

# Effect of Zinc Substitution on Structural and Infrared Properties of Spinel Cobalt Ferrite Nanoparticles

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**Abstract:** In the present work, effect of zinc ions substitution on the structural and infrared properties of cobalt ferrite nanoparticles was reported. Zinc substituted cobalt ferrite ( $Co_{1-x}Zn_xFe_2O_4$ ,  $x = 0.0, 0.4$  and  $0.8$ ) have been prepared for various compositions using sol-gel auto combustion method. The obtained nanoparticles were structurally characterized by X-ray diffraction method. X-ray diffraction pattern (XRD) recorded at room temperature shows well defined Bragg's reflections belonging to cubic spinel structure. The analysis of XRD pattern clearly indicates the formation of single phase cubic spinel structure as well as nanocrystalline nature of the prepared samples. The crystallite size calculated using Scherrer's formula is found to be in the range 16 to 22 nm. The lattice constant found to increase with increasing zinc composition  $x$ . Using XRD data, various structural parameters viz. X-ray density, bulk density, porosity, dislocation density etc. were obtained and their variation as a function of zinc composition is explained herein. The prepared nanoparticles were also characterized by infrared spectroscopic (IR) technique, IR spectra reveals presence of two absorption bands approximately near to  $400\text{ cm}^{-1}$  and  $600\text{ cm}^{-1}$ . These two bands show the characteristics feature of spinel ferrite and these bands are attributed to tetrahedral (A) and octahedral [B] metal stretching.

**Key Words:** Cobalt-Zinc, Sol-gel synthesis, XRD, IR

## 1. INTRODUCTION:

Spinel ferrites recognized by the formula  $MFe_2O_4$ , where M is a divalent cation like Co, Ni, Mn, Mg etc. are one of the most interesting magnetic nanoparticles due to their applications in many fields. The unit cell of a spinel ferrite crystal structure consists of a cubic closed pack arrangement of oxygen ions with 64 tetrahedral (A-site) and 16 of octahedral [B-site]. Out of this, 8 of tetrahedral (A-sites) and 16 of octahedral [B-site] sites are occupied by the metal cations. The properties of ferrites are strongly influenced by the material composition, microstructure (which is sensitive to preparation method), type and amount of dopant etc [1]. Many synthesis processes have been illustrated in the literature for the synthesis of spinel ferrite nanoparticles. The synthesis methods include ball milling, sol-gel, coprecipitation, hydrothermal etc [2]. The cubic spinel structured cobalt ferrite,  $CoFe_2O_4$ , represents a well-known and important class of iron oxide materials. The  $O^{2-}$  ions form f.c.c. close packing, and the  $Co^{2+}$  and  $Fe^{3+}$  occupy either tetrahedral (A) or octahedral (B) interstitial sites. Cobalt ferrites, typically inverse spinel ferrites, have been extensively used in electronic devices because of their large permeability at high frequency, remarkably high electrical resistivity and high saturation magnetization [3]. Substituted cobalt ferrites are widely used as magnetic materials due to their low dielectric losses [4].

Zinc (Zn) substitution plays a vital role in determining the various properties of ferrites. Mixed Zn ferrites and especially Co–Zn ferrites are the most important magnetic materials. As, cobalt ferrite having inverse structure and zinc ferrite having normal structure, the resultant mixed cobalt-zinc ferrite may have the mixed structure. It will be more interested to study the structural and infrared properties of Co-Zn spinel ferrite nanoparticles. Here, we report the results of structural and infrared properties of Zn substituted cobalt ferrite ( $Co_{1-x}Zn_xFe_2O_4$ ) nanoparticles.

## 2. MATERIALS:

Cobalt nitrate ( $Co(NO_3)_2 \cdot 6H_2O$ ), zinc nitrate ( $Zn(NO_3)_2 \cdot 6H_2O$ ), ferric nitrate ( $Fe(NO_3)_3 \cdot 9H_2O$ ) and citric acid ( $C_6H_8O_7 \cdot H_2O$ ) were used as a raw materials for sol-gel auto combustion synthesis of  $Co_{1-x}Zn_xFe_2O_4$  ( $x = 0.0, 0.4$  and  $0.8$ ) spinel ferrite nanoparticles. All the reagents used for the synthesis of Co-Zn ferrite nanoparticles were analytical grade (AR) and used as received without further purification.

