



# Synthesis of $Zn_{0.5}Co_xMg_{0.5-x}Fe_2O_4$ Nano-Ferrites Using Co-Precipitation Method and Its Structural and Optical Properties

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**Abstract:** In this work, cobalt (Co) substituted magnesium Zinc nanocrystalline spinel ferrites having general formula  $Zn_{0.5}Co_xMg_{0.5-x}Fe_2O_4$  (with  $x=0.1, 0.2, 0.3, 0.4, 0.5$ ) were synthesized using chemical co-precipitation method. The Cobalt substituted magnesium was annealed at  $450^\circ C$  and characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and UV-visible spectroscopy. XRD analysis confirmed the formation of single phase spinel structure. The crystalline size was calculated using Scherer's formula and was found to be in 21.44 – 25.03 nm range. The lattice constant was found to decrease as substitution of Co is further increased. The decrease in lattice constant may attribute to the smaller ionic radius of Co as compared to Zinc ion. The FTIR spectra for the samples measured in the range of  $4000-400\text{ cm}^{-1}$  exhibited symmetric stretching mode of vibration of tetrahedral and octahedral sites. The energy band gaps of the materials were calculated and were found to be in the range of 4.5 to 4.8 eV.

**Keywords:** FTIR, Nanoferrite, Nanoparticles, Spinel Structure

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## 1. Introduction

Particles in the size range of approximately 1–100 nm can display novel optical, electronic, magnetic, chemical and structural properties because of quantum confinement and surface effects that may find many important technological applications [1,2]. The technology based on these nanoparticles, known as nanotechnology, is possible in theory, but its practical realization requires the solution of quite challenging issues of applied technology, e.g., control the geometry, the particle size, the morphology of nanoparticles and their assembly into structures performing specific functions and delivering specific effects [2,3]. Nanotechnology is well known as a very important key technology in science and industry. In the field of material science and engineering, nano-particles are considered to be a unique unit material made from atoms and molecules, to build ceramics, catalysts, or even nano-machines [4].

Ferrites are well-known magnetic nano materials intensively studied as a recording media due to their superior physical properties [5]. These properties make ferrites an ideal candidate for technical applications such as magnetic resonance imaging enhancement, catalysis, sensors and pigments [6]. Spinel nano-ferrites with chemical formula  $AB_2O_4$  are materials of today's research due to their amazing structural, dielectric, electrical and magnetic properties [7]. Such properties are dependent on the nature of cations, their charges and their distribution among tetrahedral (A) and octahedral (B) sites [8].

Various physical and chemical methods of preparation have been developed to achieve nano-sized ferrite particles such as sol-gel [9], chemical co-precipitation [10], high-energy ball milling [11], hydrothermal [12], citrate precursor [13], and Chemical combustion route [14]. Among them chemical co-precipitation method seems to be the most convenient method for the synthesis of Zn-Co-Mg ferrites. It is very simple and has better control over crystalline size and

other properties of the materials [15]. Several researchers used co-precipitation method to successfully prepare their different samples. Among those, Nikumbh et al. [16] used the method in order to prepare  $\text{CoRE}_x\text{Fe}_{2-x}\text{O}_4$  nano-phase, while P. Kumar et al. [17] used it to prepare  $\text{CoFe}_{2-x}\text{GdO}_4$ . The preparation of  $\text{TiO}_2$  nanoparticles using a wet chemical technique was carried out by Suresh Sagadevan [18].

In this work, the aim is to synthesis nano-ferrites using chemical co-precipitation method and to investigate its structural and optical properties. Moreover, the effect of doping of Cobalt (Co) substituted magnesium was investigated. X-ray diffraction (XRD) was used to confirm the formation of single phase spinel structure and to determine the crystalline size. Fourier Transform Infrared Spectroscopy (FTIR), and Ultraviolet visible spectrometer (UV-visible) were used in order to explore the effect of Co substituted zinc magnesium nano-ferrites on the optical properties.

