

# Energy Band Gap and Vibrational Bond Structure Analysis of Cobalt Doped Nickel Ferrite Material by Self-Combustion Method

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## Abstract:

Cobalt Doped Nickel Ferrites with the general formula  $Ni_{1-x}Co_xFe_2O_4$  ( $x = 0.0, 0.1, 0.2$  and  $0.3$ ) were prepared by self-combustion method. Nickel II Nitrate Hexahydrate  $[Ni(NO_3)_2 \cdot 6H_2O]$ , Cobalt II Nitrate Hexahydrate  $[Co(NO_3)_2 \cdot 6H_2O]$  and Iron (III) Nanohydrate  $[Fe(NO_3)_3 \cdot 9H_2O]$  were used as the starting chemicals. The X-ray diffraction analysis was carried out to investigate the crystalline phase formation. The FTIR spectra of the spinel phase calcinated at  $600^\circ C$  exhibit two prominent fundamental absorption bands in the range of  $350-600\text{ cm}^{-1}$  assigned to the intrinsic stretching vibrations of the metal at the tetrahedral and octahedral sites. The Raman spectra analysis and the energy band gap of these samples were also investigated. The energy band gap of all samples was nearly the same around  $5.2\text{ eV}$  and it was agreed with the standard value.

## Keywords:

Cobalt Doped Nickel Ferrites, XRD, FTIR, RT & UV

## 1. Introduction

Nanoparticles of magnetic ferrites have attracted great research interest because of their applications in permanent magnets, drug delivery, microwave devices and high-density information storage. Cobalt ferrite has been extensively investigated because of its interesting magnetic behavior, chemical stability and mechanical hardness. Cobalt ferrite  $CoFe_2O_4$ , crystallizes in a partially inverse spinel structure. Nickel-ferrite is an inverse spinel magnetic material. Nickel ferrite is well known hard magnetic material with high coercivity and saturation magnetization while nickel ferrite is soft material with low coercivity and saturation magnetization. Many of these hard and soft magnetic properties make them very promising for candidates for a variety of applications. Nano size ferrites have been prepared by various techniques such as sol-gel, self-combustion, modified oxidation process, forced hydrolysis, hydrothermal process, ball milling and the micro-emulsion method. In the present study, Nano-ferrites of the composition  $Ni_{1-x}Co_xFe_2O_4$  (where  $x = 0.0, 0.1, 0.2$  and

0.3) were synthesized by citrate-gel self- combustion method and sol-gel method. Structural, microstructure properties and atomic and weight concentration of fabricated nano-ferrite were studied by X-ray diffraction (XRD), Fourier Transform Infrared( FTIR ), Raman spectroscopy and the energy band gap of different samples by measuring the absorption spectrum using UV-VISIBLE spectrometer.

