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# Zinc Doped Cobalt Ferrite: Tuning the Vibrations by Chemical Composition

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## ABSTRACT

The implement of Zn-doping in $CoFe_2O_4$ nanoparticles (NPs) through chemical co-precipitation route reviewed in the describe of structural and vibrational system. XRD and FTIR analyses corroborate the development of the cubic spinel structure, where the crystallite size varies with zinc content from 32 to 29 nm. The NPs are affected by Zn doping; lattice constant (a) rises then decreases while size decreases, which is related with helpful site occupancy and the change in particle size. The vibrational stretching modes of tetrahedral (490-508 $cm^{-1}$) and octahedral (389-405$cm^{-1}$) sites were confirmed by FTIR. These ferrites hold the promise of magnetic sensors.

**Keywords:** Structural; cobalt ferrite; cubic spinel phase; lattice constant; magnetic sensors.

## INTRODUCTION

Magnetic ferrite (MF) semiconductors with a general formula of $AFe_2O_4$, where 'A' stands for metals as (Mn, Co, Ni, Mg, or Zn), are well known of their remarkable optical, magnetically, and electric properties, particularly in nanometer range. Nanocrystalline cobalt ferrite with unique properties has potential applications in memory core, antennas, high frequency device, converters, recording media, hyperthermia, in a biomedical field, magneto resonance imaging (MRI) magnetic sensing, ferrofluid, solar hydrogen production, inductors, spintronics, drug delivery, catalysts, magneto-optical recording, humidity sensors, and energy storage fields [1-3].

We realize that zinc cations ($Zn^{2+}$) with diamagnetic types are noted for carrying out perfect control over magnetic parameters in producing effective materials. Substitution of magnetic ($Co^{2+}$) by a nonmagnetic

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($Zn^{2+}$) cations in spinel ferrite phase may cause significant variations in their structural, optical, magnetic, and others properties, for the order of cations in between the applicable A and B sites [4]. However, a detailed application on the structural, elastic, optical, and magnetic properties of $Zn^{2+}$-doped $CoFe_2O_4$ nanoparticles got by co-precipitation technique in the region has not yet reported so far. The aim of the present work is to incorporate nanoparticles of $Co_{1-x}Zn_xFe_2O_4$ with x varying from 0 to 0.5 from metal salts by co-precipitation of hydroxides. The prompt of Zn substitution on the structural, optical, and magnetic properties of this practice has been conferred.

## EXPERIMENTAL

### Synthesis of PVP Coated $Ni_{1-x}Cu_xFe_2O_4$ Nanoscale Particles

Synthesis of Zn-Doped Cobalt Ferrites The detailed description of synthesis route has been presented in our earlier work [1]. For preparing $Co_{1-x}Zn_xFe_2O_4$ (x = 0.2) samples through co-precipitation technique, iron, cobalt, and zinc sulfates drawn in stoichiometric ratios and dispersed in distilled water as stated in Fig.1. The as-prepared solutions were incorporated and stirred for 1 h to promote homogeneity.

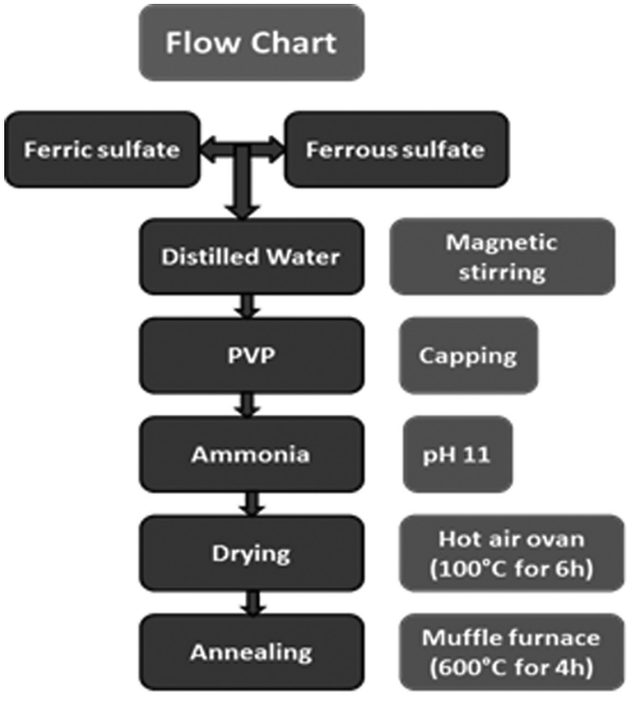


**Fig 1: 1 Synthesis of PVP Coated $Ni_{1-x}Cu_xFe_2O_4$ Mixed Ferrite**

They exposed the solutions to constant heating at 80°C under repeated stirring. Again, 4 M solution of $NH_3$ added drop wise in needed proportion. They washed the black precipitate several times with distilled water and warmed at 100°C for 6h for drying. The dried powders were heated at 800°C for 2 h and then were left to cool down slowly to room temperature.