## 2. Experimental

The  $\text{Zn}_{0.5}\text{Co}_x\text{Mg}_{0.5-x}\text{Fe}_2\text{O}_4$  ( $x = 0.0, 0.1, 0.2, 0.3, 0.4$ ) nano-crystalline ferrites were prepared using chemical co-precipitation method as reported in the literature [19, 20]. Following chemicals were purchase from Sigma Aldrich and used in the preparation of  $\text{Zn}_{0.5}\text{Co}_x\text{Mg}_{0.5-x}\text{Fe}_2\text{O}_4$  nano-crystalline ferrites; namely  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99%),  $\text{Zn}(\text{NO}_3)_2$  (98%),  $\text{CONO}_3$  (99%), and  $\text{MgNO}_3$  (99%). Required volumes of metal salts solutions having concentrations 0.15 M were mixed and stirred on a magnetic hot plate at  $80^\circ\text{C}$  for 1 hour. Specific amount of oleic acid was used as surfactant and for coating. The pH value was adjusted using 3M NaOH solution and the pH value was maintained 11-13 for all of the samples. The precipitates were washed with deionized water until the pH reduced to 7. Water was, then, evaporated using the oven at  $100^\circ\text{C}$ , and annealing was carried out at  $450^\circ\text{C}$  for 6 h in a temperature controlled muffle furnace Vulcan A-550 at a heating rate  $10^\circ\text{C}/\text{min}$ . The obtained materials were grinded into powder form and were made ready for characterization using various techniques.

The XRD analysis was carried out to confirm the purity of the synthesized materials using Shimadzu 6000 X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation of a wavelength of  $\lambda = 1.5406 \text{ \AA}$  source.

FTIR measurements were performed using (Mattson, model 960m0016) spectra, while, the absorption of solution with different concentration was calculated using UV min 1240 spectrometer Shimadzu.

## 3. Results and Discussion

The crystalline and structure of prepared particles are confirmed by XRD patterns. Figure 1 displays the typical XRD spectra of cobalt substituted magnesium nanoferrites with composition ( $x = 0$ ). XRD patterns are well indexed using MDI jade 5.0 [21]. Several peaks have been observed and indexed and assigned as (111), (220), (311), (400), (422),

(511), (440) and (533) which are the characteristics planes of single phase cubic spinel structure with space group  $\text{Fd-}3\text{m}$  and most intense (311) reflection [22].

From the XRD data, the crystallite size of  $\text{Zn}_{0.5}\text{Co}_x\text{Mg}_{0.5-x}\text{Fe}_2\text{O}_4$  prepared nanoparticles is calculated using Scherer's formula [23].

$$D_c = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

where  $D_c$  is crystallite size,  $\beta$  is full width at half maximum (FWHM) of the most intense (311) peak,  $\lambda$  is X-ray wavelength and  $\theta$  is diffraction angle. The results of X-ray diffraction are listed in Table 1.

Figure 2 (a) shows the intensity versus  $2\theta$  for samples with different concentration of cobalt. It can be observed that the crystalline sizes are found to increase from 23.60 nm to 25.03 nm as the concentration of cobalt increases from  $x=0$  to  $x=0.4$ . The lattice constant as a function of cobalt concentrations is shown in figure 2 (b). It is clear, from the figure, that the lattice constant,  $a$ , increase from 8.375 to 8.392  $\text{\AA}$ . The increasing in lattice constant is attributed to the larger ionic radius of  $\text{Co}^{+2}$  (0.74  $\text{\AA}$ ) in compare with  $\text{Mg}^{+2}$  (0.72  $\text{\AA}$ ) [11]. Sonal Singhal et al. showed in their results that the lattice parameter,  $a$ , was increase with cobalt concentration and attributed to the smaller ionic radius of nickel [24]. Rapolu Sridhar et al., studied Copper Substituted Nickel Nano-Ferrites by Citrate-Gel Technique and they found the lattice parameter was decreased when  $\text{Cu}^{+2}$  concentration was further increase [25].

The density of composition is estimated using the following relation [26]

$$D_x(\text{ferrite}) = \frac{8M}{N \times a^3} \quad (2)$$

where,  $M$  is molecular weight of the ferrite,  $N$  is the Avogadro's number and  $a^3$  is the volume of the cubic unit cell. It can be observed from table 1 that, the composition density increases with increasing Co content. The increase in density may be due to the ionic radii of constituent ions causing increase in lattice constant. The density of pure  $\text{CoFe}_2\text{O}_4$  is (5.29  $\text{g}/\text{cm}^3$ ) [14], while for pure  $\text{MgFe}_2\text{O}_4$  is (4.52  $\text{g}/\text{cm}^3$ ) [27].