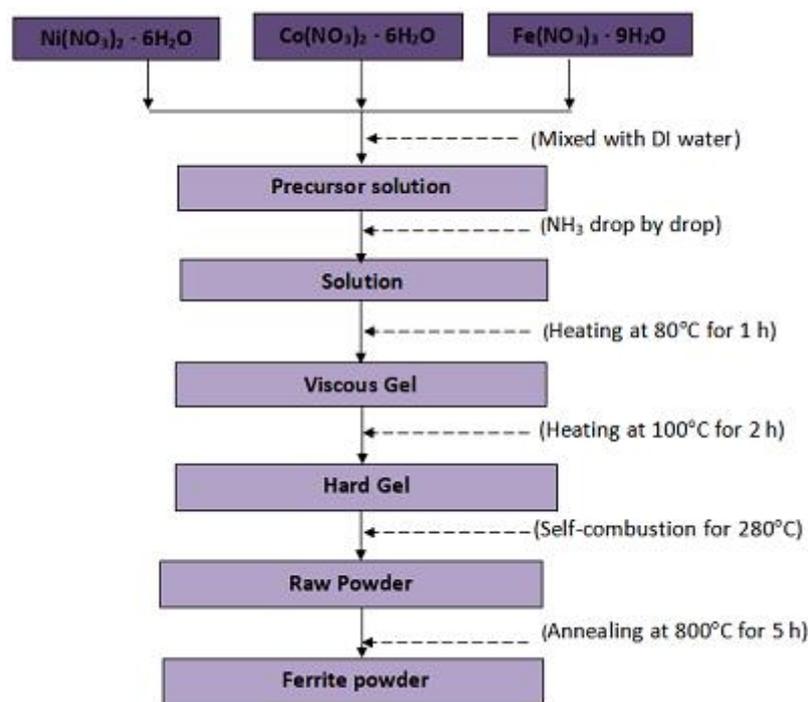
## 2. Experimental Details

In this research spinel like ferrites belonging to the series  $Ni_{1-x}Co_xFe_2O_4$ , where  $x$  varies from 0.0 to 0.3 in steps of 0.1 were prepared by self-combustion method.  $Ni(NO_3)_2 \cdot 6H_2O$ , Nickel nitrate hydrate,  $Fe(NO_3)_3 \cdot 9H_2O$ , iron nitrate hydrate and  $Co(NO_3)_2 \cdot 6H_2O$ , cobalt nitrate hydrate were used as raw materials for  $Ni_{1-x}Co_xFe_2O_4$  ferrite. Before preparation of spinel like ferrites the purification of starting materials was checked by X-ray diffraction.

### Experimental Sequence for Nano-ferrites by Self-combustion Method:

The self-combustion method was used for preparation because the followings two advantages.

- (1) heat generated in the exothermic reaction accelerates the process and
- (2) the resulting as prepared powder is fine grained with grain size smaller than that of the starting powers.



**Figure 1.** Experimental sequence of Cobalt Doped Nickel ferrites for Self-combustion method.

Nickel II Nitrate Hexahydrate [ $Ni(NO_3)_2 \cdot 6H_2O$ ], cobalt II Nitrate Hexahydrate [ $Co(NO_3)_2 \cdot 6H_2O$ ] Iron (III) Nanohydrate [ $Fe(NO_3)_3 \cdot 9H_2O$ ] were weighed with desired stoichiometric compositions. The precursor solutions were prepared by dissolving the necessary powders in deionized water by molarity ratio. The mixture solution was stirred by magnetic stirrer at  $80^\circ C$ . Ammonium Hydroxide( $NH_4OH$ ) was added to control pH level of mixture solution. After stirring 1h, the mixture solution became viscous gel. Hard gel was obtained by continuous heating at  $100^\circ C$  for 2h. As

the temperature increased from 100°C to 190°C, the colour of hard gel changed to black colour. Finally, self-combustion process was done at 280°C and reddish-brown powder was obtained. It was cooled down at room temperature and then ground by agate mortar. After sieved by mesh sieve,  $Ni_{1-x}Co_xFe_2O_4$  nano ferrite powder was obtained. Experimental sequence of Cobalt doped Nickel Ferrites using self-combustion method was shown in Figure 1.

