**Effect of isovalent ion (Co2+) substitution on Structural Properties of ZnFe2O4**

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**Abstract**

This work is summarizes the synthesis of cobalt doped zinc ferrite (Co-doped ZnFe2O4) nano-composite materials via solution-gelation method followed by auto combustion process using nitrate precursors. The prepared material samples were characterized by X-ray diffraction (XRD) for structural properties. Further Match3! and VESTA software were employed for the observations of structural properties of the synthesized nanomaterials Co-doped ZnFe2O4.

**Keywords:** Zinc ferrite, Nano-composites materials, X-ray diffraction.

1. **Introduction**

In general, ferrite is a ceramic class material that includes iron oxide as a core ingredient and metallic element such as Mn, Co, Ni, Mg, and Zn in small scale[[1-3](#_gjdgxs)]. It has been investigated that the properties of a bulk materials changes as its dimensions reduces. These significant changes are caused to an increase in surface area to volume ratio. The similar reports have been considered for the case of magnetic materials also. In recent years due to vital applications and utility of spinel ferrites like memory storage, high frequency power supply, biomedicines a number of ways have been found to synthesis and investigate for their functional applications in information storage systems, sensors, actuators, magnetic fluid, microwave absorbers and medical diagnostics. Therefore, much attention has been focused on the preparation and characterization of spinel ferrites [[4](#_30j0zll), [5](#_1fob9te)]. The spinel structure is abbreviated in form of AB2O4, where A and B are tetrahedral and octahedral interstitial sites respectively. Spinel structure possess a big unit cell which is made up of 8 small unit cells having face centered cubic structure with tetrahedral(A) site and octahedral(B) site in each. There are 64 A sites and 32 B sites in total and 32 oxygen atoms form a unit cell of closed packed structure [[6](#_3znysh7)]. In spinel ferrites A is represented by divalent metal ions like Mn2+,Co2+,Ni2+, Mg2+,Cd2+ etc. and that of B by Fe3+ ions. In Mn-Zn ferrites Zn2+ ions located on A sites while Mn2+ and Fe3+ ions could be positioned on B sites. Basically, zinc ferrite adopts the normal spinel group possessing no net magnetic moment by its unit cell due to d0[Zn2+] and d5,d5[Fe3+,Fe3+] while on the other hand manganese ferrite belongs to inverse spinel group in which two magnetic sub lattices are antiferromagnetically aligned[[7](#_2et92p0)].

1. **Experimental section**

**2.1. Material synthesis process**

A series of the system MnxZn(1–x)Fe2O4(for x=0.0, 0.1, 0.2, 0.3) was synthesized via solution-gelation method followed by auto combustion using nitrate precursors. Metal nitrates were utilized as starting chemical regents, Ferric nitrate Nona hydrate [FeN3O9.9H2O] 98+% (metals basis) crystalline from Alfa Aesar, Zinc nitrate hexahydrate [Zn(NO3)2.6H2O] 99% (metals basis) crystalline from Alfa Aesar, Manganese(II) nitrate tetra hydrate [Co(NO3)2.4H2O]98% (metals basis) crystalline from Alfa Aesar and citric acid Anhydrous[C6H8O7.H2O] 99.8% Fizmerk India, for the synthesis of Co-Zn ferrite nanomaterial. The Mn-Zn ferrites nano particles were synthesized by solution-gelation methods followed by auto combustion. In this process, a mixture of [Fe(NO3)3.9H2O], Mn(NO3)2.6H2O, Zn(NO3)2.6H2O salts were dissolved in 100 ml de-ionized water for distinct composition and 6.3042gm of citric acid was added as a fuel to manage the ratio of the fuel to the oxidizer *ϕ* = 1.35[[8](#_tyjcwt)]. The prepared mixture was stirred in beaker on hot plate for two hours at 80 0C to get a homogeneous solution. The pH was maintained up to 7 by adding drop wise the ammonia solution (NH4OH). Further the temperature of the hot plate was increased to 235-240 °C and prepared solution was gradually evaporated and transformed into gel form. Later this gel was auto ignited and converted into ash powder. After cooling at normal temperature, the ash formed was ground using agate mortar and pestle to obtain homogeneous mixing of powder sample. The powder was calcined in furnace at 600 °C for 4 hours.

