

## Effect of Aluminium Doping on Structural Properties of $\text{CoFe}_2\text{O}_4$ Nanoparticles

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**Abstract:** The present work deals with the synthesis and structural properties of pure and aluminium doped cobalt ferrite ( $\text{CoFe}_2\text{O}_4$  and  $\text{CoAl}_{0.2}\text{Fe}_{1.8}\text{O}_4$ ) nanoparticles. The  $\text{CoFe}_2\text{O}_4$  and  $\text{CoAl}_{0.2}\text{Fe}_{1.8}\text{O}_4$  nanoparticles were synthesized by sol-gel auto combustion method. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques were used for the characterization of the prepared samples. The structural properties were estimated from X-ray diffraction (XRD) studies. The average particle size was calculated by using Debye Scherrer's formula and the obtained values are of few nanometre. The principle absorption band corresponding to octahedral lattice site was observed from FTIR spectra.

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### I. INTRODUCTION

Ferrites are magnetic ceramics of great importance in many technological applications on account of their various electrical, dielectric and magnetic properties. Ferrites with cubic spinel structure forms an important class of magnetic materials and exhibit interesting electrical and magnetic properties. Owing to their numerous applications ferrites are being studied from last six to seven decades with a view to understand and improve their properties for suitable applications. On account of their combined electric and magnetic properties they show wide applications in technology, particularly at high frequency [1, 2]. Ferrite materials find high frequency applications due to their high permeability and permittivity [3-7]. These materials are being used in transformer cores, antennas, radio frequency coil and radar absorbing materials (RAM) [8].

The literature report mainly focuses on nanosize magnetic materials having significant potential for many applications. Research in this area for better and improved materials still continues as they find some new applications. During the last decades there has been an interest in developing and understanding the basic magnetic and electrical properties of spinel ferrite at nanometric scale. The progress made in the area of nanotechnology in the recent years has motivated the scientist and technologist to synthesize spinel ferrites in nanometric size and characterize them for their structural, electrical and magnetic properties. It is well known that the properties of spinel ferrites are changed when the size of the particle reduces from bulk to nano.

In the recent years, the design and synthesis of magnetic nanoparticles of spinel ferrites in nanosize has been the focus of intense fundamental and applied research due to their enhanced properties that are different from those of their bulk counterparts [9]. Technological demand of high performance devices has triggered the synthesis and research in nanoscale spinel ferrite. Nanosize spinel ferrites find applications in high density magnetic data storage [10], microwave absorbing material [11], magnetic resonance imaging [12], targeted drug delivery [13], magnetic fluids [14], biotechnology [15] etc.

Cobalt ferrite is a well-known magnetic material with inverse spinel structure. The saturation magnetization and coercivity of cobalt ferrite is higher than the other cobalt, manganese spinel ferrites [16]. Cobalt ferrite is the most important and abundant magnetic materials that have large magnetic anisotropy, moderate saturation magnetization, remarkable chemical stability and mechanical hardness, which make it good candidate for the recording media [17, 18]. The chemical composition method of synthesis, nature of dopant, site preference of dopants etc parameters strongly influences the structural, electrical and magnetic properties of spinel ferrites [19, 20]. In the present study, the effect of aluminium doping on the structural properties of nanocrystalline cobalt ferrite prepared by sol-gel auto combustion method is reported.

### II. MATERIAL AND METHODS

#### Preparation

$\text{CoFe}_2\text{O}_4$  and  $\text{CoAl}_{0.2}\text{Fe}_{1.8}\text{O}_4$  nanoparticles 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

