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Original Research

Effect of Particle Size on the Structural and Magnetic Properties of Nanocrystalline Zinc Ferrite

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Abstract

$ZnFe_2O_4$ is one of the most important technological material having applications in radio engineering, radio technology, semiconductors, bio-medical applications etc. $ZnFe_2O_4$ when in bulk form shows paramagnetic behavior at room temperature. When $ZnFe_2O_4$ is synthesized by some techniques it was possible to see the ferromagnetic behavior. Also, $ZnFe_2O_4$ in nanocrystalline form exhibit different magnetic properties. Therefore in the present work we intend to present the properties of particle size behavior of $ZnFe_2O_4$ nanoparticles. $ZnFe_2O_4$ nanoparticles were synthesized by oxalic acid based precursor method. The obtained $ZnFe_2O_4$ nano powders were thermally annealed from 300 to 600 °C. The structural and magnetic characterization were measured using X-ray diffraction (XRD), scanning electron microscope (SEM), IR measurements and vibrating sample magnetometer (VSM). XRD patterns clearly showed the formation of zinc ferrite. The particle size was observed to increase from 19 to 35 nm with increasing annealing temperature. The lattice constants were observed to decrease with increasing particle size. The nanoparticles size were confirmed using SEM measurements. IR measurements were carried to confirm the phase formation of $ZnFe_2O_4$ nanoparticles. The Infrared spectra showed the characteristic features of vibrational bands corresponding to spinel ferrite. Room temperature ferromagnetic properties were observed for zinc ferrite having particle sizes 19 and 21 nm. For the particle size 29 and 35 nm it showed paramagnetic nature. The magnetic properties of zinc ferrite nanoparticles were observed to be dependent on the particle size.

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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 and Durka Prasad *et al*., 2014). $ZnFe_2O_4$ is one of the most important technological material having applications in radio engineering, radio technology, semiconductors etc. Bulk $ZnFe_2O_4$ has the normal spinel structure with Zn^{2+} ions occupying tetrahedral (A) sites and Fe^{3+} ions being occupied in octahedral [B] sites and is antiferromagnetic material having Neel temperature around 10 K (Pettit *et al.,* 1971). The magnetic properties of $ZnFe_2O_4$ significantly depends, when a small amount of Fe^{3+} ions occupy A site (Choi *et al.,* 2008).

The magnetic properties of $ZnFe_2O_4$ nanoparticles were 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 $ZnFe_2O_4$ (Choi *et al.,* 1980). It was observed that the magnetic properties of $ZnFe_2O_4$ were also dependent on the particle size (Choi *et al.,*

1980; Singh *et al.,* 2010 and Thirupathi *et al.,* 2012). Several researchers suggested that, $ZnFe_2O_4$ having lower particle size shows ferromagnetic nature and higher particle size as paramagnetic and vice-versa. But still there is no clear evidence on such behavior. In this article we made an attempt to synthesize $ZnFe_2O_4$ nanopowders in order to observe the room temperature ferromagnetic nature. Also we are presenting the results observed for the particle size dependent structural and magnetic properties of nanocrystalline $ZnFe_2O_4$ synthesized by oxalate based precursor method.