**2.2 Characterizations**

The X-ray diffraction patterns of system MnxZn(1–x)Fe2O4 (for x=0.0, 0.1, 0.2, 0.3) were recorded at room temperature employing Miniflex II, Rigaku, Japan with Cu-Kα radiation (λ≈1.5406 Å , 20° ≤ 2θ ≤ 80° and step size of Δ2θ=0.02˚) and Ni filter at a scanning rate of 2°C/min. Further all these structures were optimized using crystallography open database and Material Project**.** VESTA software (OpenGL version: 3.3.0, Tsukuba, Japan) was utilized for simulation studies**.** Additionally, Match3! software was utilized for theoretical studies of the polycrystalline composite system**.**

**3. Results and Discussion**

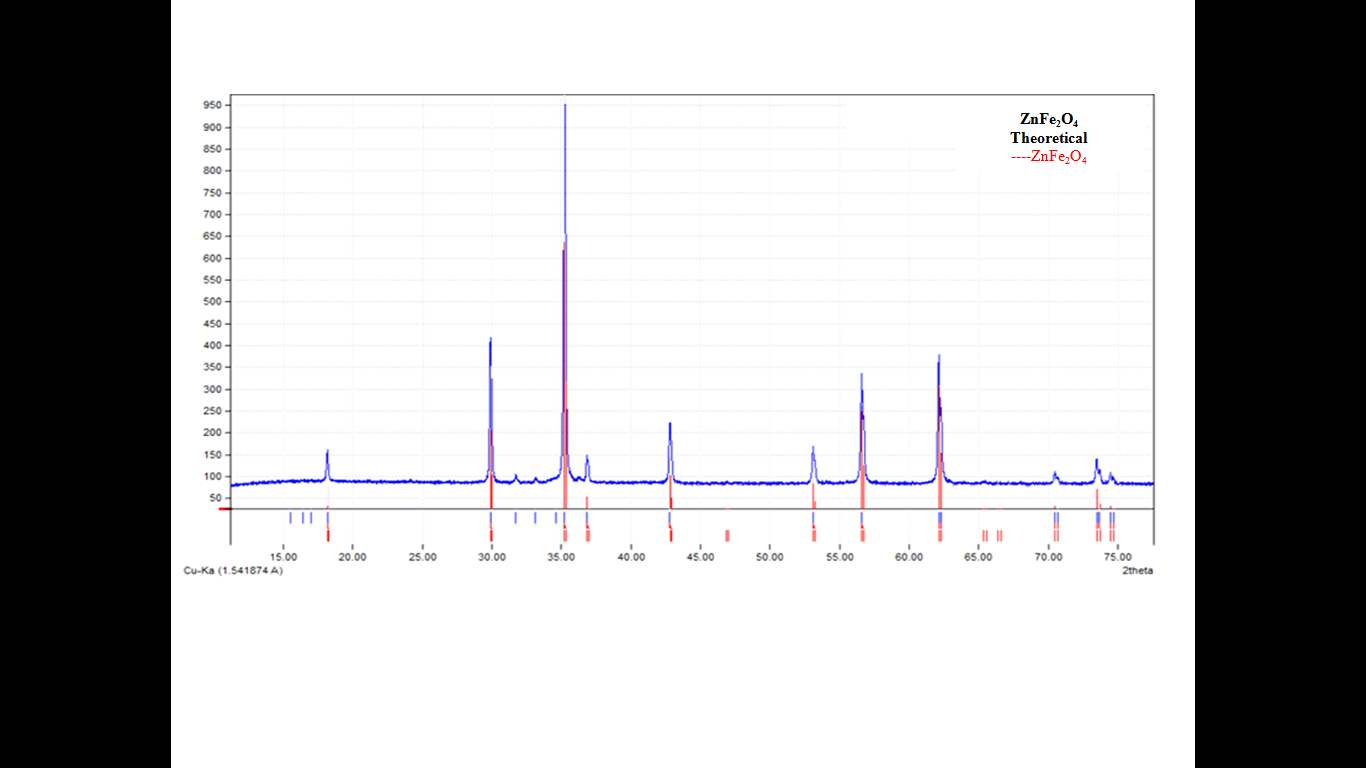
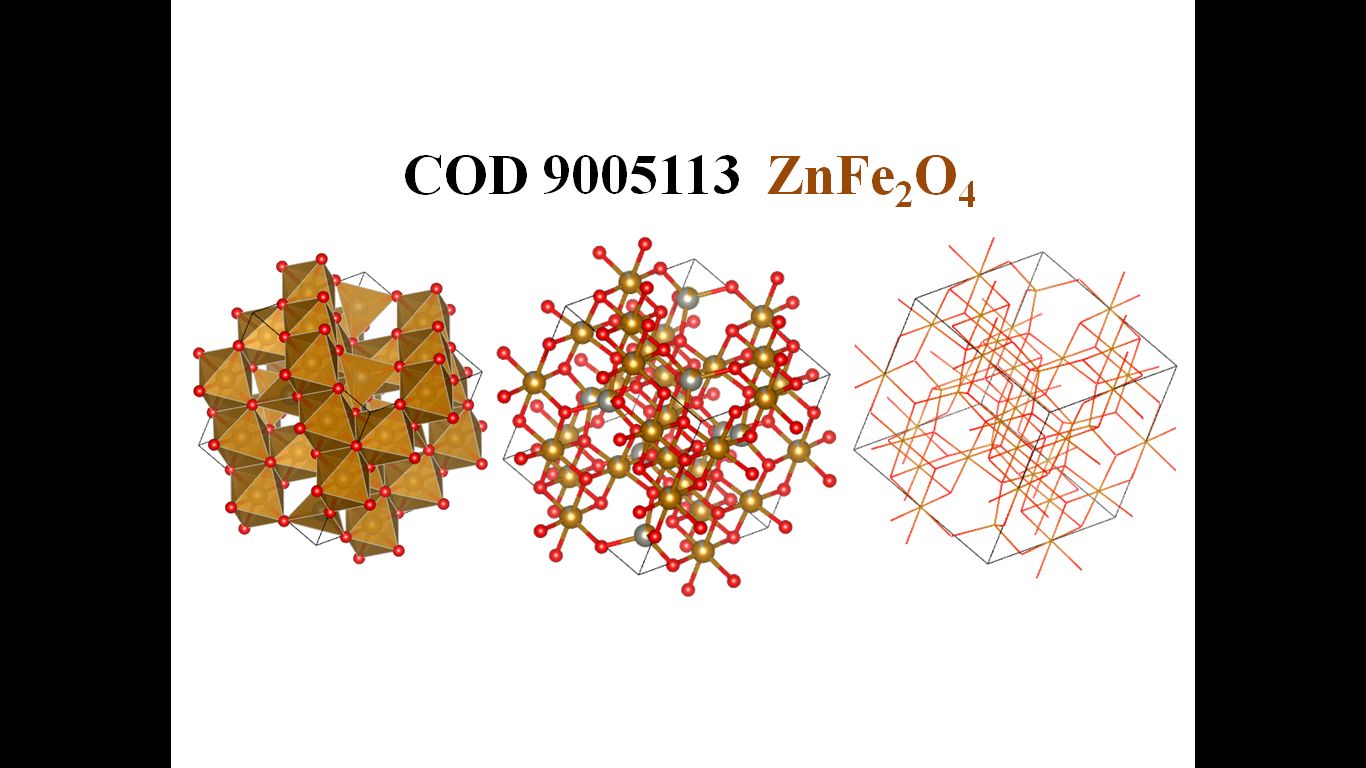


