zn²⁺ ions occupying tetrahedral (A) site and Fe³⁺ ions being occupied in octahedral (B) site and is antiferromagnetic material having Neel temperature around 10 K (Pettit *et al.*, 1971). The magnetic properties of zinc ferrites significantly depend when a small amount of Fe³⁺ ions occupy A site (Choi *et al.*, 2008).

The magnetic properties of zinc ferrite nanoparticles was observed to have higher magnetization values compared to the bulk materials and also the synthesis technique might also play important role in achieving the ferromagnetic nature of zinc ferrite (Chen *et al.*, 1980, Singh *et al.*, 2010 and Thirupathi *et al.*, 2012). Several

reports on ZnFe₂O₄ have showed that, ZnFe₂O₄ is paramagnetic at room temperature with Néel temperature T_N≈10 K. But, recently when ZnFe₂O₄ synthesized by different techniques and due to creation of oxygen vacancies ferromagnetic behavior was observed. Based on the above interesting properties of ZnFe₂O₄ nanoparticles, in this work we aimed to achieve room temperature ferromagnetic behavior of ZnFe₂O₄ nanoparticles synthesized using coprecipitation technique.

MATERIALS AND METHODS

ZnFe₂O₄ nanoparticles were synthesized using coprecipitation method (Raghavender *et al.*, 2011). The AR grade sodium hydroxide (NaOH), zinc (II) nitrate hydrate (Zn(NO₃)₂·6H₂O), ferric (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O) (98%) were used as starting materials. The metal nitrates were dissolved together in a minimum amount of deionized water to get a clear solution. In the metal nitrates precursor solution NaOH solution was added drop by drop under vigorous stirring. The precipitation occurred immediately to change the reaction solution to dark brown. The entire reaction was carried out at 75 °C for 2 h. The pH of the solution was varied by NaOH. The precipitate was filtered using a filter paper and

then dried at 220 °C for 3 h in oven. The structural characterization of zinc ferrite powders was carried out using Philips (France) X-ray diffraction (XRD) system with Ni filter using Cu –K α radiation (wave length $\lambda = 1.54 \text{ \AA}$). The ZnFe₂O₄ structure was confirmed by ABB Bomem MB 102 (Canada) infrared (FTIR) spectrometer. The samples were mixed with KBr and made in the form of pellets for IR transmission measurements. The particle size and morphology was verified using FEI Quanta (USA) FEG 200 High Resolution Scanning Electron Microscope (HR-SEM) and DLS measurements using LS spectrometer (Switzerland). The ZnFe₂O₄ powder was made in the form of pellet by applying 5 Tons of pressure and then SEM measurements was carried. For DLS measurements ZnFe₂O₄ powder was dissolved in ethanol and a high intensity laser beam was passed on to the dissolved sample to capture the particle size image. Room temperature magnetic properties were investigated using Lakeshore (USA) VSM 7410.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of ZnFe₂O₄ nanoparticles. The XRD pattern shows the formation of single phase spinel structure. The lattice constant a from the XRD analysis was observed to be 8.409 Å, which is in agreement with the ZnFe₂O₄ nanoparticles synthesized by different techniques (Anjaneyulu *et al.*, 2014). The average particle size D was calculated using most intense peak (3 1 1) employing the Scherrer formula (Raghavender 2013).

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

where β is the angular line width at half maximum intensity and θ is the Bragg angle for the actual peak.