Figure 3 shows the infrared spectra of synthesized  $\text{Zn}_{0.5}\text{Co}_x\text{Mg}_{0.5-x}\text{Fe}_2\text{O}_4$  nano ferrite powders where  $x = 0.0, 0.1, 0.2, 0.3,$  and  $0.4$  (as pellets in KBr) in the range of 400 to 4000  $\text{cm}^{-1}$ . The spectra of all the ferrites have been used to locate the band positions which are given in the Table 2. In the present study the absorption bands  $\nu_1, \nu_2, \nu_3, \nu_4,$  and  $\nu_5$  are found to be around 603, 1142, 1405, 1643 and 3111  $\text{cm}^{-1}$ , respectively for all the compositions. The absorption bands observed within these specific limits revealed the formation of single-phase spinel structure having two sub-lattices tetrahedral (A) site and octahedral (B) site [24]. There is a band, not very clear, appear around 465  $\text{cm}^{-1}$  which may be caused by the metal-oxygen vibration in the octahedral side. The ( $\nu_1$ ) band usually observed around 600  $\text{cm}^{-1}$  is caused by the metal-oxygen vibration in the tetrahedral sides [24]. The difference in the spectral positions may be due to the different of distances of metal ion- $\text{O}^{2-}$  for octahedral and

tetrahedral sites. The band ( $\nu_2$ ) around  $1142\text{ cm}^{-1}$  is due to formation of Co substituted spinel ferrites. The ( $\nu_3$ ) around  $1405\text{ cm}^{-1}$  is associated with the bending vibration related to the  $CH_2$  groups [11]. ( $\nu_4, \nu_5$ ) which observed around 1643 and  $3111\text{ cm}^{-1}$  are due to the stretching mode of H-O-H bending vibration of free or absorbed water which implies that the hydroxyl groups are retained in ferrites [28].

The absorption as a function of wavelength for  $Zn_{0.5}Co_xMg_{0.5-x}Fe_2O_4$  samples is performed. In case of sample  $5Zn_{0.5}Mg_{0.1}Co_{0.4}Fe_2O_4$  (figure not shown), the maximum absorption is observed at wavelength 235nm. The optical band gap energy of the nanostructured was obtained using the following equation [28]

$$(\alpha h\nu) = A(h\nu - E_g)^m \quad (3)$$

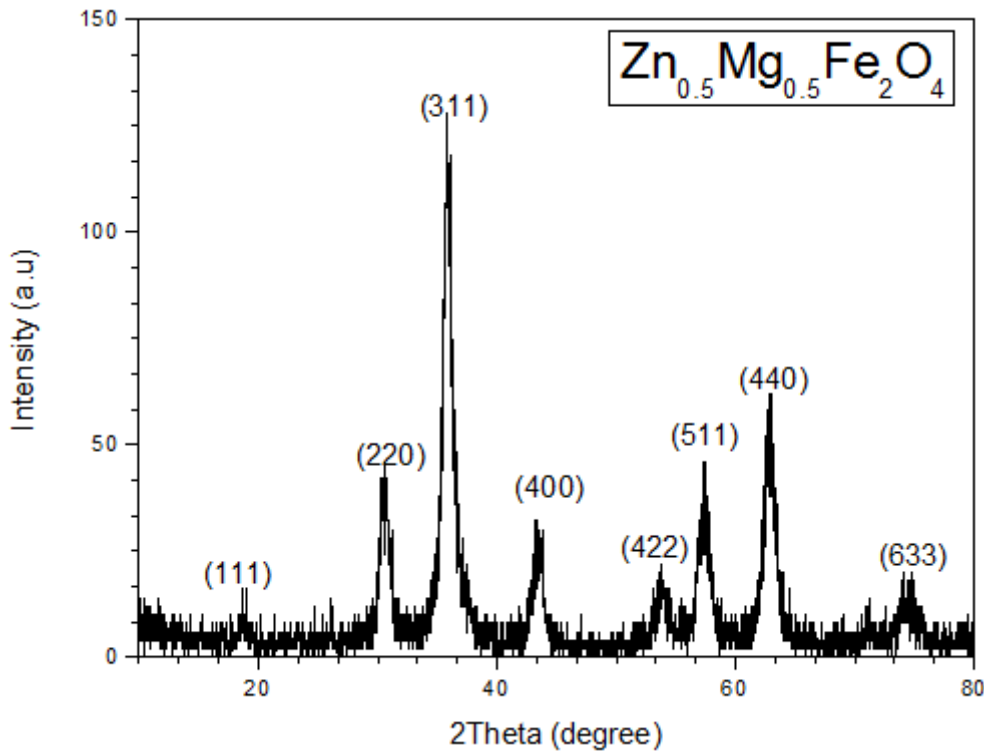
In Eq. (3)  $E_g$ , the optical band gap whereas  $m$  represents

**Table 1.** Particle size ( $D_c$ ), Lattice constant ( $a$ ), Cell volume ( $V$ ) and the cell Density of  $Zn_{0.5}Co_xMg_{0.5-x}Fe_2O_4$ .