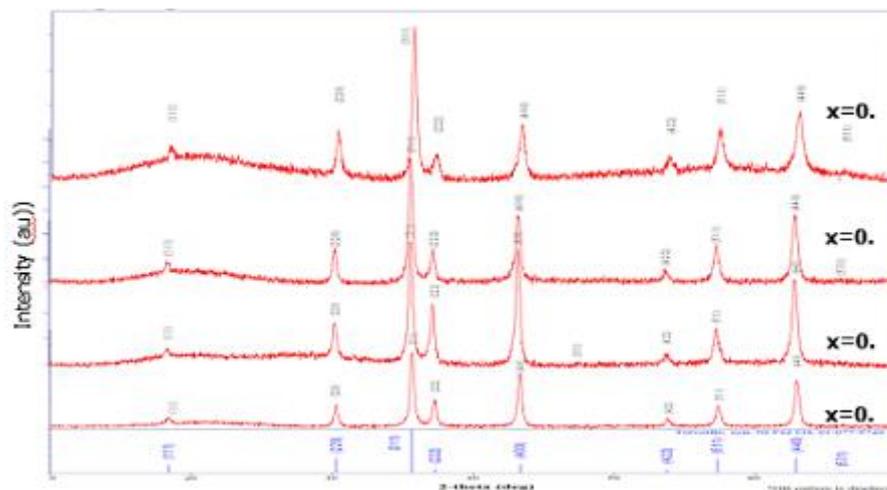
### 3. Results and Discussion

#### 3.1. Structural Investigation of Nano-ferrite

The XRD spectra of the cobalt Doped Nickel ferrites,  $Ni_{1-x}Co_xFe_2O_4$  ( $x = 0.1, 0.1, 0.2$  and  $0.3$ ) nano-ferrite were investigate by X-Ray Diffractometer. Figure 2 showed XRD profile of nano-ferrite fabricated by self-combustion method with different Co concentration.

In these figures, eight diffraction patterns were clearly observed and all of these patterns were consistent with JCPDS library file No 01-077-9720. It can be seen that all the compounds thus prepared show crystallinity and the diffraction pattern is characteristic of a spinel structure. The interatomic spacing ( $d$ ) values were in good conformity with that of the reported values. Moreover no other impurity lines corresponding to possible oxides of precursors used for synthesis were noticed. Thus it was ensured that the prepared compounds were single phasic in nature and they exhibit an inverse/ normal spinel structure.

In Figure 2, all the reflections in the XRD patterns correspond to that of cobalt ferrite and no additional reflections were observed for the samples indicating the phase purity of the samples. The X-ray diffractograms clearly indicate the formation of single phase spinel structure.



**Figure 2.** XRD Spectrum of  $Ni_{1-x}Co_xFe_2O_4$  ferrites with different Co concentration by self-combustion method.

The X-ray density of all the  $Ni_{1-x}Co_xFe_2O_4$  ( $0 \leq x \leq 0.3$ ) ferrites has been calculated from the molecular weight and the volume of the unit cell using the relation;

$$d_x = \frac{8M}{Na^3}$$

The calculated values were also listed in Table 1.

The average particle size of the synthesized ferrite samples was estimated from X-ray peak broadening of diffraction peaks using Scherrer formula. The calculated average crystallite sizes of these starting materials were listed in Table 2. From this results, the average crystallite size was decreased with the increasing of Co content. But at the Co content (0.3%), the average crystallite size increased again due to the material concentration. But, as the sintering temperature and sintering time (800°C for 5 h) were very high, this resulted for larger grain size in the prepared ferrite samples. Likelihood, all of fabricated nano ferrite confirmed nano meter range.

**Table 1.** Variation of X- ray density values for  $Ni_{1-x}Co_xFe_2O_4$  nano-ferrite.

$Ni_{1-x}Co_xFe_2O_4$ Nano-ferrite	X-ray density (g cm <sup>-3</sup> )
	Self-combustion Method
x =0.0	5.35
x =0.1	6.72
x = 0.2	7.29
x= 0.3	6.81