Figure 1. Theoretical XRD pattern of ZnFe2O4



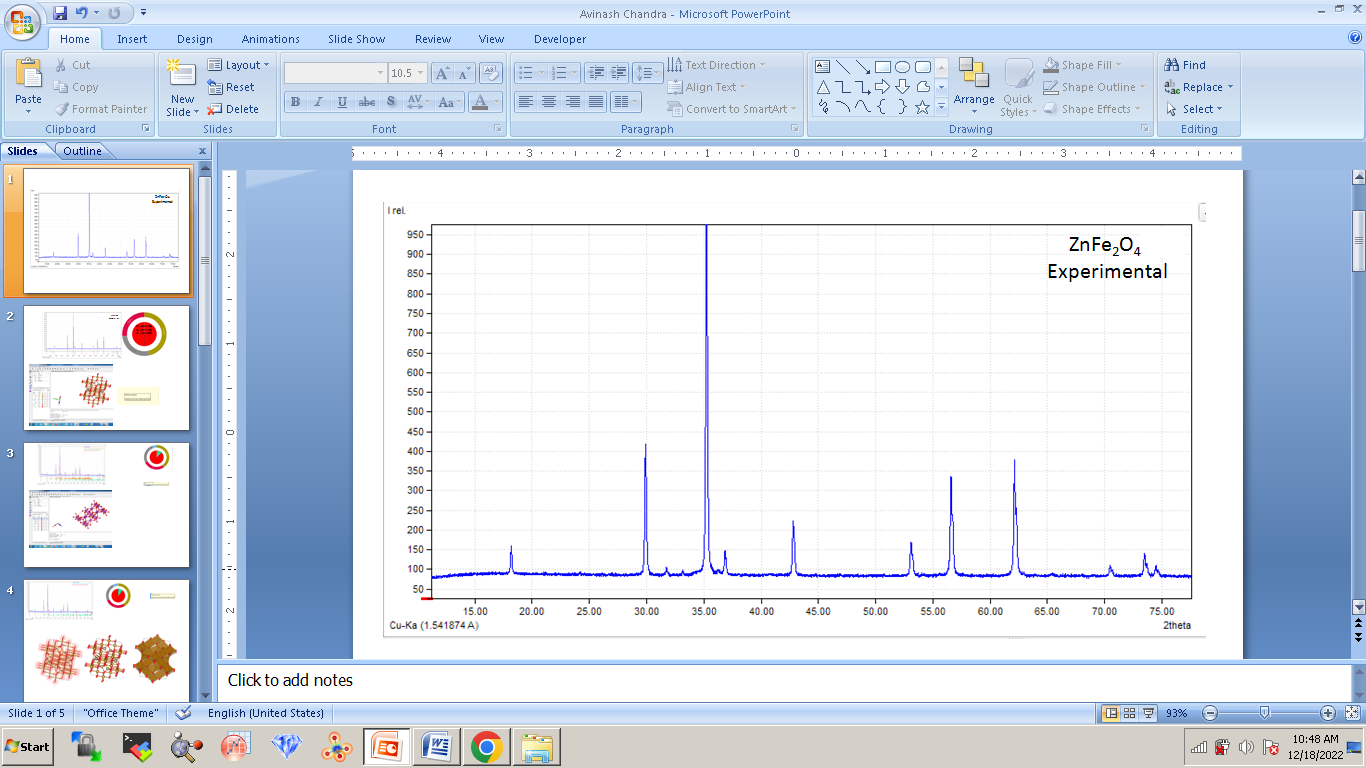
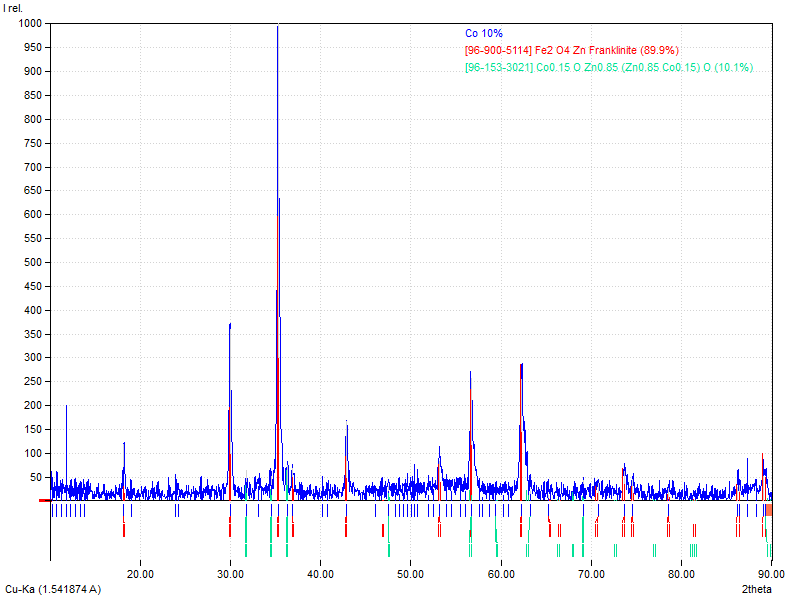


