

# STRUCTURAL, MORPHOLOGICAL AND MAGNETIC PROPERTIES OF $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$ NANO-CRYSTALLINE

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## ABSTRACT

*Nanocrystalline Gallium substituted cobalt ferrite materials have been synthesized by coprecipitation route. The structural, morphological and magnetic properties of  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$  ( $0.0 \leq x \leq 0.8$ ) were determined by XRD, SEM, EDX spectroscopy and VSM. SEM images reveal that the sample surface exhibits well defined crystalline nanoparticles of spherical shapes with small agglomeration. Energy dispersive x-ray (EDAX) analysis confirms the presence of Co, Fe, Ga and oxygen in the prepared nanoparticles. From the HR-TEM, the average particle size is found to be 21 nm that is similar to that of the particle size obtained from the XRD data. The saturation magnetization ( $M_s$ ), coercivity ( $H_c$ ) and remanent magnetization ( $M_r$ ) increase with Ga content and the phase transformation from Para to ferromagnetic takes place with increase of Gallium.*

**Keywords:** *Coprecipitation method, Magnetic material, Nanoparticles, SEM, TEM analysis.*

## 1. INTRODUCTION

Ferrites general structure  $[\text{A}^{2+}]_{\text{tet}} [\text{B}^{3+}]_{\text{octa}} \text{O}_4$  are well known for their electrical, magnetic and catalytic properties [1,2]. In a spinel structured compound  $\text{AB}_2\text{O}_4$  (A site = divalent cations and B site = trivalent Fe ions) one unit cell contains 32 oxygen atoms that are in direct contact to one another forming a closed-pack face-centered cubic structure with 8 tetrahedral (A) and 16 octahedral (B) occupied sites [3,4].  $\text{CoFe}_2\text{O}_4$  has an inverse spinel structure with  $\text{Co}^{2+}$  ions in the (B) sites and  $\text{Fe}^{3+}$  ions equally distributed between tetrahedral (A) and octahedral (B) sites. Therefore, by substituting various metal cations change in properties can be observed in these nanoferrites [5, 6].

The literature survey reveals that bulk growth of  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$  has been carried out by ceramic method; Ranvah et al [7] studied the effect of Ga substitution on the temperature dependence of magnetization, magnetic anisotropy, and coercive field of gallium-substituted cobalt ferrite. S.H.Song et al [8] investigated the magnetic

and magnetoelastic properties of Ga substituted Cobalt ferrite found that the Curie temperature  $T_c$  and hysteresis properties vary with Ga content which indicates that exchange and anisotropy energy changed as a result of Ga substitution in Fe. S.J.Lee et al [9] observed the magneto – optic spectra particularly polar Kerr rotations in Ga substituted cobalt ferrite where the Kerr rotation can be controlled by adjusting the Ga content in cobalt ferrite. In the present study, Ga substituted Co ferrites nanoparticles have been investigated.  $Ga^{3+}$  is known to prefer the tetrahedral sites[10], therefore, the properties and the results are expected to be different from Al, Mn, Cr, Ni, Zn, Zr substituted cobalt ferrites.

