Structural and Chemical Properties of ZnFe$_2$O$_4$ Nanoparticles Synthesised by Chemical Co-Precipitation Technique

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Abstract. In the present work, Zn-ferrite nanoparticles have been synthesized by chemical co-precipitation method. Prepared samples were characterized by XRD and FTIR to study its structural and chemical properties. The formation of single phase with Fd-3m space group of Zn-ferrite was revealed by XRD and also studied the effect of synthesis techniques on structural parameters. Crystallite size of ZnFe$_2$O$_4$ was found to be 26.11 nm. The FTIR spectra showed two expected bands in the range 550-560 cm$^{-1}$ (i.e. $\nu_1$) and 400-410 cm$^{-1}$ (i.e. $\nu_2$) which confirms the formation of ferrite phase.

1. Introduction

Nonmaterial have been recently become one of the most important science and technology research priorities due to their advantages in the effects of surface chemistry[1]. The nano materials have excellent structural, electrical, magnetic properties than that of bulk material. Among the nonmaterial magnetic nonmaterial becomes promising candidate in the various applications because of its enhanced structural and magnetic properties[2]. Any magnetic properties can be enhanced by preparing samples in nano form due to an increase in the surface to volume ratio of particles[3]. In the family of magnetic material ferrites nanoparticles are predominant material due to its novelty and applicability in various field for example gas sensor, magnetic hyperthermia, drug delivery, memories storage, etc[4, 5]. Nano ferrites are the combination of iron oxide Fe$_2$O$_3$ and metal ions (Zn$^{2+}$, Co$^{2+}$, Mn$^{2+}$, etc.). On the basis of structure ferrites are classified into three categories such as spinel ferrite, garnet ferrite and hexagonal ferrite. MFe$_2$O$_4$ is the general spinel ferrite formula, where M is a divalent metal ion like Zn$^{2+}$, Co$^{2+}$, Mn$^{2+}$, etc. in the spinel ferrite family zinc ferrites are most promising material for biomedical application because of its low toxic and soft ferrite nature[6]. Application of Zinc ferrite nanoparticles in the industrial and medical sector has been growing tremendously since the last decade. Cobalt ferrite nanoparticles have also been used for media storage, magnetic refrigeration, ferrofluids, spintronic, drug delivery to particular areas of the body, biosensor and hyperthermia etc[7], because of its different characteristics such as low saturation magnetization, exceptional chemical stability and low toxicity. The magnetic and structural properties of nanoparticles depend on the phase purity, shape and size of these particles. A significant field of research and development becomes the synthesis of ZnFe$_2$O$_4$ nanoparticles with sufficient physical and chemical properties. The ZnFe$_2$O$_4$ nanoparticles are synthesized by many techniques of synthesis such as sol-gel, hydrothermal, combustion, co-precipitation, thermal decomposition and micro-emulsion. Among
these synthesis techniques co-precipitation method is easy, cost effective and no any organic fuel required in the synthesis. The low temperature, small particle size, high porosity, short time of preparation, high purity, strong chemical homogeneity, crystallinity and a simple process, these are some of the great benefits of the co-precipitation process. L.C. Sonia et. al[8]. Reported the co-precipitation method is better rout for synthesis of required sized nanoparticles as compare to other methods.

In the present work, synthesis of ZnFe$_2$O$_4$ nanoparticles was carried out by chemical co-precipitation method. Synthesized Zn-ferrite nanoparticles were characterized by standard characterization techniques to study the structural and chemical properties.

2 Experimental

Materials
Analytical grade Zinc Chloride (ZnCl$_2$), Ferric chloride (FeCl$_3$) and Sodium Hydroxide (NaOH) were used as raw materials for synthesis of ZnFe$_2$O$_4$ nanoparticles by chemical co-precipitation method.

Preparation of zinc ferrite
Zn-ferrite nanoparticles have been synthesized by chemical co-precipitation method. The chemical co-precipitation method was applied for the synthesis of zinc ferrite nanoparticles and accordingly the molar ratio of 1:2 ZnCl$_2$ and FeCl$_3$ was dissolved in distilled water. 1M sodium hydroxide (NaOH) was added drop wise to keep the pH of the solution at 7 under constant stirring at 60 ℃ temperature. After the 60 min the ageing process was completed; the solution was cooled down to room temperature under constant stirring condition. The precipitation was washed with hot DI water or acetone to remove sodium chloride and traces of water. The centrifugal separator is then used to settle the precipitate over several times before washing with acetone and filtering. The nanoparticles have been dried 48 h at room temperature. The loose zinc ferrite as-prepared powder was grind for 40 minutes and sintered into the furnace at 900 ℃ for 4 h. The flow chart of ZnFe$_2$O$_4$ nanoparticles were synthesized by co-precipitation method shown in figure 1.

![Figure 1](image)

**Figure 1.** Schematical version of co-precipitation rout for preparation of ZnFe$_2$O$_4$ nanoparticles.
Characterization

The prepared samples were characterized for identification of structural properties by using X-ray diffractometer (Bruker) with Cu-Kα (λ=1.5406Å) radiation, operated at 20 mA current and 40 kV voltage in the 2θ range from 20° to 80°. FT-IR spectra were recorded for prepared nanoparticles with a Shimadzu FTIR spectrometer at room temperature within the wavenumber range 400cm⁻¹ to 2000cm⁻¹ and transmittance spectrum was obtained.