Figure 2. Experimental XRD pattern of ZnFe2O4



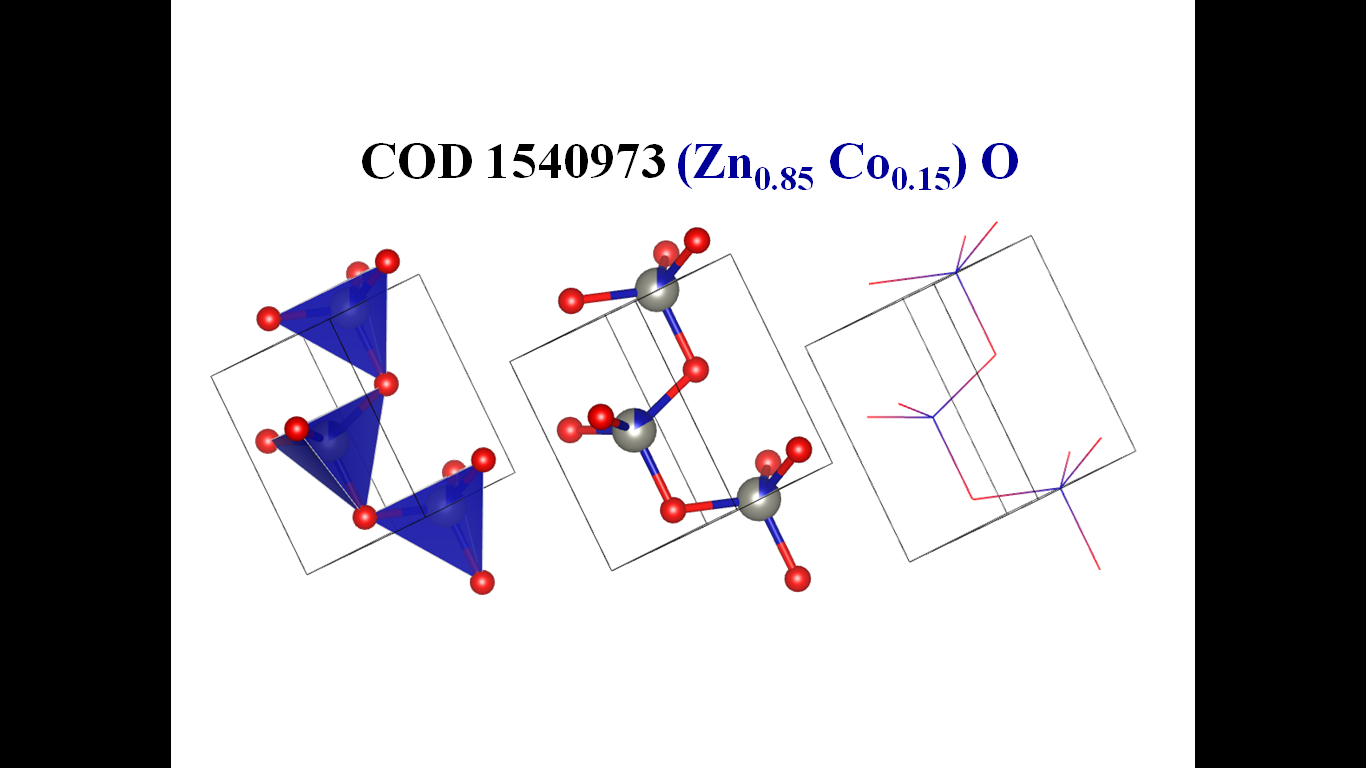
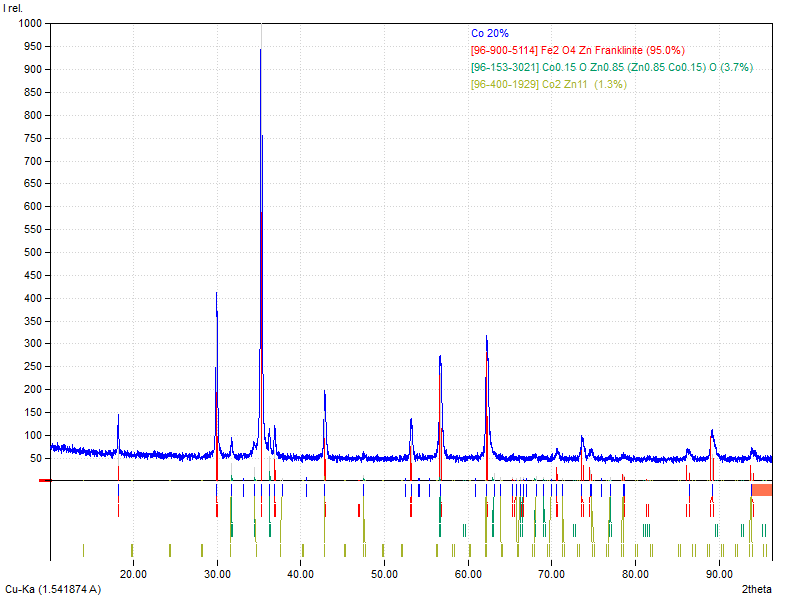