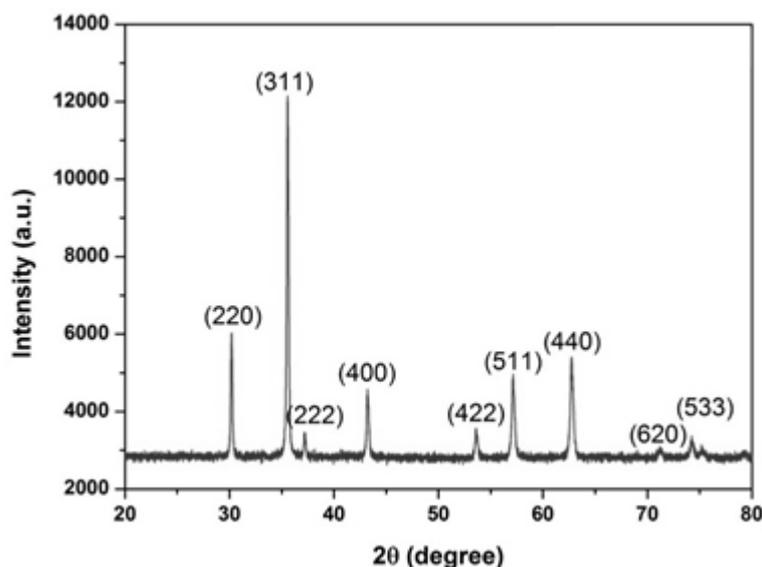
into separate glass beakers. The mixed solution was stirred for 15-20 minutes to dissolve completely into distilled water. After complete dissolution they were mixed together. Ammonia was added drop-wise into the solution to adjust pH value to about 7 and stabilize the nitrate-citric acid solution. Then the neutralized solution was constantly magnetically stirred and heated at 80-90°C for 6 h on a hot plate. On the formation of sol-gel, very viscous gel the temperature was further raised up to 120 °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 30 minutes and annealed at 700°C for 4 h in muffle furnace.

### Characterizations

In the present work, pure and aluminium substituted cobalt ferrite samples were synthesized by sol-gel auto combustion method and characterized by X-ray diffraction technique. X-ray diffraction patterns of all the samples were recorded at room temperature by using a Regaku Miniflex-II X-ray powder diffractometer operated at 40 kV and 30 mA. The diffraction patterns were recorded in the 2θ range 20° to 80° with scanning rate of 2° per minute using Cu-K<sub>α</sub> radiation of wavelength 1.5406 Å. The vibrational band position was estimated from the FTIR spectroscopy.

### III. RESULTS AND DISCUSSION

Fig. 1 depicts the XRD pattern of aluminium doped cobalt ferrite nanoparticles (CoAl<sub>0.2</sub>Fe<sub>1.8</sub>O<sub>4</sub>) recorded at room temperature. The analysis of XRD patterns reveals the formation of single phase cubic spinel structure for doped and undoped Cobalt ferrite. All the peaks in the XRD pattern were indexed by using Bragg's law. The presence of planes (220), (311), (222), (400), (422), (511) and (440) in the XRD pattern reveals the cubic spinel structure of all the samples. It is also evident that all the peaks are intense and sharp. No impurity peaks were observed, thus the samples are single phase in nature. It is also evident from XRD pattern that the intensity of Bragg's peak is higher and the peaks are broader. Similar XRD patterns have been observed for spinel ferrites in the literature [14].



**Fig.1:** XRD pattern of CoAl<sub>0.2</sub>Fe<sub>1.8</sub>O<sub>4</sub>

The intensity of (311) plane is more as compared to other planes. The lattice constant (a) values were calculated using standard relation,

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

Where, (d) is interplanar spacing; (h k l) is Miller Indices.

The obtained values of the lattice constant (a) are listed in table 1. It is observed that, the lattice constant decreases after aluminium doping. The doping of Al<sup>3+</sup> (0.51 Å) ions in place of Fe<sup>3+</sup> (0.67 Å) leads to decrease in lattice constant. Similar behaviour of lattice constant was reported in the literature [15]. The values of structural parameters such as X-ray density and unit cell volume were also calculated and listed in table 1.