Table 1: Particle size D from XRD, DLS, lattice constant a , IR bands ν_1, ν_2, ν_3 , Coercivity H_c , remanence magnetization M_r , maximum magnetization M for ZnFe₂O₄ nanoparticles

D_{XRD} (nm)	D_{DLS} (nm)	a (Å)	ν_1	ν_2	ν_3	H_c (Oe)	M_r (emu/g)	M (emu/g)
45	42	8.409	544	388	329	57	1.2	10.6

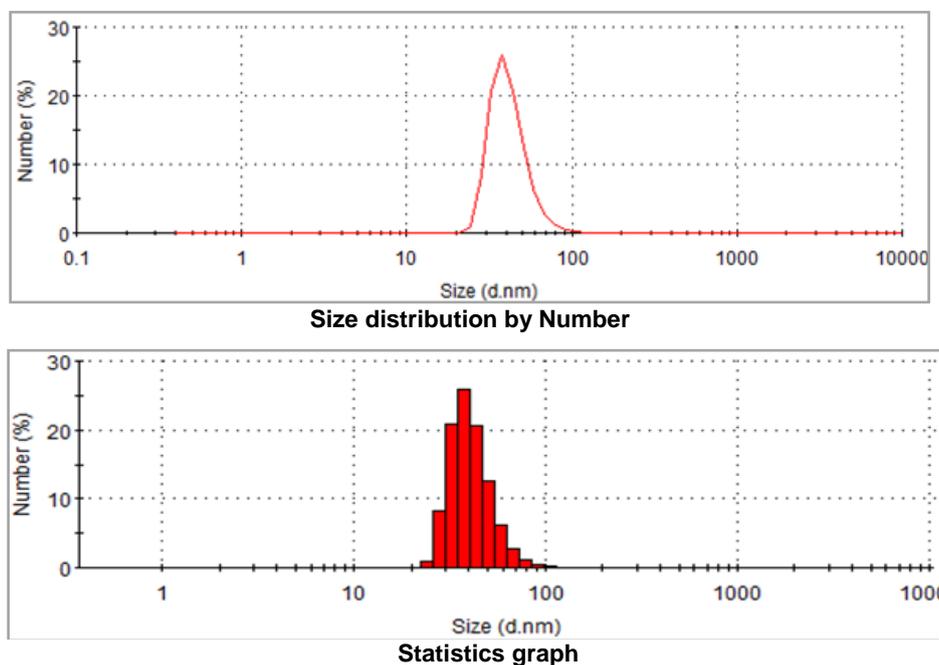


Figure 2: DLS image by distribution and statistics graph of ZnFe₂O₄ nanoparticles.

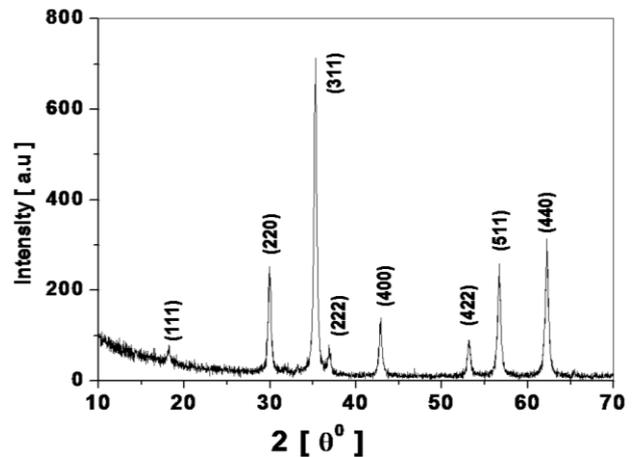


Figure 1: X-ray diffraction patterns of ZnFe₂O₄ nanoparticles

The average particle size calculated from XRD spectra was observed to be 45 nm (Table 1). The particle size was also measured from DLS system. The DLS measurement shows the particle size to be 42 (Figure 2). Therefore the average particle sizes calculated from XRD and DLS measurements are very well in agreement. Figure 3 shows the SEM image of synthesized ZnFe₂O₄ nanoparticles. Due to agglomeration in the synthesized nanoparticles we could not clearly observe the particle size distribution. Generally, when the particle size is in nano regime, due to nature and forces between them, agglomeration occurs which seems to be unavoidable when synthesized by few techniques. However, the XRD and DLS measurements support the existence of the nanoparticles in the synthesized ZnFe₂O₄ powder.