$Zn_{0.5}Co_xMg_{0.5-x}Fe_2O_4$	$D_c$ (nm)	Lattice constants ( $\text{\AA}$ )	$V$ ( $\text{nm}^3$ )	Density ( $\text{g/cm}^3$ )
X=0.0	23.60	8.375	0.587	4.52
X=0.1	23.88	8.377	0.588	5.30
X=0.2	21.69	8.387	0.590	4.50
X=0.3	25.03	8.391	0.591	5.18
X=0.4	21.44	8.392	0.591	5.30

**Table 2.** Wave numbers and band gaps of  $Zn_{0.5}Co_xMg_{0.5-x}Fe_2O_4$  nanoferrite.

No	$Zn_{0.5}Co_xMg_{0.5-x}Fe_2O_4$	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	Band gap (eV)
1	X=0.0	603	1142	1405	1646	3132	4.8
2	X=0.1	601	1142	1405	1643	3111	4.7
3	X=0.2	600	1142	1404	1643	3111	4.8
4	X=0.3	603	1142	1405	1643	3101	4.8
5	X=0.4	603	1111	1405	1643	3111	4.5



**Figure 1.** XRD patterns of  $Zn_{0.5}Mg_{0.5}Fe_2O_4$  nanoferrite.

the nature of the transition band gap, constant  $A$  is an energy-independent constant,  $(h\nu)$  is energy of photon. Assuming direct band gap transition for the samples,  $m$  was assigned a value of  $1/2$ . To evaluate a precise value for the optical band gap, we plotted  $(\alpha h\nu)^2$  versus energy  $(h\nu)$  for  $Zn_{0.5}Mg_{0.5}Co_{0.1}Fe_2O_4$  (sample 2) as shown in figure 4. The optical band gap was determined by extrapolating the linear portion of the plot to  $(\alpha h\nu)^2 = 0$  and is found to be 4.8, 4.7, 4.8, 4.8 and 4.5eV for the studied samples, respectively. The results of wave numbers and band gaps of all the compounds are listed in Table 2. The effect of substitution is profound when the Co concentration is further increased to 0.4 as optical band gap energy dropped to 4.5. The reduction in optical band gap may be due to increase in lattice constant with Co concentration.