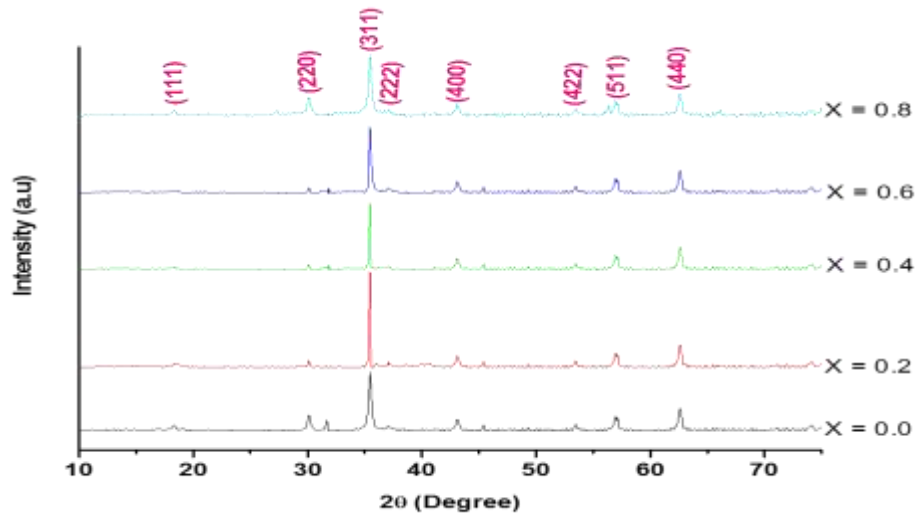
## II EXPERIMENTAL SYNTHESIS

Nanoparticles of Ga doped Cobalt ferrite with the stoichiometry ratio  $CoGa_xFe_{2-x}O_4$  ( $0.0 \leq x \leq 0.8$ ) samples were prepared by co-precipitation method. The starting materials used were Cobaltous chloride ( $CoCl_2 \cdot 6H_2O$ ), Ferric chloride anhydrous ( $FeCl_3$ ), Gallium (III) chloride ( $GaCl_3$ ) of 99.999% purity and Sodium hydroxide (NaOH), all from Alfa Aesar and Analytical Grade. Polyethylene glycol – 400(PEG -400) is used as a surfactant. The salts were dissolved in double distilled water separately according to their mole ratio. 0.1M of cobalt and 1.8M of iron was dissolved and mixed together. Then 0.2M of gallium was added to this mixture. All the processes were carried out with continuous stirring. Sodium hydroxide solution of 0.3M is added drop by drop to the above mixture till the pH of the solution reaches between 10 - 12. Finally, few drops of PEG -400 were added to the solution. The aqueous solution was heated at  $80^\circ C$  with continuous stirring for 1hr. The heated solution was brought to room temperature and washed thoroughly with 2D –water until the precipitate is free from sodium and chloride ions. The precipitate was dried in the oven at  $100^\circ C$  for overnight to remove water contents. The dried sample was fluffy mass in appearance and grinded for 1hr using a motor and pestle to get a homogeneous mixture and the resulting powder was sintered for 5 hrs at  $500^\circ C$ . The sintered samples were grinded using Ball milling for 2hrs and proceeded for further characterization.

## III RESULTS AND DISCUSSION

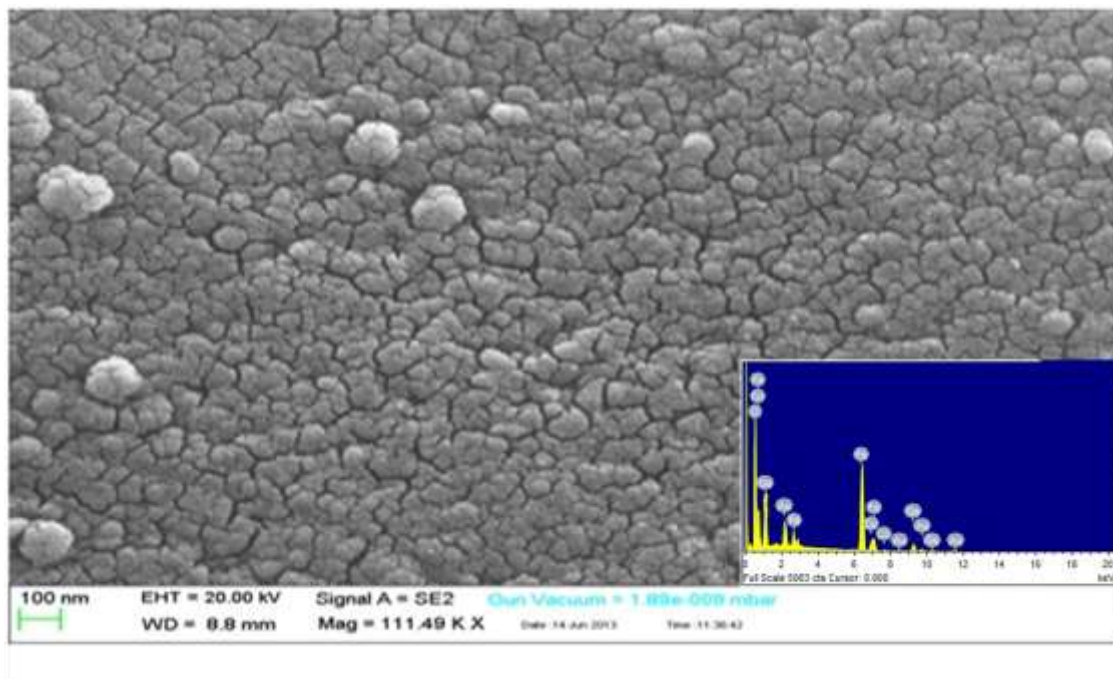
### 3.1. Structural

The XRD pattern for each sample was recorded (Fig: 1) and confirms the incorporation of  $Ga^{3+}$  ions into the cubic spinel structure. The phase analysis was done with JCPDS card number 22- 1086. According to the Debye – Scherrer formula, the crystalline size  $D_{hkl}$  [11] for the samples was calculated and the average crystalline size was found to be in the range of 16-24 nm.