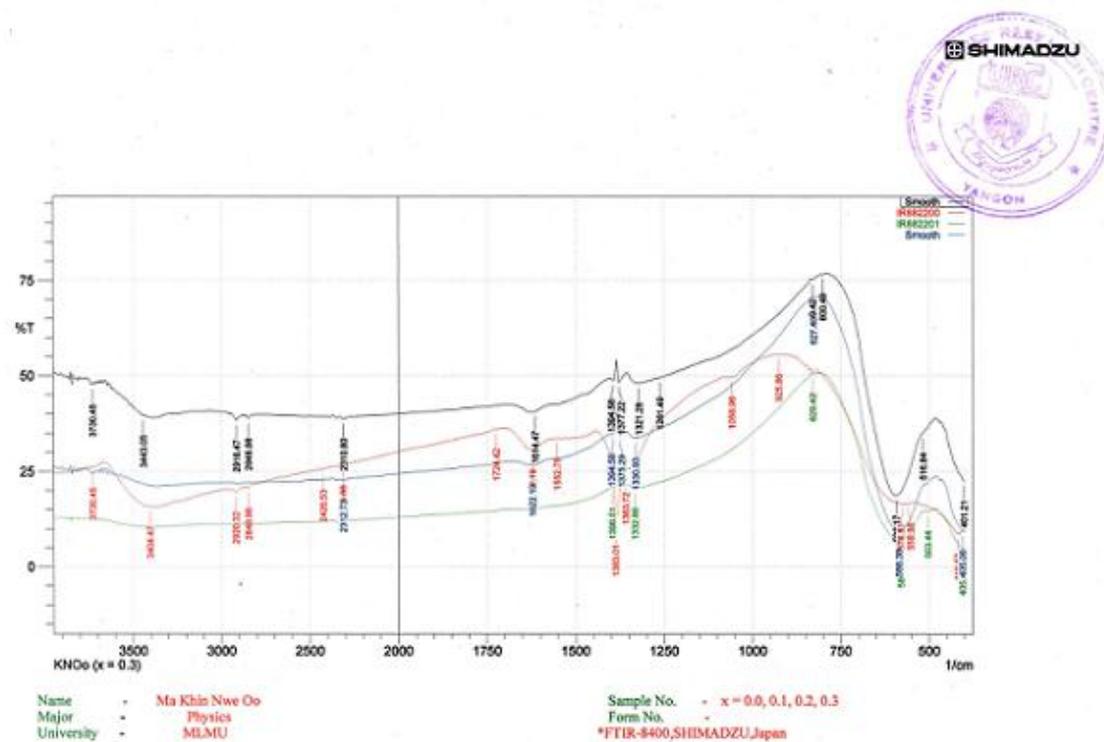
**Table 2.** The crystallite size of starting materials.

$Ni_{1-x}Co_xFe_2O_4$ Nano-ferrite	Crystallite Size(nm)
	Self-combustion Method
x =0.0	45.79
x =0.1	43.12
x = 0.2	41.43
x= 0.3	42.51

### 3.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier transform infrared (FTIR) studies were carried out to ascertain the metal-oxygen bonding. Fourier Transform Infrared absorption spectrum in the range of 4000-400 cm<sup>-1</sup> was recorded at room temperature by using SHIMADZU using KBr pellet method. The spectrum transmittance (%) against wave number was used for interpretation of the results. The FT-IR spectrum of the investigated cobalt doped nickel ferrite ( $Ni_{1-x}Co_xFe_2O_4$ ) nanoparticles synthesized by self-combustion was shown in Figure 3. Following Waldron, the ferrites were described as continuously bonded crystals in which the atoms were bonded to all nearest neighbors by equivalent strength of ionic, covalent or van der Waals interactions. The spinel structure are attributed to the stretching vibrations of the unit cell of the spinel in the tetrahedral (A) Site and The metal-oxygen vibration in the octahedral (B) site. These absorption bands are highly sensitive to changes in interaction between oxygen and cations, as well as to the size of the obtained nano-particles. The broadening of the spectral band depends on the statistical distribution of cations over A and B sites. The vibration frequency depends on the cation mass, cation-oxygen distance and bending force. In ferrites the metal ions occupy two different sub-lattices designated as

tetrahedral (A-site) and octahedral (B-site) positions with respect to the geometrical configuration of the oxygen nearest neighbors. The one with the higher wave number,  $\nu_1$  observed in the range of 580–600  $\text{cm}^{-1}$  corresponds to the intrinsic stretching vibrations of the metal at the tetrahedral site ( $M_{\text{tetra}} \leftrightarrow O$ ).



**Figure 3.** The FT-IR spectrum of the cobalt doped nickel ferrite nanoparticles synthesized by self-combustion method .