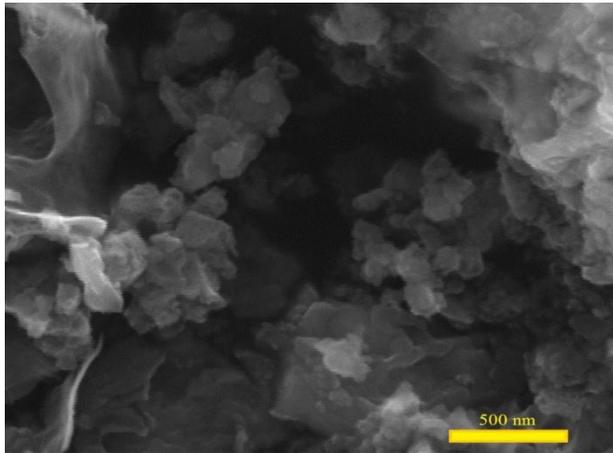


Figure 3: SEM image of ZnFe₂O₄ nanoparticles

The IR spectra of ZnFe₂O₄ nanoparticles are shown in Figure 4. IR spectra shows the bands corresponding to ZnFe₂O₄. The IR spectra shows the three absorption bands. The first band, ν_1 , is located in the 800 – 500 cm⁻¹ range, the second band, ν_2 , in the 500 – 350 cm⁻¹ range, while the third band, ν_3 , occurs between 350 and 280 cm⁻¹ range. According to Waldron (Waldron 1955), ν_1 band corresponds to the stretching vibrations of Zn²⁺-O band in tetrahedral sites, while ν_2 is assigned to Fe³⁺-O stretching of octahedral sites. On the other hand, ν_3 is result of oscillations of metal atoms in the isotropic force fields of their tetrahedral or octahedral environment. The IR results observed for ZnFe₂O₄ are in support with the reported data in the literature (Raghavender *et al.*, 2011; Raghavender 2013; Anjaneyulu *et al.*, 2014).

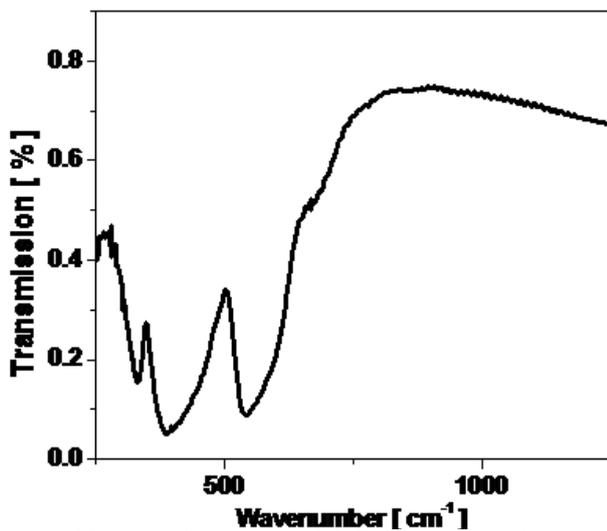


Figure 4: IR spectra of ZnFe₂O₄ nanoparticles

Figure 5 shows the room temperature hysteresis curve of ZnFe₂O₄ nanoparticles. The derived parameters are listed in Table 1. The hysteresis curve shows ferromagnetic nature of ZnFe₂O₄ nanoparticles. The magnetization curve does not seem to be saturated even with the maximum applied field of 10 kOe. From the hysteresis curve, the coercivity H_c was observed to be 57 Oe, remanence magnetization M_r was observed to be 1.2 emu/g and the maximum magnetization M to be 10.6 emu/g. ZnFe₂O₄ nanoparticles / bulk materials measured at low temperatures or synthesized at low temperatures shows ferromagnetic behavior. Generally, ZnFe₂O₄ shows