MATERIALS AND METHODS

Nanocrystalline $ZnFe_2O_4$ powders were synthesized using oxalate based precursor method (Raghavender *et al.,* 2011). The A.R Grade citric acid ($C_6H_8O_7.H_2O$), zinc nitrate ($Zn(NO_3)_2.6H_2O$), ferric nitrate ($Fe(NO_3)_3.9H_2O$) (≥99%) were used as starting materials. The obtained $ZnFe_2O_4$ nanopowders were annealed at temperatures 300, 400, 500 and 600 °C to study the particle size dependent structural and magnetic properties. The structural characterization of zinc ferrite powders was carried out using Philips (France) X-ray diffraction (XRD) system with Ni filter using Cu –Kα radiation (wave length λ = 1.54 A°). The structural changes with annealing temperature are observed 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). Room temperature magnetic properties were investigated using Lakeshore (USA) VSM 7410.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of $ZnFe_2O_4$ nanoparticles annealed at different temperatures 300, 400, 500 and 600 °C. XRD patterns clearly showed the formation of single phase spinel structure without any secondary phases. It is observed that, as the annealing temperatures was increased the particle size was observed to increase. The XRD peaks become sharp and the full width half maximum decreased. The decrease in the full width half maximum is the evidence of increased particle size with increasing annealing temperatures as shown in Table 1. The particle size was observed to increase from 19 nm to 35 nm with the increase of annealing temperature (Figure 2). It is observed from Figure 2 that, the lattice constants decreased with increasing particle size. The decrease in the lattice constant is due to the larger ionic radii of Zn^{2+} (0.82 Å) than of Fe^{3+} (0.67 Å). It is observed in ultrafine particles that surface energy and surface tension of particles is high, resulting in a tendency to shrink the lattice, which causes reduced lattice constant (Scott *et al.,* 1983). Literature suggests that, lattice constants and particle size are directly related; stating that, as particle size increases, this causes a corresponding increase or decrease in the lattice constants. From our investigations we observed that as the particle size increases the lattice constant continues to decrease. Figure 3 shows the typical SEM picture of $ZnFe_2O_4$ nanoparticles annealed at 400 °C. The SEM picture clearly shows the nanoparticles in the prepared sample. The average grain size for the $ZnFe_2O_4$ nanoparticles were observed to be in the range of 40 – 50 nm.

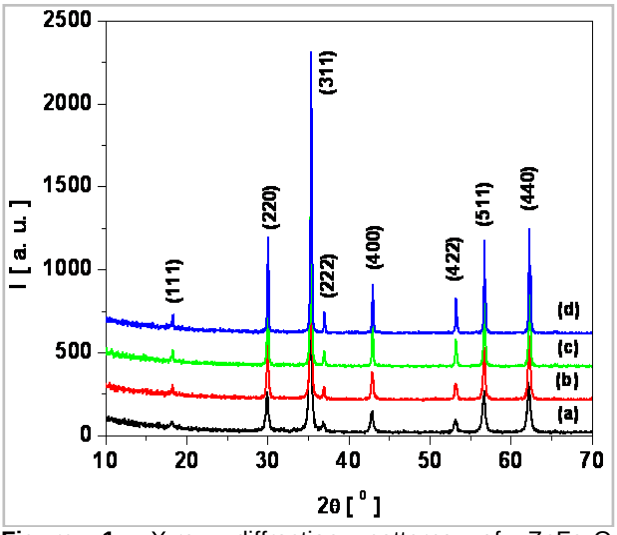

Figure 1: X-ray diffraction patterns of $ZnFe_2O_4$ nanoparticles annealed at (a) 300 °C, (b) 400 °C, (c) 500 °C and (d) 600 °C temperatures

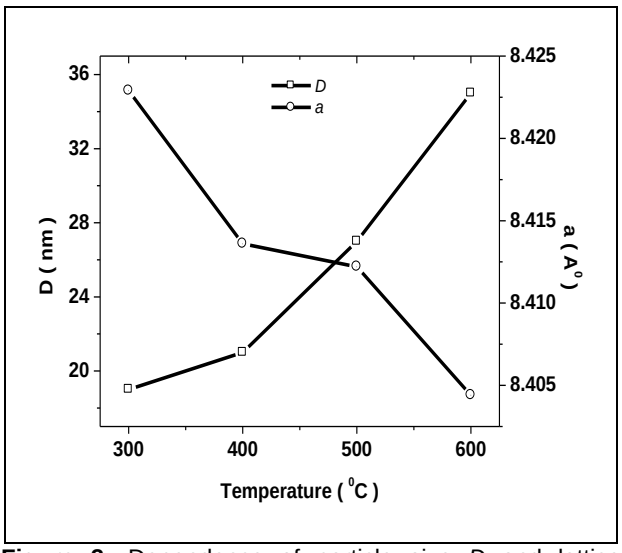

Figure 2: Dependence of particle size *D* and lattice constant *a* of $ZnFe_2O_4$ nanoparticles on the annealing temperatures