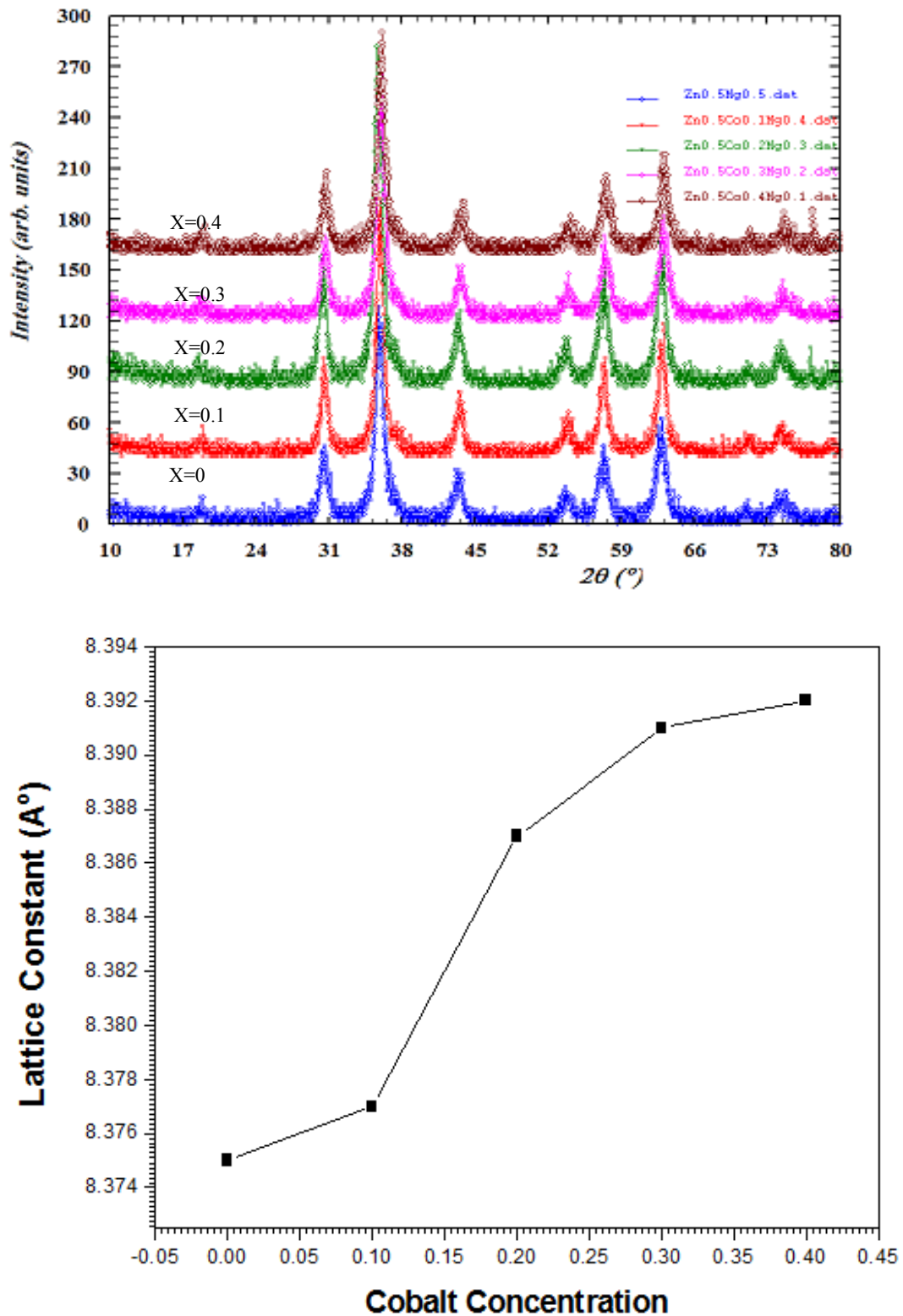


Figure 2. (a) XRD patterns of Zn<sub>0.5</sub>Co<sub>x</sub>Mg<sub>0.5-x</sub>Fe<sub>2</sub>O<sub>4</sub> nano-ferrites. (b) Lattice constant as a function of different concentration of Co of Zn<sub>0.5</sub>Co<sub>x</sub>Mg<sub>0.5-x</sub>Fe<sub>2</sub>O<sub>4</sub> nano-ferrites.