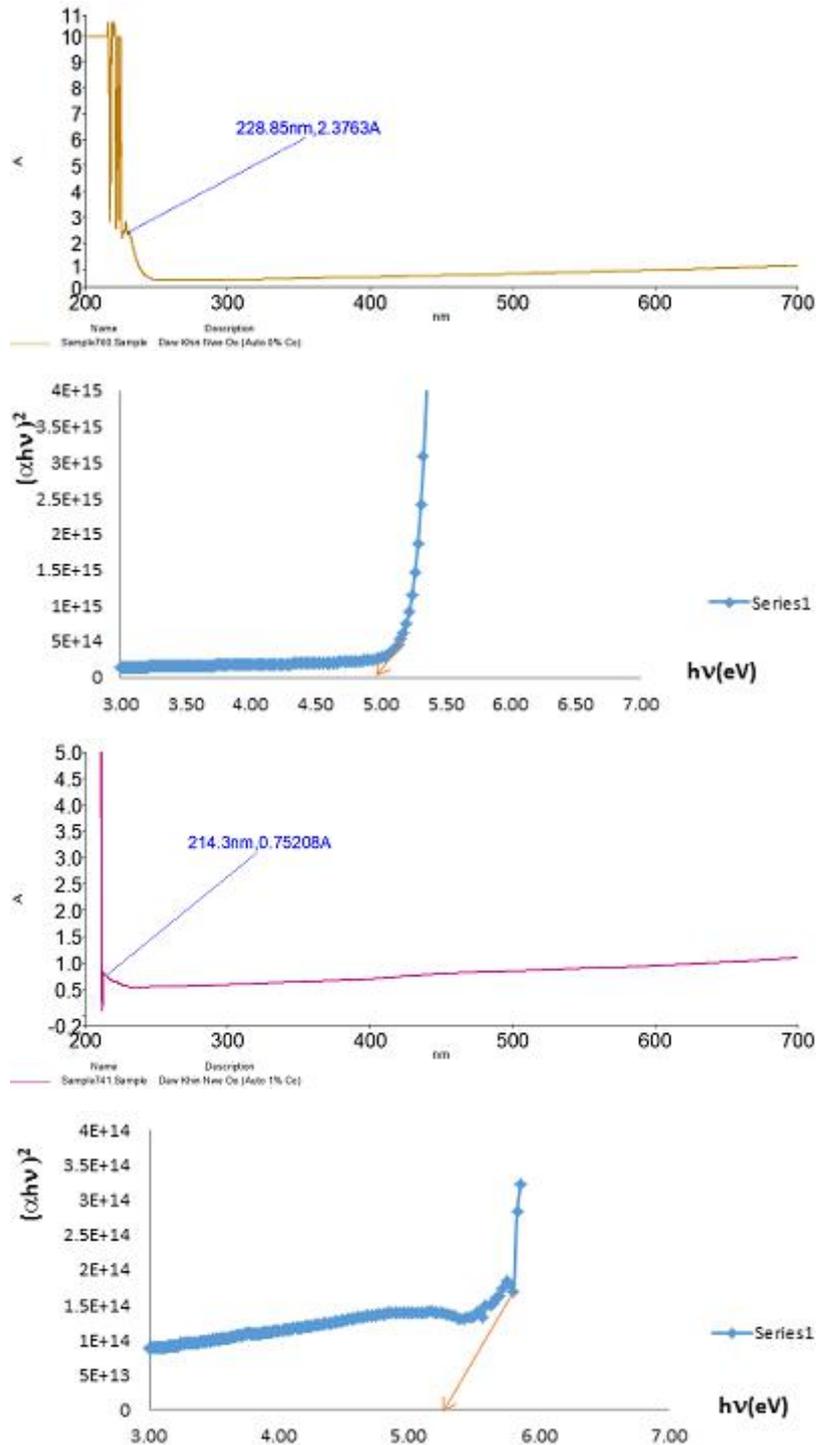
While the lower wave number one,  $\nu_2$  which is usually observed around 375–450  $\text{cm}^{-1}$  is attributed to the octahedral metal stretching ( $M_{\text{octa}} \leftrightarrow O$ ). The two main broad metal–oxygen bands are seen in the infrared spectrum of all spinels, especially ferrites. The higher absorption band observed in the range 578  $\text{cm}^{-1}$ , was caused by the stretching vibrations of the tetrahedral metal–oxygen bond and the lowest band observed in the range 406  $\text{cm}^{-1}$ , was caused by the metal–oxygen vibrations in the octahedral sites. The absorption band around 3560  $\text{cm}^{-1}$  indicated the presence of hydroxyl group. The absorption peaks at 1435  $\text{cm}^{-1}$ , 1627  $\text{cm}^{-1}$  and 3520  $\text{cm}^{-1}$  was due to traces of adsorbed or atmospheric  $\text{CO}_2$ . The decomposition of hydroxide to oxide phase for the formation of spinel ferrites was well reflected in the FTIR spectrum. It has been reported that the IR bands of solids are usually attributed to the vibration of ions in the crystal lattice. The bands at 552  $\text{cm}^{-1}$  and 461  $\text{cm}^{-1}$  represented tetrahedral and octahedral modes of  $\text{NiFe}_2\text{O}_4$ , respectively. The band located at 3336  $\text{cm}^{-1}$  could be attributed to the symmetric vibration of  $-\text{OH}$  groups. The bands with peaks observed at 1038  $\text{cm}^{-1}$  could be assigned to O-H bending vibration. The peak at 2333  $\text{cm}^{-1}$  was ascribed to H-O-H bending vibration of the free or absorbed water. The appearance of much weaker absorption bands around 1100–1300  $\text{cm}^{-1}$ , 1400–1700  $\text{cm}^{-1}$ , 2850–3000  $\text{cm}^{-1}$  and 3400  $\text{cm}^{-1}$  are assigned to the vibrations of  $\text{NO}_3^-$  ions, carboxyl group  $\text{COO}^-$ , the stretching of the C–H bands and hydrogen