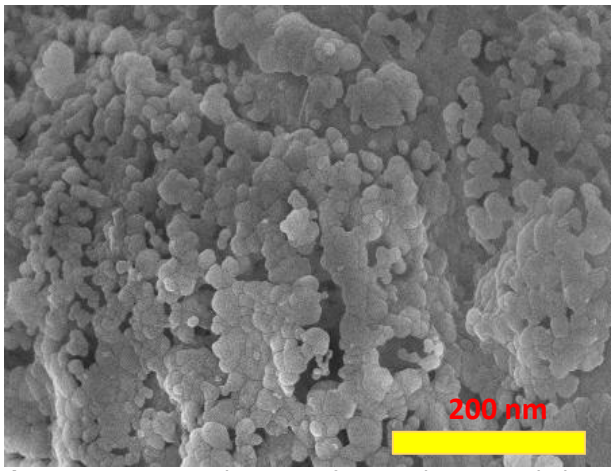

Figure 3: SEM image of sample annealed at temperatures 400 °C

Table 1: Particle size *D*, lattice constant *a*, IR bands v_1, v_2, v_3, Coercivity H_c, remanence magnetization M_r and maximum magnetization *M* for $ZnFe_2O_4$ nanoparticles

Temp. °C	*D* (nm)	*a*(A°)	v_1 (cm^{-1})	v_2 (cm^{-1})	v_3 (cm^{-1})	H_c (Oe)	M_r (emu/g)	*M* (emu/g)
200	19	8.422	540	378	332	480	4.42	9.8
300	21	8.414	523	387	331	192	3.41	8.6
400	29	8.412	539	391	334	-	-	-
500	35	8.404	545	393	333	-	-	-

The IR spectra of $ZnFe_2O_4$ nanoparticles having different particles sizes are shown in Figure 4. It is clearly observed from Figure 4 that, the IR spectra shows the three absorption bands. The first band, v_1, is located in the 800 – 500 cm^{-1} range, the second band, v_2, in the 500 – 350 cm^{-1} range, while the third band, v_3, occurs between 350 and 280 cm^{-1} range. According to Waldron (Waldron 1955), v_1 band corresponds to the stretching vibrations of Zn^{2+}- O band in tetrahedral sites, while v_2 is assigned to Fe^{3+}- O stretching of octahedral sites. On the other hand, v_3 is result of oscillations of metal atoms in the isotropic force fields of their tetrahedral or octahedral environment. It is evident from Table 1 that, the v_2 band significantly changes its position towards the higher wave numbers. Simultaneously, it gradually changes its shape, due to the growth of broad shoulder on the high-wave number side of the band (Andres-Verges *et al.,* 1993; Raghavender *et al.,* 2011). So it can be concluded that the change of the size of nanoparticles causes the variation in infrared bands positions which was reported in the literature (Raghavender *et al.,* 2011and Raghavender 2013).

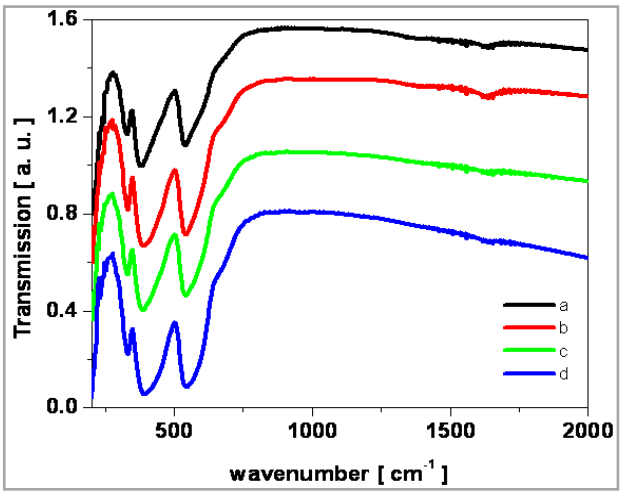

Figure 4: IR spectra of $ZnFe_2O_4$ nanoparticles annealed at (a) 300 °C, (b) 400 °C, (c) 500 °C and (d) 600 °C temperatures

Figure 5 shows the room temperature M-H loops of $ZnFe_2O_4$ nanoparticles with different particle sizes. The derived parameters are given in Table 1. It is observed that, as the particle size increases the magnetization was observed to decrease. $ZnFe_2O_4$ having particle sizes 19 and 21 nm showed the ferromagnetic behavior with clear hysteresis curve. In the case of 29 and 35 nm particles it showed paramagnetic behavior. Also the magnetization was observed to decrease with increasing particle size. Similar results have been reported by Uniyal *et al.* (2010). The decrease in the magnetization for $ZnFe_2O_4$ nanoparticles can be explained on the basis of grain growth. Due to the grain growth, grain traps the inter-granular pores. This inter-granular porosity may lead to decrease of magnetic properties. Magnetically ordered nature of $ZnFe_2O_4$ is evident from the magnetization loops for the samples having particle size 19 and 21 nm.