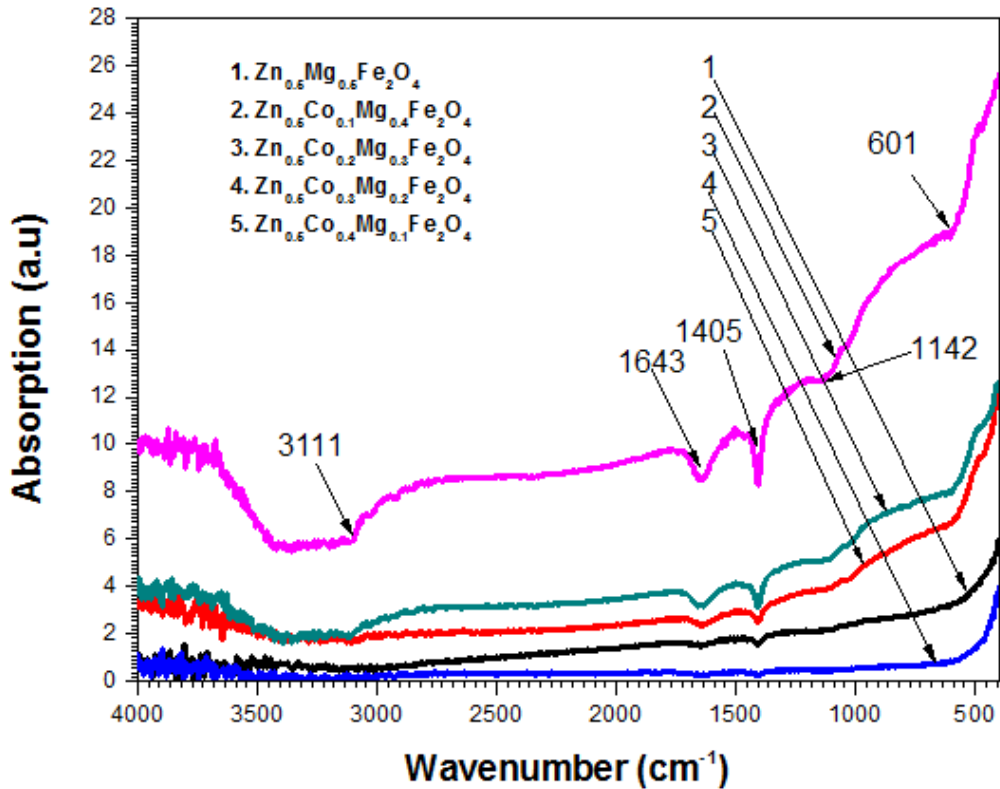


Figure 3. FTIR spectra of  $Zn_{0.5}Co_xMg_{0.5-x}Fe_2O_4$  nanoferrites of different concentration of Co.

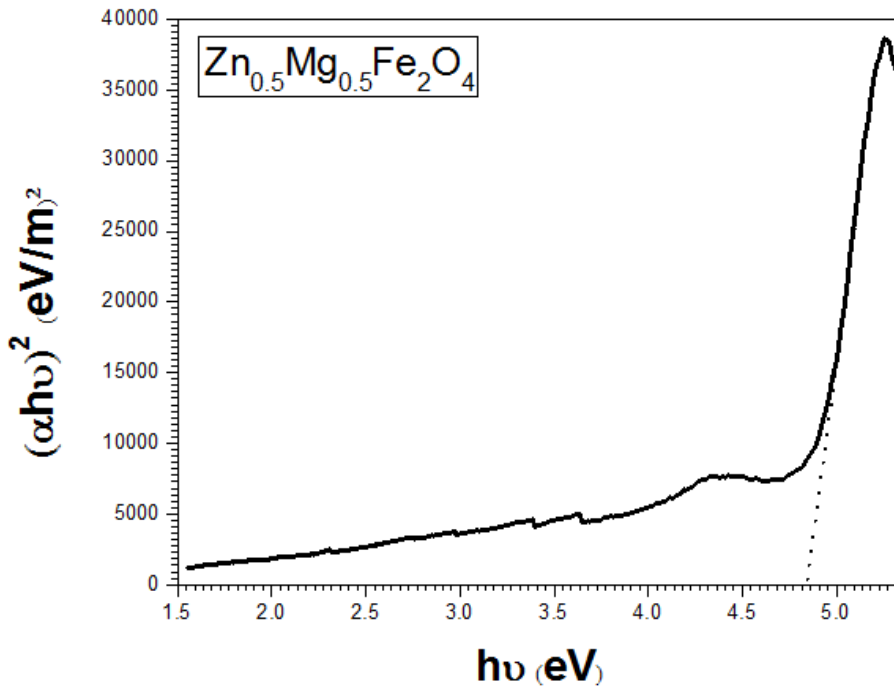


Figure 4. Plot of  $(\alpha h\nu)^2$  versus  $h\nu$  for  $Zn_{0.5}Mg_{0.5}Fe_2O_4$  nanoferrite

#### 4. Conclusion

The effect of cobalt substitution on magnesium nanocrystalline ferrites was studied. The formation of single phase crystalline structure with size in the range 23.60 – 25.03 nm was confirmed by X-ray diffraction. FTIR

spectrum exhibited expected main absorption bands, thereby confirming the spinel structure. Optical band gap energy of  $Zn_{0.5}Co_xMg_{0.5-x}Fe_2O_4$  nanoferrite was found to be in the range 4.5 to 4.8eV for samples with different cobalt concentration. The substitution was resulted in slight increased in the lattice constant and that sequentially may lead to the slightly decreased in the energy gap. The synthesized nanoferrites are

expected to be useful in several technological applications such as soft magnets and magnetic fluids for hyperthermia. The structural and properties of spinel ferrites depend upon the method of preparation, the nature of substitutional element and the concentration of the substitution element. Attempts can be made to prepare the samples by different methods to get desired properties and particle sizes.

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