## RESULTS AND DISCUSSION

### X-ray Diffraction Analysis

X-ray Diffract ion Analysis X-ray diffraction (XRD) was performed on the powders calcined at 800°C, and the XRD patterns of all the samples were shown in Fig.2.

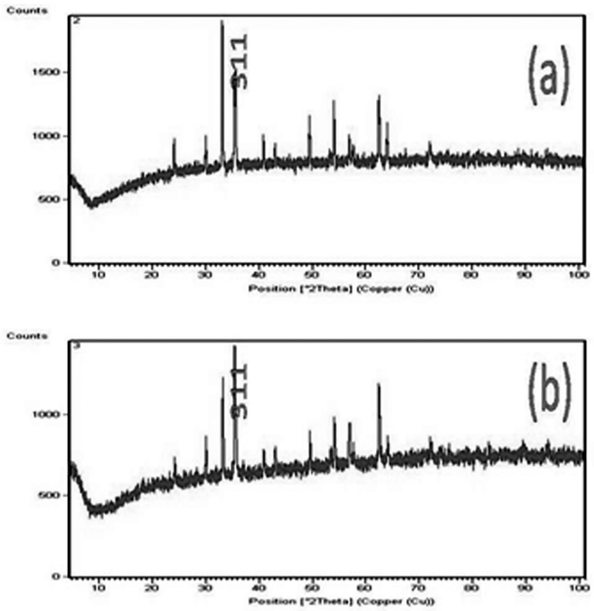


**Fig 2: X-ray Difraction of Zinc Doped Cobalt Ferrite Nanoparticles**

**(a) $Co_{0.8M}$ $Zn_{0.2M}Fe_{2M}O_4$, (b) $Co_{0.2M}Zn_{0.8M}Fe_{2M}O_4$**

The obtained patterns confirm the formation of a homogeneous single phase having cubic spinel structure with the space group Fd3m. The patterns show diffraction peaks of $C_{o_{1-x}}Zn_xFe_2O_4$ (x = 0.2M), corresponding to peak (311) estimated crystal parameters. The results show that the lattice parameter a slightly increases with $Zn^{2+}$ - doping content as shown in Table 1. The increase of a with x can be explained on the basis of the difference in ionic radii of $Zn^{2+}$ and $Co^{2+}$. The smaller ionic radius of Co (0.58 Å) was replaced by the larger ionic radius of Zn (0.6 Å) so the lattice parameter increased due to the expansion of the unit cell [5].

**Table 1: Zinc Doped Cobalt Ferrite Nanoparticles**

| Materials | 2θ Deg | FWHM β | d Spacing Å | Cos θ | Crystalline Size (nm) | Lattice Constant Å | Volume $V = a^3$ $(Å)^3$ |
|---|---|---|---|---|---|---|---|
| $Co_{0.8}Zn_{0.2}Fe_2O_4$ | 35.75 | 0.45 | 2.51 | 0.9517 | 32 | 8.30 | 571.787 |
| $Co_{0.2}Zn_{0.8}Fe_2O_4$ | 35.35 | 0.50 | 2.53 | 0.9528 | 29 | 8.37 | 586.376 |

Considering that, the forms of mathematical functions that describe different types of physical broadening are unknown; thereby different methods were proposed to determine microstructural parameters (crystallite size and microstrain). It carried the interpret the crystallite size out using the increase of the XRD peaks. We know that peak increase results from both limited crystallite size and strain effect within the crystal lattice. The Debye temperature falloff with rising $Zn^{2+}$ content and combine to the falloff in wave number of the peak attributed to Me-O bond vibration in the tetrahedral site [6]. Figure 2 presents the X-ray diffraction patterns of the ZCF-NPs prepared via the coprecipitation method calcined at 800°C. The formation of cubic spinel structure of $CoFe_2O_4$ NPs (JCPDS 3–864) with Fd3m space group can be observed in the obtained patterns. There is no secondary phase was observed in the sample. The average crystallite size was decreased with an increase in Zn-dopant (Table 1) and calculated using the following Debye–Scherrer's relation [1, 7],

$$D = K \lambda / \beta \cos \theta \text{ (nm)}$$

Where k = is the crystallite shape constant (0.89), λ is the wavelength of X-ray light source (1.540 Å), β is full width at half maximum (FWHM) and θ is the glancing angle.