### 3. METHOD:

Nanoparticles of  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  ( $x = 0.0, 0.4$  and  $0.8$ ) were synthesized by sol-gel auto combustion method using citric acid as a fuel. The stoichiometric proportions of metal nitrates to fuel (citric acid) ratio as 1:3 were taken into separate glass beakers. The mixed solution was stirred for 20-25 minutes to dissolve completely into distilled water. After complete dissolution they were mixed together. Ammonia was added drop-wise into the solution to adjust pH value at 7 and stabilize the nitrate-citric acid solution. Then the neutralized solution was constantly magnetically stirred and heated at 90-100°C for 6 h on a hot plate. On the formation of sol-gel, very viscous gel the temperature was further raised up to 110°C so that the ignition of the dried gel started and finally powder was obtained. The as prepared loose cobalt ferrite powder was grinded for 40 minutes and annealed at 600°C for 6 h in muffle furnace.

Further, X-ray diffraction (XRD) patterns of all the samples were recorded at room temperature by using a PANalytical X'pert pro diffractometer operated at 40 kV and 30 mA. The diffraction pattern were recorded in the  $2\theta$  range 20° to 80° with scanning rate of 2° per minute using  $\text{Cu-K}\alpha$  radiation of wavelength 1.5406 Å. Various structural parameters such as lattice constant, particle size, X-ray density and bulk density were calculated from the studies of X-ray diffraction. The infrared spectra of all the samples were recorded at room temperature in the range 400  $\text{cm}^{-1}$  – 1000  $\text{cm}^{-1}$  on FTIR-6100 type-A model.

### 4. RESULTS AND DISCUSSION:

#### X-ray diffraction study

The X-ray diffraction pattern (XRD) of  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  ( $x = 0.0, 0.4$  and  $0.8$ ) nanoparticles are shown in figure 1 (a-c). It is observed from figure that the XRD patterns have peaks at reflections plane indexed (220), (311), (222), (400), (422), (511) and (440) for all the compositions. The presence of all the peaks in the XRD pattern proves the formation of single phase cubic spinel structure. All the peaks in the XRD pattern are sharp and intense. The XRD peak does not show any additional peak other than mentioned above indicates the high purity of prepared samples. Similar XRD pattern for cobalt-zinc ferrite samples is reported in the literature [5].

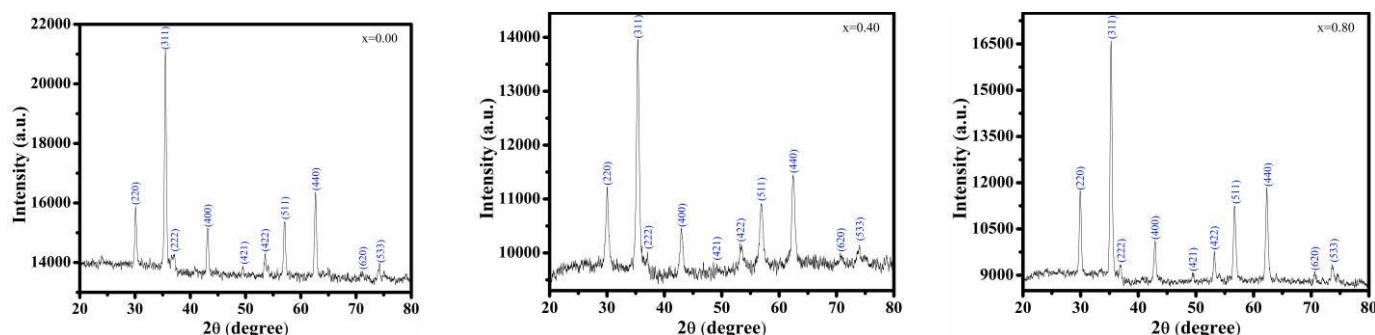


Figure 1 (a-c). X-ray diffraction pattern of  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  ( $x = 0.0, 0.4$  and  $0.8$ ) nanoparticles

- **Lattice constant (a)**

Using the values of Bragg's angle  $2\theta$  and interplanar spacing  $d$ , the values of lattice constant for all the composition are calculated using the following relation.

$$a = d\sqrt{h^2 + k^2 + l^2} \quad \text{Å} \quad \dots 1$$

The values of lattice constant are presented in table 1 and were found to be in the range of 8.37 Å to 8.42 Å. It is found that, the values of lattice constant changes with the zinc composition  $x$ . It is observed from table that lattice constant increases with increase in Zn composition  $x$ . The variation of lattice parameter with zinc composition  $x$  could be attributed to the substitution of  $\text{Zn}^{2+}$  ions of large radius (0.82 Å) in place of cobalt ions of small radius (0.74 Å). This behaviour of lattice constant is similar to the cobalt-zinc nanoparticles synthesized by other methods and other zinc substituted spinel ferrite [6].