the paramagnetic behavior at room temperature as reported in literature. The probable reason for the observed ferromagnetic behavior in our case may be due to several facts such as structural rearrangement, which may induce changes due to the superexchange interaction in the tetrahedral (A) and octahedral [B] sites (Deraz *et al.*, 2012). In the case of ZnFe₂O₄ thin films, the random distribution of Zn²⁺ and Fe³⁺ at (A) and [B] sites or the defects causes the ferromagnetic behavior (Raghavender, 2011). In ZnFe₂O₄ nanoparticles or bulk materials, the superexchange interaction between (A) and [B] sites does not seem to favor at room temperature, and when measured below room temperature ZnFe₂O₄ shows ferromagnetic behavior (Ayyapan *et al.*, 2010; Goya *et al.*, 1999). The ferromagnetic behavior in our case may also be due to nonequilibrium distribution of Fe³⁺ ions in (A) and [B] sites (Bohra *et al.*, 2006). In ZnFe₂O₄ the inversion parameter leads to the ferromagnetic behavior (Hofmann *et al.*, 2004). In fact, the magnetic properties of ZnFe₂O₄ are influenced mainly due to the synthesis routes, annealing temperature, cation distribution and the grain size (Deraz *et al.*, 2012). The synthesis route makes a lot of difference in the properties of materials while no difference in some other properties (Upadhyay *et al.*, 2007). The ferromagnetic behavior may also arise due to the spin or structural disorder when ZnFe₂O₄ is synthesized by different routes. Therefore, the observed magnetic properties in the present work may be due to the above mentioned facts. In our future work, we will try to investigate in detail the magnetic properties of ZnFe₂O₄ nanoparticles prepared under several experimental conditions to clearly understand the origin of ferromagnetic behavior.

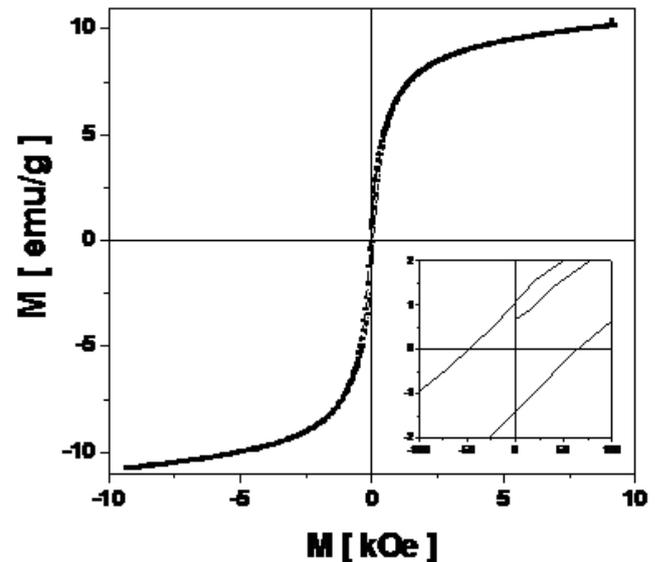


Figure 5: Room temperature M-H curve for ZnFe₂O₄ nanoparticles. The inset of the figure shows the expanded lower field curve.

CONCLUSION

ZnFe₂O₄ nanoparticles were synthesized using coprecipitation technique. The average particle size of synthesized ZnFe₂O₄ were observed to be 45 nm. DLS measurements showed the average particle size around 42 nm. The particle size calculated from XRD and DLS measurements are very well in agreement. The IR spectra showed the bands corresponding to ZnFe₂O₄.

Room temperature ferromagnetic behavior was observed for synthesized ZnFe₂O₄ nanoparticles. The ferromagnetic behavior in the synthesized ZnFe₂O₄ nanoparticles may be due to the random distribution of Zn²⁺ and Fe³⁺ at the tetrahedral (A) and octahedral [B] sites, inversion parameter, synthesis techniques etc.

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