Figure3. Theoretical XRD pattern of 10% Cobalt in ZnFe2O4



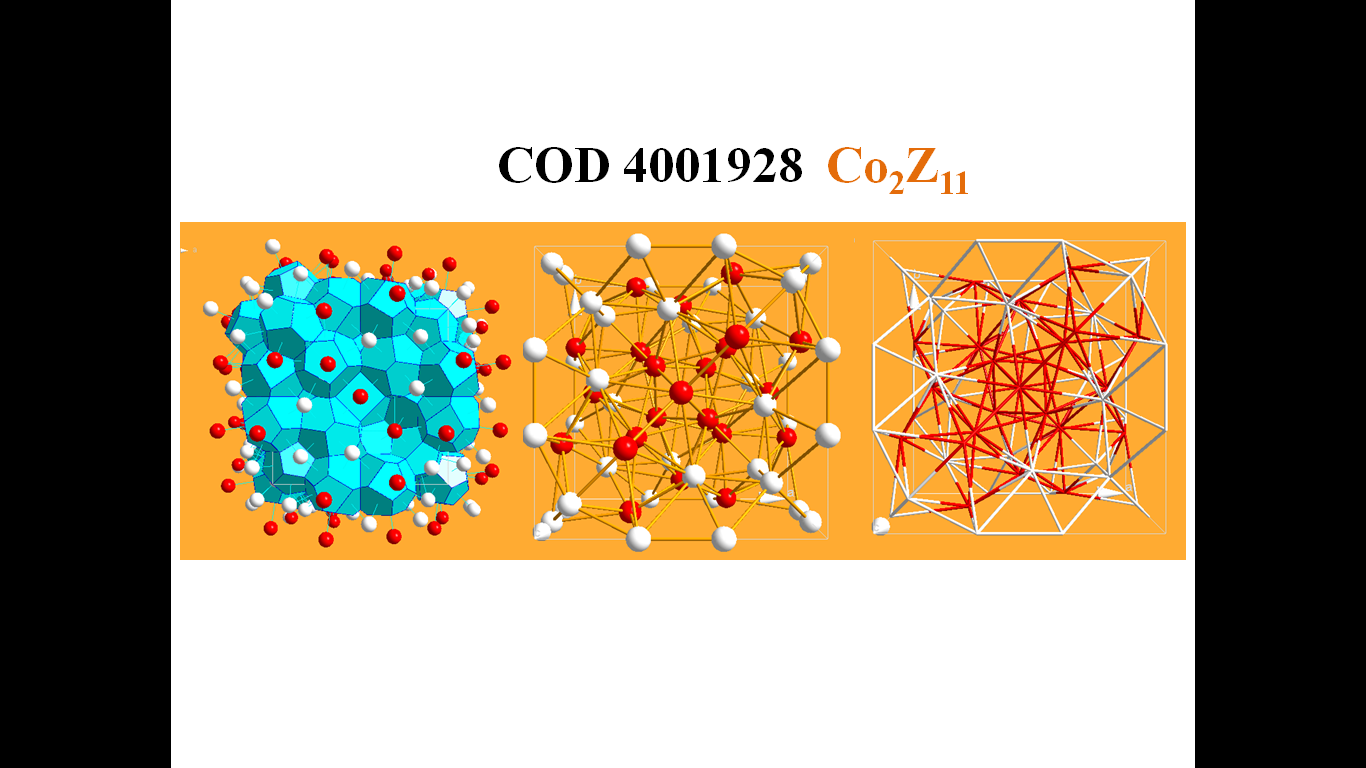
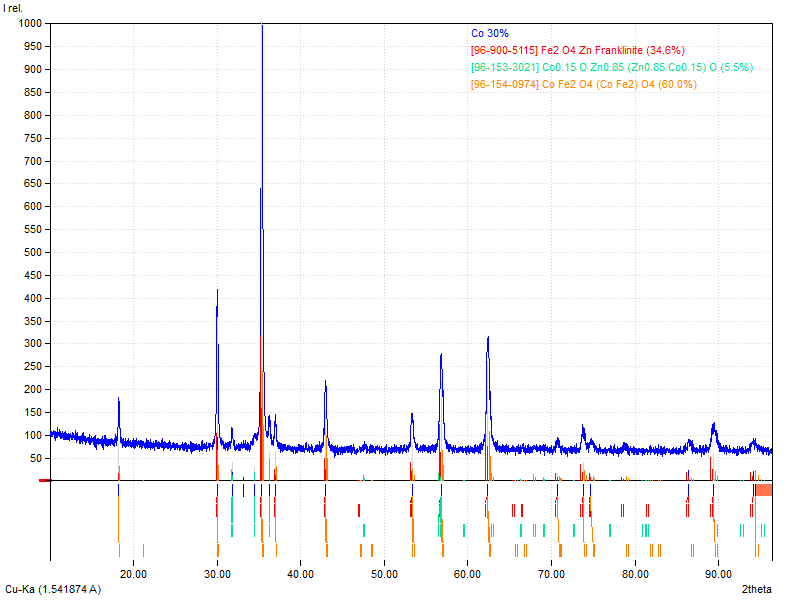