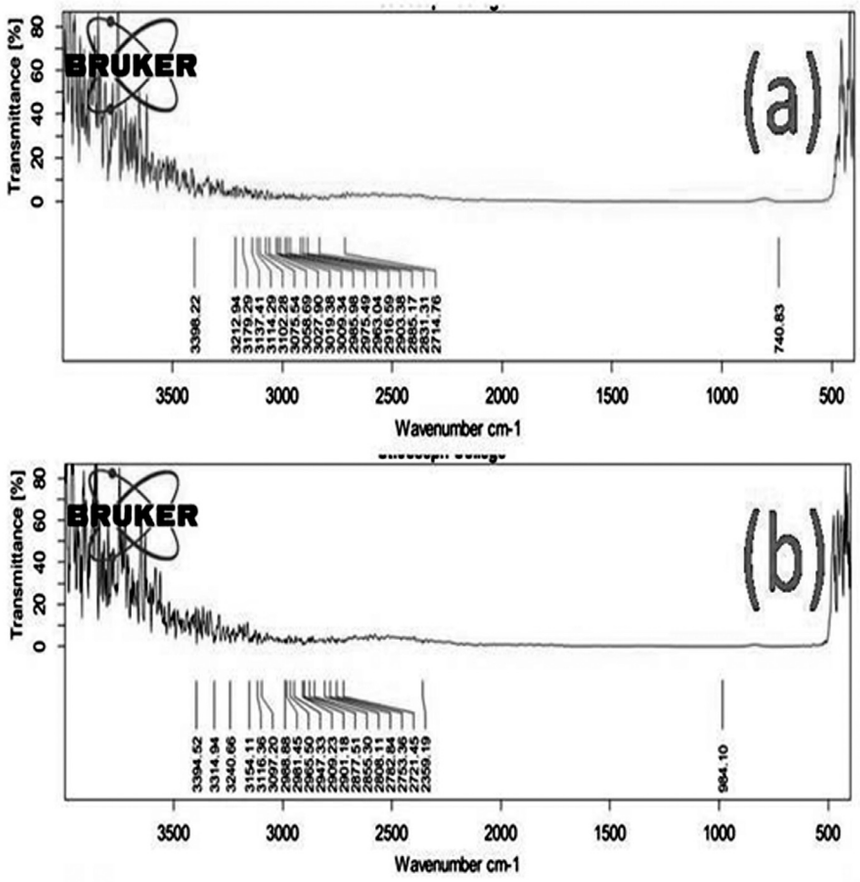


**Fig 3: FTIR Spectra of Zinc Doped Cobalt Ferrite**

**(a) $Co_{0.8M}$ $Zn_{0.2M}Fe_{2MO4}$, (b) $Co_{0.2M}Zn_{0.8M}Fe_{2MO4}$**

Further, the lattice parameter (a) values were calculated using the relation [8],

$$a = d\,(h^2+K^2+l^2)^{1/2} \quad Å$$

where, d is the interplanar distances between two planes and (h, k, l) are the Miller indices. The increase in Zn-dopant, the lattice parameter also increases from 8.30 to 8.37 Å. This is because the ionic radius of $Zn^{2+}$ (0.74 Å) is larger than the ionic radius of $Co^{2+}$ (0.70 Å) which lead to the expansion of unit cell [1, 9]. The volume of the unit cells given by (Table 1),

$$V = a^3$$

**Table 2: Vibrational Assignments of Zinc Doped Cobalt Ferrite**

| Frequencies ($cm^{-1}$) | | Vibrational Assignments |
|---|---|---|
| $Co_{0.8}Zn_{0.2}Fe_2O_4$ | $Co_{0.2}Zn_{0.8}Fe_2O_4$ | |
| 3824 | 3823 | O-H Stretching |
| 490 | 508 | Tetrahedral-metal stretching high frequency bonds |
| 389 | 405 | octahedral-metal stretching low frequency bonds |

## FT-IR ANALYSIS

Figure 2 illustrates the FTIR spectra of the ZCF NPs between 4000 and 50$cm^{-1}$ to describe the vibrational bands present in the samples. At 3097-3394$cm^{-1}$ a band noted for all sample applied to the vibrational stretching frequencies of adsorbed H − O − H or free molecule of water [2, 3]. There are recognized two main bands at 490-508$cm^{-1}$ as 389-405$cm^{-1}$ attribute to the intrinsic vibrational stretching frequency of Fe-O-Fe (tetrahedral sites) and Co-O-Fe (octahedral site) [1,7]. There is a linear increase in the molecular mass which leads to the vibrational frequency shifting towards the lower value (Table 2) because of $Zn^{2+}$ doping in the cobalt ferrite lattice.

## CONCLUSIONS

Zinc doped cobalt ferrite nano-particles of the formula $Zn_xCo_{1-x}Fe_2O_4$ (x = 0.2) was successfully synthesized using the co-precipitation method. Powder XRD studies of the samples revealed the formation of highly crystalline ferrite nano-particles with an average crystallite size of 33nm. There are two main bands observed at 490-508$cm^{-1}$ as tetrahedral-metal stretching high frequency bands (Co-O-Fe) and 389-405$cm^{-1}$ are attributed to the intrinsic vibrational stretching frequency of Fe-O-Fe (octahedral site).

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