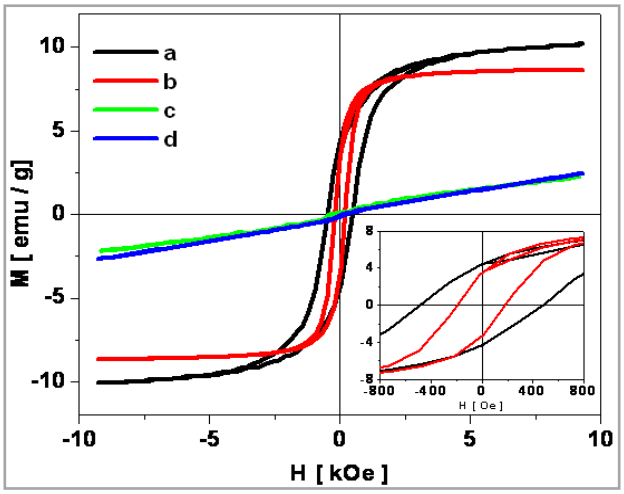

Figure 5: Room temperature M-H curves for $ZnFe_2O_4$ nanoparticles annealed at (a) 300 °C, (b) 400 °C, (c) 500 °C and (d) 600 °C temperatures. The inset of the figure shows the expanded filed curve for 300 ^{0}C and 400 ^{0}C annealed samples

We have observed the linear magnetization loops for the samples having particle size 29 and 35 nm (Figure 5). It was reported that, $ZnFe_2O_4$ is antiferromagnetic at room temperature so there should be no additive magnetic contribution at room temperature (Verma *et al.,* 1999). The antiferromagnetic spin order of $ZnFe_2O_4$ is not homogeneous (Verma *et al.,* 1999). Further for 29 and 35 nm particles it was very difficult to find the maximum magnetization value as the curves showed linear increasing behavior. For these samples the remanence and coercivity is almost zero, which is similar to the results obtained by other researchers (Zhang *et al.,* 1998 and Chen *et al.,* 1998). If the surface layer is absent, the magnetization of the particles would saturate with increase in applied field up to a particular magnetic field, when the core magnetic moments align with the magnetic field. At some magnetic field the response of the '*core mode*' of the magnetization response is saturated and the core magnetization of the system behaves in a usual Langevin likes way. Beyond this stage any increase in the magnetic field on the particles has an effect only on the surface layer of the particles and thus the increase in the magnetization of the particles slows down (Hasmonay *et al.,* 2000). The origin of surface spin disorder for ferrite nanocrystals may be due to broken exchange bonds, high anisotropy layer on the surface or loss of the long-range order in the surface layer. These effects are particularly strong in the case of ferrites because of the super exchange interaction through the oxygen ions (Caizer *et al.,* 2002). The magnetization value in our case may be

closely related with the existence of magnetically disordered surface layer in which direct completion of exchange interactions between surface spins takes place (Kumar *et al.,* 2010). Moreover we observed that, increase in particle size lead to the decreases in the magnetization. It is well known that, magnetic properties of $ZnFe_2O_4$ also depends on the type of synthesis technique.

CONCLUSIONS

$ZnFe_2O_4$ nanoparticles were synthesized using oxalic acid based precursor method. The particle size was observed to increase with increasing annealing temperature. The lattice constants were observed to decrease with increasing particle size. The IR spectra revealed the existence of the bands corresponding to spinel ferrite phase formation. The IR band positions were observed to shift towards the lower wave numbers as the particle sizes increases. The magnetic properties of nanocrystalline $ZnFe_2O_4$ compared to multidomain bulk $ZnFe_2O_4$ ferrite can be attributed to the surface effects due to finite size of nanocrystallites.

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