Figure4. Theoretical XRD pattern of 20% Cobalt in ZnFe2O4



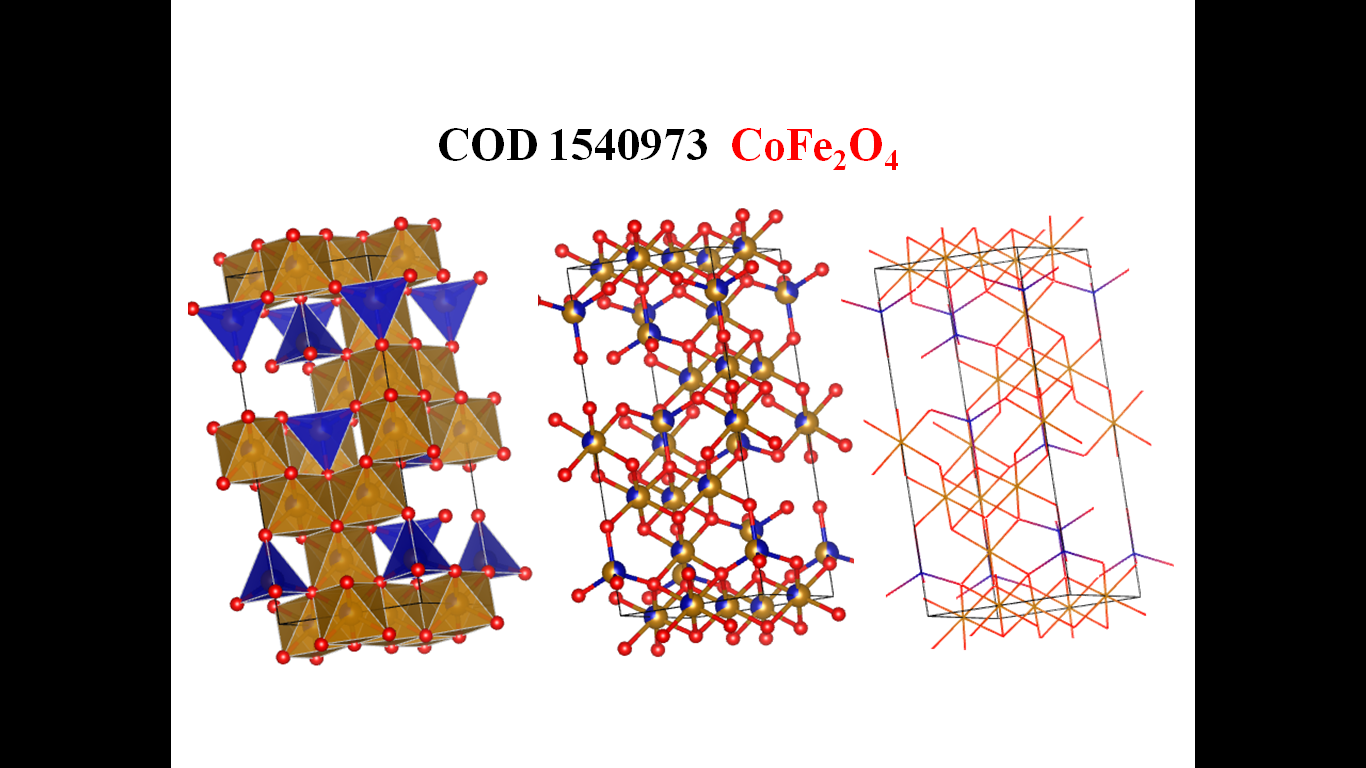


Figure5. Theoretical XRD pattern of 30% Cobalt in ZnFe2O4

Theoretical simulation of ZnFe2O4 exhibited cubic system zinc ferrite ZnFe2O4 (COD - 900511), with lattice type F, space groupFd-3m with space group number 227 and setting number two. Inside the unit cell of ZnFe2O4, a=b=c= 8.4420 Å, and α=β=γ= 90°. The unit cell volume of the system ZnFe2O4 was calculated ⁓601.660396. The experimental XRD pattern was perfectly in agreement with simulation pattern of the composite which further confirmed the single phase formation of base materials ZnFe2O4. VESTA (Open GL version: 3.3.0, Tsukuba, Japan), Material Project, and Endeavor software were utilized for polyhedral, ball-stick and wireframe representation of different phases obtained in simulation studies[[9](#_3dy6vkm)]. All theoretical structures were optimized using crystallography open database[[10](#_1t3h5sf)]. Furthermore, thorough investigations of the polycrystalline composite systems were performed by utilizing experimental XRD diffraction pattern and Match3! Software [[9-13](#_3dy6vkm)].