- **Crystallite size (t)**

The crystallite size ( $t$ ) was calculated from the most intense peak (311) present in the XRD patterns using the well known Scherrer's formula [7].

$$t = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{nm} \quad \dots 2$$

The crystallite size calculated using the above relation is presented in table 1. The particle sizes of the prepared samples were found to be between 16 nm to 22 nm. Crystallite size does not show any systematic behaviour.

• **Dislocation density**

The dislocation density ( $\delta$ ) of  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  ( $x = 0.0, 0.4$  and  $0.8$ ) nanoparticles was calculated using the standard relation given by,

$$\delta = \frac{1}{t^2} \text{ lines/m}^2 \quad \dots 3$$

Where,  $t$  is average crystallite size. The values of dislocation density are presented in table 1. The value of dislocation densities are in the range of  $20 \times 10^{14}$  lines/m<sup>2</sup> to  $22 \times 10^{14}$  lines/m<sup>2</sup>.

• **X-ray density ( $d_x$ )**

The X-ray density of  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  ( $x = 0.0, 0.4$  and  $0.8$ ) nanoparticles was calculated using the standard relation given by equation,

$$d_x = \frac{Z \times M}{V \times N_A} \text{ gm/cm}^3 \quad \dots 4$$

Where,  $Z$  is the number of molecules per formula unit ( $Z = 8$  for spinel system),  $M$  is molecular mass of the sample,  $V = a^3$  is the unit cell volume,  $N_A$  is the Avogadro's number. The obtained values of X-ray density are presented in table 1. It is evident from table 1 that, the as zinc concentration  $x$  increases the X-ray density decreases. The X-ray density is related to lattice constant inversely. The observed decrease in X-ray density can be attributed to the increase in lattice constant. In the present cobalt-zinc system, the lattice constant increases with zinc content  $x$ .

• **Bulk density ( $d_B$ )**

The bulk density of the present samples was determined using Archimedes principle. Toluene was used as a liquid medium to measure the bulk density. The values of bulk density are given in table 1. It can be observed from table 1 that bulk density of the present sample was found to be varying between  $3.48 \text{ gm/cm}^3$  to  $3.63 \text{ gm/cm}^3$ . The observed decrease in bulk density may be due to the decrease in mass. It is also observed that, the values of bulk density of the present samples are quite less than X-ray density which results in high porosity values.

• **Porosity (%P)**

The percentage porosity of the present Co-Zn samples was calculated from the following relation;

$$P = 1 - \frac{d_B}{d_x} \% \quad \dots 5$$

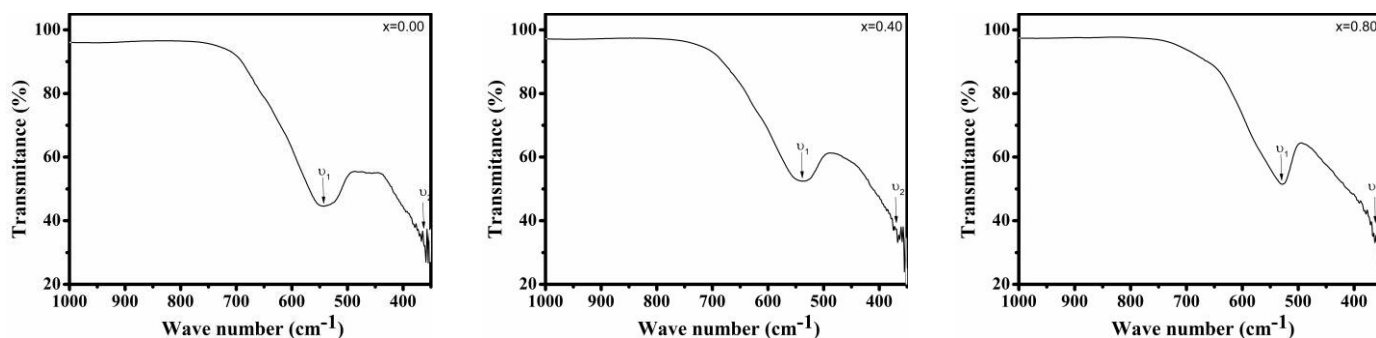
The obtained values of porosity are listed in table 1, the porosity for the cobalt ferrite sample ( $x = 0.0$ ) is less than that of zinc substituted cobalt ferrite samples ( $x = 0.4$  and  $0.8$ ). The increase in porosity may be due to increase in X-ray density and decrease in bulk density. The high values of porosity (31% to 34%) are attributed to agglomeration of particles during the synthesis procedure.