**Fig: 1 XRD pattern of  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$  ( $x = 0.0, 0.2, 0.4, 0.6$  and  $0.8$ ) annealed at  $500^\circ\text{C}$**

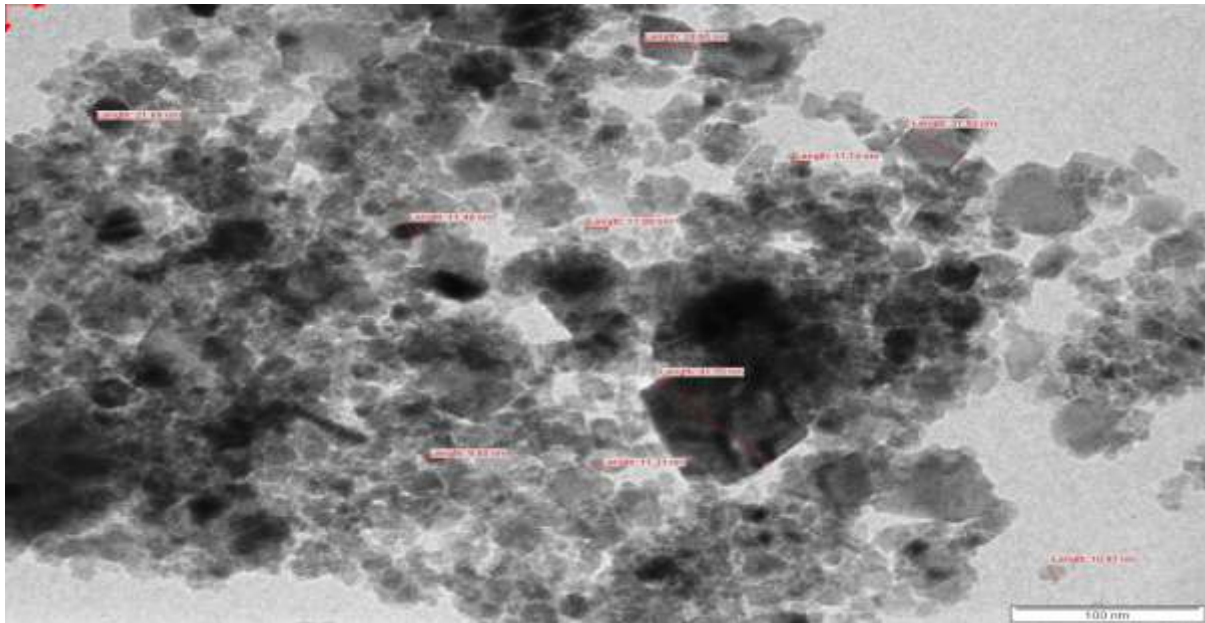
The SEM images and EDX spectra are shown in Fig.2 .SEM images indicate that the samples consist of spherical shaped nanoparticles which are dense, distributed regularly on the surface with the existence of soft agglomeration. The EDX spectrum confirms the presence of all elemental composition in the sample.



**Fig: 2 SEM with EDX Spectrum of  $\text{CoGa}_{0.6}\text{Fe}_{1.4}\text{O}_4$**

The morphology of the particle formed was examined using high- resolution transmission electron microscope for the collected samples. HR-TEM images of the  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$  ( $x = 0.6$ ) are shown in Fig 3. It can be seen that