Theoretical simulation of base materials (ZnFe2O4) exhibited cubic system zinc ferrite ZnFe2O4 (COD - 900513), with lattice type F, space group *Fd-3m* with space group number 227 and setting number two. For the unit cell of ZnFe2O4, a = b = c = 8.44210 Å, and α = β = γ = 90°. The unit cell volume of the system ZnFe2O4 was determined to be 601.660376 Å^3. The experimental XRD diffraction pattern was perfectly in good agreement with simulation pattern of the composite which confirmed the single phase formation of base materials ZnFe2O4.

When 10 % of Co was added in pure base material ZnFe2O4 then one new phase was appeared to be hexagonal Zn0.85Co0.15 as a minor phase with lattice type P, space group *P 63 m c* with space group number 186 and setting number one. Inside the unit cell of Zn0.85Co0.15, a = b = 3.25380, while c = 5.20440 Å, and α = β = 90°, with γ = 120°. The unit cell volume of the system ZnFe2O4 was found to be 601.660376Å^3.

At rising proportion of Co to be 20 %, two minor phases appeared to be Zn0.85Co0.15 and Co2Zn11 respectively. The crystal Co2Zn11 emerged due to increasing percentage of Cobalt in base material ZnFe2O4. Theoretical simulation exhibited Co2Zn11, to be cubic system with lattice type I, space group *I-43 m* with space group number 217. Inside the unit cell of ZnFe2O4, a = b = c = 8.96540 Å, and α = β = γ = 90°. The unit cell volume of the system ZnFe2O4 was found to be 720.624420 Å^3.

When the entitlement of Co is further increased to be 30%, the major phase ZnFe2O4 was replaced by CoFe2O4, which indicate that Zn was probably replaced by Co for the crystal system ZnFe2O4 while other minor phase was appeared to be Zn0.85Co0.15. Additionally, theoretical simulation exhibited CoFe2O4 to be trigonal system with lattice type R, space group *R-3m*, space group number 166 with setting number one (with hexagonal axes). Inside the unit cell of CoFe2O4, a = b = 5.93660, c = 14.54300 Å, and α = β = 90°, while γ = 120°. The unit cell volume of the system ZnFe2O4 was found to be 443.874553Å^3.

Bulk ZnFe2O4 possesses a typical cubic spinel X-Y2-O4 atomic arrangement, in which oxygen anions occupy 32e Wyckoff sites and form a distorted face-centered cubic (FCC) lattice as well as large interstices between O2− are partially occupied by iron and zinc cations. One eighth of the tetrahedral positions are occupied by divalent Zn2+ cations, whereas half of the octahedral positions are engaged by trivalent Fe3+ cations, leading to the formula [Zn2+]A[Fe3+2]BO2−4[[11](#_2s8eyo1)]. Moreover, the spinel structure is relatively “open”, and various vacant crystallographic sites can ease the intercalation of dopant, which in turn can enlarge the number of applications of such material [[11](#_2s8eyo1), [14](#_17dp8vu), [15](#_3rdcrjn)]. In the crystal system ZnFe2O4 depicts Zn and Fe is surrounded by Oxygens with potential bonding between Zn-O, Fe-O, Zn-O-Zn or Fe-O-Fe.

1. **Conclusion**

Cobalt-doped nano zinc ferrites were synthesized by the sol-gel method followed by auto-combustion. XRD, Match3! And VESTAwasusedas the characterization techniques for the structural properties of the synthesized nanoparticles. The XRD pattern reveals that the synthesized nanoparticles have a cubic spinel ferrite phase with space group *Fd3m*. The experimental XRD diffraction pattern was perfectly in agreement with simulation pattern of the composite which further confirmed the single phase formation of base materials ZnFe2O4. It was seen that some minor phases Zn0.85Co0.15 for 10 % Co, Zn0.85Co0.15 and Co2Zn11 for 20% Co were found along with major phase of Zinc Ferrites. When Co is further increased to be 30%, the major phase ZnFe2O4 was replaced by CoFe2O4. These minor phases definitely will affect the Vibrational and Magnetic properties of the synthesized nanomaterials.

**Acknowledgement**

Although we have used freely available Match3! And VESTA software but authors are sincerely thankful to the developer of Match3! And VESTA software and to make it freely available for worldwide researchers.

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