3 Results and Discussions

X-ray Diffraction

The XRD pattern of ZnFe₂O₄ nanoparticles recorded at room temperature in the 2θ ranges from 20-80° C with Cu Kα radiation having wavelength 1.5406 Å shown in figure 2. There is no any impurity peak observed in XRD pattern of ZnFe₂O₄ which indicates the purity of sample. From figure 1 it is clear that the reflection planes (h k l) indicated the cubic spinel structure with Fd-3m space group of both samples. The lattice parameter value were calculated by using the following equation [9].

\[ \sin^2 \theta = \left( \frac{\lambda^2}{a^2} \right)(h^2 + k^2 + l^2) \]

Where, \( \lambda \) is the X-ray wavelength (1.540 Å), \( a \) is the lattice constant, \( h \ k \ l \) are the miller indices of the reflection planes, \( \theta \) is the angle of diffraction. The lattice parameter value of ZnFe₂O₄ was found to be 8.434 Å. The crystallite size of ZnFe₂O₄ sample was observed 26 nm. Crystallite size of nanoparticles affected by pH, Temperature, etc. like synthesis parameters. The crystallite size of samples was calculated by using Debye-Scherrer’s formula as follow[10],

\[ t = \frac{k \lambda}{\beta \cos \theta} \]

Where, \( \lambda \) is the X-ray wavelength (1.540 Å), \( t \) is the crystallite size, \( \beta \) is the FWHM and \( \theta \) is the angle of diffraction. All the structural parameters calculated from the XRD pattern tabulated in the table 1. The x-ray density of ZnFe₂O₄ sample was found to be 5.336 g/cm³. The unit cell volume of ZnFe₂O₄ was observed 600 Å³. The calculated bulk density of ZnFe₂O₄ sample was found to be 3.617 g/cm³. Other structural parameters such as Hopping Length (Lₐ, Lₖ), tetrahedral bond length (dₐL), octahedral bond length (dₖL), Tetra edge (dₐE), Ionic radii (rₐ, rₖ) were calculated by using the lattice parameter value, calculated parameters tabulated in table 2. From the XRD result it is clear that the co-precipitation technique is excellent rout of synthesis of required sized nanoparticles.

### Table 1. Lattice constant (a), unit cell volume (V), X-ray density (dₓ), particle size (t), bulk density (dₜ) and porosity (%) of the ZnFe₂O₄ nanoparticles

| Sample   | a (Å) | V (Å³) | t (nm) | dₓ (g/cm³) | dₜ (g/cm³) | Porosity % |
|----------|-------|--------|--------|------------|------------|------------|
| ZnFe₂O₄ | 8.434 | 600.1  | 26.11  | 5.336      | 3.617      | 32.21      |

### Table 2. Hopping Length (Lₐ, Lₖ), tetrahedral bond length (dₐL), octahedral bond length (dₖL), Tetra edge (dₐE), Ionic radii (rₐ, rₖ) of ZnFe₂O₄ nanoparticles

| Sample   | Lₐ(Å) | Lₖ(Å) | dₐL(Å) | dₖL(Å) | dₐE(Å) | rₐ(Å) | rₖ(Å) |
|----------|-------|-------|--------|--------|--------|-------|-------|
| ZnFe₂O₄ | 2.5417| 2.4622| 1.9138 | 2.0593 | 3.1252 | 0.5938| 0.7381|
FTIR (Fourier-transform infrared spectroscopy)

Typical FT-IR spectra at room temperature for the sample \( \text{ZnFe}_2\text{O}_4 \) annealed at 900 °C are shown in figure 3. FTIR spectra revealed the formation of ferrite phase. FTIR spectra of \( \text{ZnFe}_2\text{O}_4 \) sample shows two absorption peaks which indicated the intrinsic stretching vibrations of metal – oxygen at A and B site; this is the characteristic feature of formation of spinel ferrite\([11]\). The first higher wavenumber band \( \nu_1 \) corresponds to the intrinsic stretching vibration of metal-oxygen at tetrahedral site and second lower wavenumber band \( \nu_2 \) corresponds to the intrinsic stretching vibrations of metal-oxygen at octahedral site. FTIR spectra of \( \text{ZnFe}_2\text{O}_4 \) sample revealed that the lower wave numbered (\( \nu_2 \)) band observed in the range 400-410 cm\(^{-1}\) and higher wave numbered (\( \nu_1 \)) band observed in the range 550-560 cm\(^{-1}\) for both samples shown in table 3.
4. Conclusions
Zinc ferrite (ZnFe₂O₄) nanoparticles using Co-precipitation chemical routes were successfully synthesized with an ideal core-shell structure. XRD pattern showed the cubic spinel structure of Fd3m space group. Further, observed that the particle size of sample prepared by the co-precipitation method is very small. Thus, it is concluded that the co-precipitation is a better route for the synthesis of fine Zinc ferrite nanoparticles. The formation of ferrite phase was confirmed by the two absorption bands occurred 400 cm⁻¹ and 600 cm⁻¹ characterizing the ferrite nature of the sample.

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