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# Synthesis and magneto-electrical properties of $MFe_2O_4$ (Co, Zn) nanoparticles by oleylamine route

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ABSTRACT

In this study, nearly monodisperse cobalt ferrite ($CoFe_2O_4$) and zinc ferrite ($ZnFe_2O_4$) nanoparticles (NPs) without any size-selection process have been fabricated through an alluring method in an oleylamine (OAM)/benzyl ether system. Samples were synthesized by thermal decomposition of metal acetylacetonates in a high-boiling solvent and in the presence of oleylamine as surfactant and reducing agent. XRD analysis confirmed the purity and nanosized of both products and TEM analysis showed the monodispersion of them also. The oleylamine coated nanoparticles exhibited semiconducting nature at lower frequencies i.e. conductivity enhances with temperature. The dc conductivity curves of $ZnFe_2O_4$@OAm and $CoFe_2O_4$@OAm NPs indicate significant temperature-dependent behavior. The temperature and frequency-dependent variations of dielectric loss ($\varepsilon''$) of $MFe_2O_4$@OAm NPs display an almost sharp exponential decrease with frequency which becomes more considerable at higher temperatures and at low at low frequency regime. From $^{57}$Fe Mössbauer spectroscopy data, the variation in line width, isomer shift, quadrupole splitting and hyperfine magnetic field values have been determined. Although the Mössbauer spectra for the $ZnFe_2O_4$@OAm consists only one paramagnetic central doublet and $CoFe_2O_4$@OAm NPs have also one paramagnetic doublet and three magnetic Zeeman sextet.

## 1. Introduction

Magnetic nanoparticles (MNPs) which have been the most investigated materials are current research due to the their potential applications in a wide range of fields such as magnetic resonance imaging [1], magneto-optical devices [2–4], biomedical drug delivery [5,6] and gene delivery [7] and catalysts [8,9]. Among the various magnetic nanoparticles, spinel $CoFe_2O_4$ and $ZnFe_2O_4$ NPs have drawn recent interest with the aim to form stable non-toxic aqueous dispersion.

Spinel ferrites have been known for a long time because of their unique electric and magnetic characteristics and are thus possible for various industrial applications, ranging from magnetic cores and high-frequency devices to clinical and biological applications [10,11]. As a typical ferrite spinel ($AFe_2O_4$; A=Mn, Zn, Co, Ni, Cd), cobalt ferrite ($CoFe_2O_4$) has received great interests due to its high magnetic and thermal stability and high anisotropy field. On the other hand, zinc ferrite is one of the most important spinel ferrite versatile and technologically important soft ferrite [12,13]. Thus, cobalt ferrite and zinc ferrite MNPs are comparable in size to the other MNPs, which have high coercivity and moderate saturation of magnetization, making them excellent candidates for similar uses to those of iron oxides for biomedical applications. Previous studies have shown that $CoFe_2O_4$ exhibits greater magnetic abilities than MNPs, and are therefore, subject to greater manipulation. By comparing pure cobalt ferrite and pure zinc ferrite MNPs in uncoated and functionalized forms, they tend to agglomerate to form larger clusters resulting in increased particle sizes thus they have been needed to coat with surfactants such as polymeric materials [14]. Proper surface coatings not only avoid such agglomerations, but also can provide multiple functional role such as stabilizing agent, surfactant and reducing agent. The use of oleylamine alone as coating substance has been studied by Sun's group before [15,16]. In their study $Fe_3O_4$ nanoparticles were prepared by this method with a narrow size distribution and the effects of oleylamine on the phase composition, morphology and magnetic properties of $Fe_3O_4$ were investigated.

To the best of our knowledge, there is no any study about the magnetic and electrical characterization of OAM coated $CoFe_2O_4$ and $ZnFe_2O_4$ NPs. Based on the research mentioned above, this study is an attempt to describe complete structural, magnetic and

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electrical characterization of $CoFe_2O_4$ and $ZnFe_2O_4$ coated with oleylamine, OAm.

## 2. Experimental

### 2.1. Chemicals and instrumentations

Co(acac)$_2$, Zn(acac)$_2$, Fe(acac)$_3$, oleylamine (OAm), benzyl ether, hexane and ethanol were acquired from Merck and used as-received without further purification.

The phases were identified by power X-ray diffraction (XRD, Shimadzu XRD-6000) with Cu Ka radiation. The morphology and structure were examined by scanning electron microscope (SEM, Hitachi S-4800) and transmission electron microscope (TEM, JEOL-2100, Philips CM200). Fourier transform infrared (FT-IR) measurements were recorded on Perkin Elmer BX in the range 4000–400 cm$^{-1}$ to investigate the nature of the chemical bonds formed. Thermogravimetry (TG) analysis was carried out on SDT Q600 thermal analyzer under air atmosphere in a temperature range of 30–800 °C. The electrical conductivity of the $ZnFe_2O_4$ and $CoFe_2O_4$ NPs were studied in the temperature range of 20–120 °C with a heating rate of 10 °C/s. The sample was used in the form of circular pellets of 13 mm diameter and 3 mm thickness. The pellets (both nanocomposite and pristine) were sandwiched between gold electrodes and the conductivities were measured using Novocontrol dielectric impedance analyzer in the frequency range of 1 Hz–3 MHz, respectively. The temperature (between 100 and 250 °C) was controlled with a Novocool Cryosystem. The Mössbauer spectra were recorded at room temperature using a spectrometer working in the mode of constant accelerations with the use of $^{57}$Co in Rh matrix and activity of 50 mCi. The speed scale was calibrated using α- Fe and the velocity calibration was done with laser interferometry. The obtained spectrums were analyzed and fitted with Win-Normos fit program.