**Table 1:** Lattice constant (a), unit cell volume (V), X-ray density (d<sub>x</sub>) and crystallite size (t) for doped and un-doped cobalt ferrite

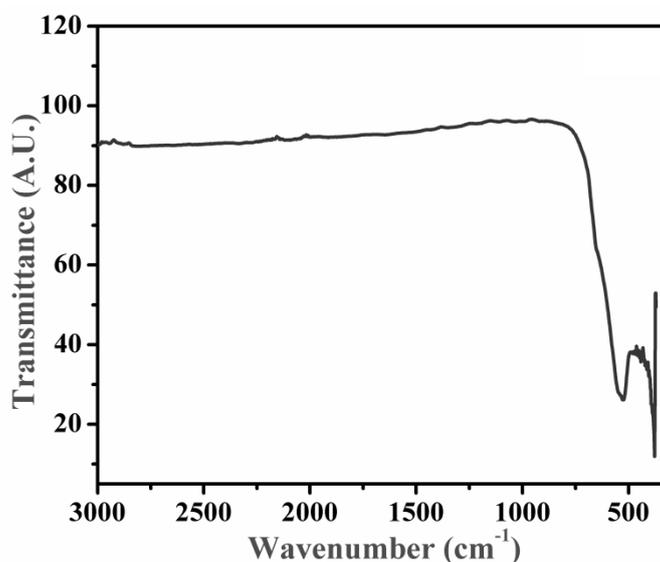
Sample	a (Å)	V (Å <sup>3</sup> )	d <sub>x</sub> (gm/cm <sup>3</sup> )	t (nm)
CoFe <sub>2</sub> O <sub>4</sub>	8.312	574.31	5.42	31
CoAl <sub>0.2</sub> Fe <sub>1.8</sub> O <sub>4</sub>	8.302	572.20	5.31	28

The particle size was calculated by using the most intense peak (311) and using the Debye-Scherrer relation for small and uniform sized cubic crystals mentioned below [16] and is found to be in nanometer size (Table 1).

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

**Fourier transform infrared spectroscopy**

Fig. 2 shows the FTIR spectra of aluminium doped cobalt ferrite (CoAl<sub>0.2</sub>Fe<sub>1.8</sub>O<sub>4</sub>) nano particles. These spectra were recorded in the frequency range 500-4000 cm<sup>-1</sup>. Two main broad metal-oxygen bands can be seen in the IR spectra. These two bands, according to Waldron attributed, band around at 500 cm<sup>-1</sup> and 600 cm<sup>-1</sup> which confirms the spinel ferrite structure. The high frequency band ν<sub>1</sub> is caused by stretching vibrations of tetrahedral metal-oxygen band and low frequency absorption band ν<sub>2</sub> is due to the metal-oxygen vibrations in octahedral sites. The difference in frequencies of bands ν<sub>1</sub> and ν<sub>2</sub>, may be due to changes in the bond length Fe<sup>3+</sup>- O<sup>2-</sup> at tetrahedral and octahedral sites. However, in the present study we observed only one band corresponding to 545 cm<sup>-1</sup> is observed because the spectrum is recorded in the range 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. The observed absorption band shows characteristics features of spinel ferrites. The values of absorption bands for undoped and Al doped cobalt ferrite nanoparticles are given in table 2.



**Fig. 2** FTIR for CoAl<sub>0.2</sub>Fe<sub>1.8</sub>O<sub>4</sub> nano crystalline material

**Table 2:** Values of absorption bands for Al doped and un-doped cobalt ferrite

Sample	ν <sub>1</sub> (cm <sup>-1</sup> )	ν <sub>2</sub> (cm <sup>-1</sup> )
CoFe <sub>2</sub> O <sub>4</sub>	381.55	395.25
CoAl <sub>0.2</sub> Fe <sub>1.8</sub> O <sub>4</sub>	525.36	552.13

**IV. CONCLUSION**

The nanocrystalline pure and aluminium doped cobalt ferrite were successfully synthesized by sol-gel auto combustion technique. The X-ray diffraction results showed the formation of single phase cubic spinel structure. The value of crystallite size confirms the nanocrystalline nature of the prepared sample. The structural parameters are found in the reported range. The substitution on Al ions in Cobalt ferrite decreases lattice constant. The absorption bands in FTIR spectra show formation of spinel cubic structure.

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