<b>Table 1.</b> Values of Lattice constant ( $a$ ), X-ray density ( $d_x$ ), Bulk density ( $d_B$ ), Porosity ( $P$ ), crystallite size ( $t$ ), dislocation density ( $\delta$ ) for $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanoparticles						
Composition	$a$ (nm)	$d_x$ (gm/cm <sup>3</sup> )	$d_B$ (gm/cm <sup>3</sup> )	$P$ (%)	$t$ (nm)	$\delta$ (lines/m <sup>2</sup> )
0.0	8.378	5.300	3.638	31.36	22	20.66E+14
0.4	8.408	5.302	3.587	32.25	16	39.06E+14
0.8	8.426	5.325	3.488	34.49	21	22.67E+14

**Infrared studies**

The infrared (IR) spectra of  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  ( $x = 0.0, 0.4$  and  $0.8$ ) nanoparticles were recorded in the range  $400 \text{ cm}^{-1} - 1000 \text{ cm}^{-1}$ . The spectra of all the samples are depicted in fig 2 (a-c). It reveals from the spectra that, two absorption bands near  $600 \text{ cm}^{-1}$  and  $400 \text{ cm}^{-1}$  are observed. The higher frequency band  $\nu_1$  and lower frequency band  $\nu_2$  were observed in the range of  $600 - 500 \text{ cm}^{-1}$  and  $450 - 380 \text{ cm}^{-1}$  and was assigned to tetrahedral (A) and octahedral [B] metal stretching, which are consider to be the typical bands of spinel structure. The values of absorption frequency  $\nu_1$  and  $\nu_2$  are listed in table 2. It is observed from table 2 that the absorption frequency  $\nu_2$  was slightly shifted towards higher frequency and  $\nu_1$  towards lower frequency side with increasing  $\text{Zn}^{2+}$  content. This can be attributed to shifting of  $\text{Fe}^{3+}$  ions towards oxygen ion on the tetrahedral site which decreases with  $\text{Fe}^{3+}-\text{O}^{2-}$  distance. The increase in site radius results in the

reduction of fundamental frequency and central frequency which shifts towards the lower side. Similar reports were reported in literature [8].



**Figure 2 (a-c).** IR spectra of  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  ( $x = 0.0, 0.4$  and  $0.8$ ) nanoparticles

**Table 2.** Values of infrared absorption frequency band positions ( $\nu_1$  and  $\nu_2$ ) for  $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  nanoparticles

Composition	$\nu_1$ ( $\text{cm}^{-1}$ )	$\nu_2$ ( $\text{cm}^{-1}$ )
0.0	527.71	357.33
0.4	536.14	360.60
0.8	541.30	361.30

## 5. CONCLUSION:

The zinc substituted cobalt ferrite nanoparticles ( $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  with  $x = 0.0, 0.4$  and  $0.8$ ) were successfully prepared using sol-gel auto combustion technique. Pure phase with cubic spinel structure was observed for all the compositions through the analysis of X-ray diffraction data. Lattice constant increased with zinc substitution  $x$ , which is attributed to difference in ionic radii of cobalt and zinc. The crystallite size obtained through Scherrer's equation shows nanocrystalline nature of all the compositions. The other structural parameter shows strong dependence of zinc substitution  $x$ . Infrared spectra showed two prominent absorption peaks near  $600 \text{ cm}^{-1}$  and  $400 \text{ cm}^{-1}$  indicating the characteristics features of cubic spinel ferrite.

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