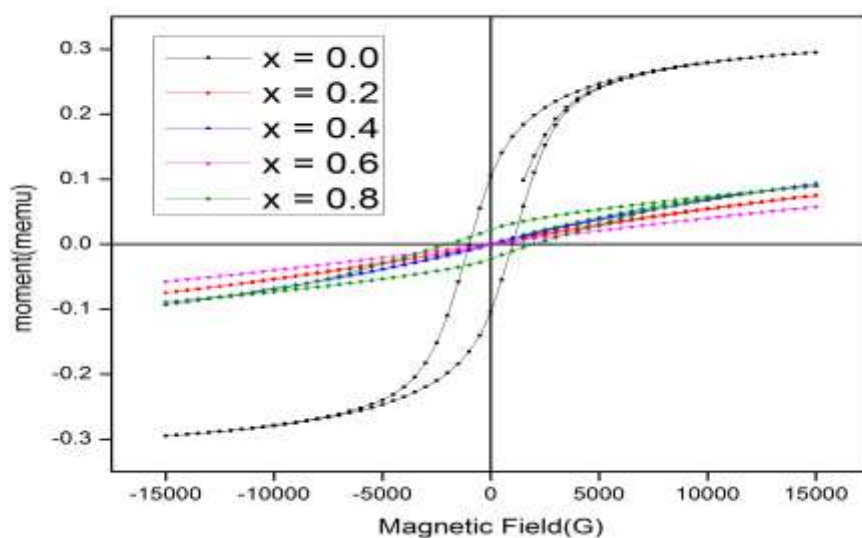
the entire powder sample is composed of small nanoparticles with a spherical shape. The average particle size is found to be 21 nm that is similar to that of the particle size obtained from the XRD data.



**Fig: 3 TEM image of  $\text{CoGa}_{0.6}\text{Fe}_{1.4}\text{O}_4$**

### 3.2 Magnetic studies

The room temperature hysteresis loops for  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$  samples ( $x = 0.2, 0.4, 0.6$  and  $0.8$ ) which were annealed at  $500^\circ\text{C}$  are shown in Fig: 4. In spinel ferrites, the magnetic order is due to a superexchange interaction between the metal ion in the A and B sublattices. The substitution of nonmagnetic ion Gallium, which has a preferentially A site occupancy results in the reduction of the exchange interaction between A and B sites. Hence, by varying the Ga content, it is possible to vary magnetic properties of the nanoparticles. The saturation magnetization ( $M_s$ ), remanent magnetization ( $M_r$ ) and coercivity ( $H_c$ ) values are listed in TABLE: 1 for the given samples. It can be seen that both saturation magnetization ( $M_s$ ) and remanent magnetization ( $M_r$ ) increase with an increase in Ga content. The saturation magnetization ( $M_s$ ) increases with increase of crystallite size. Alignment of number of atomic spins along with the applied magnetic field increases with the increase of magnetic domain, which leads to enhancement of the saturation magnetisation with the crystallite size [5]. The coercivity ( $H_c$ ) value, also increases with an increase in gallium content. Pure Cobalt ferrite is ferromagnetic which changes to paramagnetic with the addition of Gallium content at  $x = 0.0$ , and an increases in Ga content the material is changing back to ferromagnetic at  $x = 0.8$ . Phase transition takes place with the addition of Gallium to pure Cobalt ferrite. Hence, we observe that the  $M_s$ ,  $M_r$  and  $H_c$  values obtained for the  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$  nanoparticles are less than that of the values obtained by S.H.Song et al [8] in bulk growth.



**Fig: 4 Hysteresis loop of  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$  annealed at  $500^\circ\text{C}$**

Compound $\text{CoFe}_{2-x}\text{Ga}_x\text{O}_4$	Saturation Magnetization $M_s(\text{emu/g})$	Retentivity $M_r(\text{emu/g})$	Coercivity $H_c(\text{K Oe})$
X = 0.0	2.67	0.0116	131.09
X = 0.2	1.057	0.0208	219.76
X = 0.4	1.684	0.0216	511.03
X = 0.6	1.692	0.1992	1534.9
X = 0.8	1.988	0.5009	1986.9

**Table.1: The saturation magnetization ( $M_s$ ), remanent magnetization ( $M_r$ ) and coercivity ( $H_c$ ) values of  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$  annealed at  $500^\circ\text{C}$ .**

#### IV CONCLUSION

The nanoparticles of  $\text{CoGa}_x\text{Fe}_{2-x}\text{O}_4$  were synthesized by coprecipitation method. The size of the nanoparticles is in the range of 16-24 nm which are in good agreement with the values obtained by XRD, SEM and TEM indicating that there are no agglomerations. The EDX spectrum confirms the presence of all elemental composition in the sample. No impurity phase is found in the spectra. The saturation magnetization ( $M_s$ ),

remanent magnetization ( $M_r$ ) and coercivity ( $H_c$ ) increase with an increase in Ga content. The saturation magnetization ( $M_s$ ) increases due to increase in the crystallite size with the annealing temperature.

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