### 2.2. Synthesis procedure

$MFe_2O_4$ (Co, Zn) NPs were prepared via thermal decomposition of metal acetylacetonates in the presence of benzyl ether and oleylamine. M(acac)$_2$ and Fe(acac)$_3$ were used as 1:2 ratio (1:2 mmol) and dissolved in 15 ml benzyl ether. Then, 15 ml of oleylamine was added into the mixture by stirring to get a homogeneous solution respectively. After, the solution dehydrated at 110 °C for 1 h under $N_2$ atmosphere by magnetically stirred and the temperature was rapidly increased to 300 °C by keeping at that temperature for 1 h. Final solutions were cooled down to room temperature and solid products were extracted by ethylacetate-ethanol mixture with the help of centrifugation and were washed ethanol again and centrifuged once more. Finally, OAm capped $ZnFe_2O_4$ and $CoFe_2O_4$ NPs were further hold at 150 °C until they completely become a dry powders [17].

## 3. Results and discussion

### 3.1. XRD analysis

Fig. 1 represents the XRD powder patterns of $CoFe_2O_4$@OAm and $ZnFe_2O_4$@ OAm NPs. All of the observed diffraction peaks were indexed by the cubic structure of $CoFe_2O_4$ (JCPDS no. 72-1174) and $ZnFe_2O_4$ (JCPDS no.89-1012) NPs revealing a high phase purity of the products. The broadening of diffractions peaks also confirmed the nanosized products. The average crystallite size, L, was estimated by the Scherrer equation from the X-ray peak broadening (full-width at half maximum, FWHM) of the most intense peak (3 1 1):

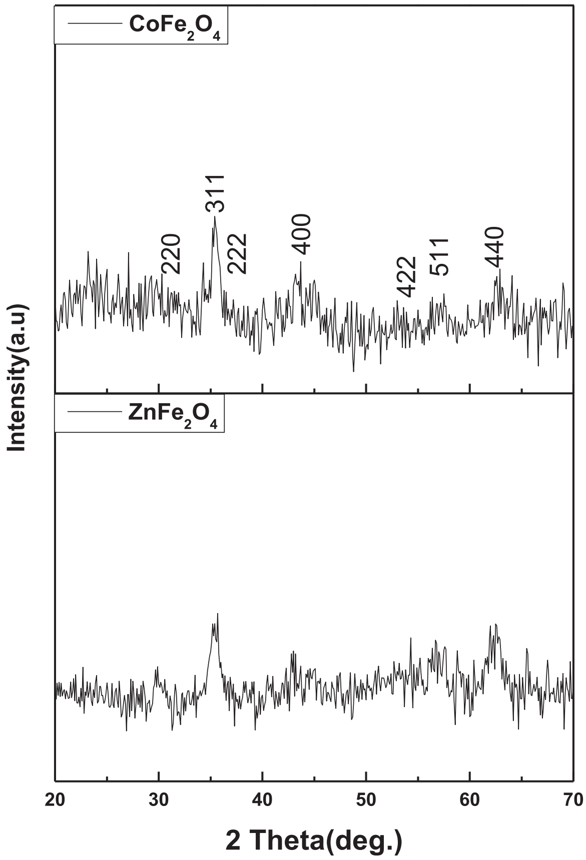

**Fig. 1.** XRD patterns of $CoFe_2O_4$@OAm and $ZnFe_2O_4$@ OAm NPs.

$$L = 0.9\,\lambda / (\beta \cos \theta)$$

where λ is the wavelength of Cu Kα (154,059 Å), θ is the angle of Bragg diffraction, and $\beta = B - b$. B is the full width at half maximum (FWHM) and b represents the instrumental line broadening [18]. Crystallite size of synthesized $CoFe_2O_4$ and $ZnFe_2O_4$ NPs, based on this equation, was calculated as ~9.9 and 8.3 nm, respectively.

### 3.2. FT-IR analysis

FTIR spectra of the samples capped with oleylamine were performed in the range of 400–4000 cm$^{-1}$ to confirm the organic part which is oleylamine, OAm. Fig. 2 shows the representative FT-

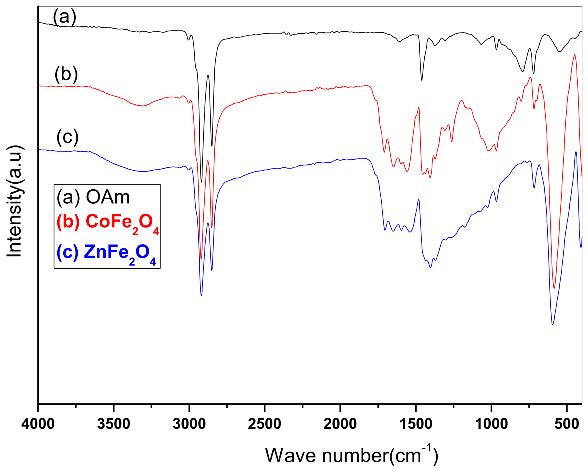

**Fig. 2.** FT-IR spectra of (a) oleylamine, (b) $CoFe_2O_4$@OAm and (c) $ZnFe_2O_4$@OAm NPs.