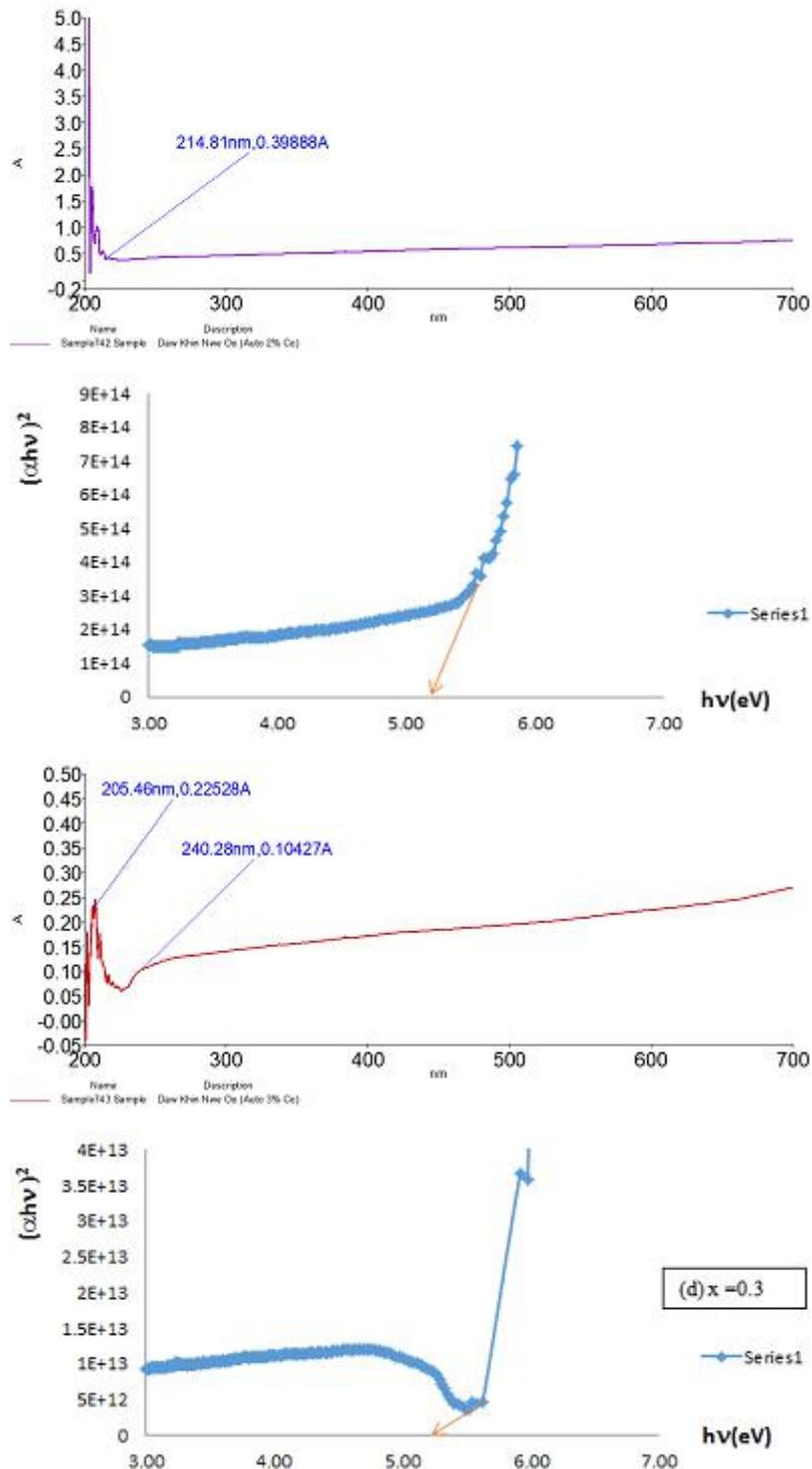


for allowed and 2 for forbidden direct energy gap for ferrites. Further, the value of  $\alpha$  been calculated by the following relation,

$$\alpha = 4\pi \frac{k}{\lambda}$$

where  $\lambda$  is wavelength in nm and k is absorptin index .





**Figure 5.** The UV absorbance spectrum and the energy band gap of  $\text{Co}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$  material (a)  $x = 0.0$ , (b)  $x = 0.1$  (c)  $x = 0.2$  (d)  $x = 0.3$  by self-combustion method.

The optical band gap of the synthesized ferrites was calculated by equation (1). The UV- visible absorbance spectra and calculated band gap of the Co substituted Ni ferrites were also shown in Figure 5 (a) to (d). From the analysis, the energy band gap of these materials was linearly the same (about 5.2 eV) in all samples.

## 4. Conclusions

Nanocrystalline Cobalt Doped Nickel Ferrites,  $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  (where  $x = 0.0, 0.1, 0.2$  and  $0.3$ ) samples were successfully prepared by self-combustion and sol-gel methods. The structural analysis was reported by using XRD. The process involved no impurity pick up and materials loss. It is a very simple and economical method where no specific heating or cooling rate is required. X-ray diffraction pattern confirms the formation of cubic spinel structure in single phased without any impurity peak. The lattice parameter was not remarkably changed with the increase of Co substitution in Ni-Co ferrites which indicates that Co content was totally substituted in Ni. Average crystallite size of fabricated nano ferrite observed that in the range between 41 and 46 nm. FT-IR measurement for the ferrite powders shows two characteristic bands in the range  $500\text{-}600\text{ cm}^{-1}$  and  $385\text{-}450\text{ cm}^{-1}$ , which could be attributed to the tetrahedral and octahedral complexes respectively. The substantial invariance of the Raman features for all the samples indicated a good stability of the spinel structure.

The energy band gap of these materials was obtained nearly the same of 5.2 eV in all samples.

## Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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