Structural and Magnetic Studies of Zinc Substituted Cobalt Ferrite Nanoparticles prepared by Sol–Gel Technique

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Abstract. All Magnetic nanoparticles are newly explored materials due to its large surface to volume ratio, smaller grain size, quantum confinement effect, large uni-axial anisotropy and superparamagnetism. In the present study, Zinc substituted cobalt ferrite nanoparticles are prepared by sol-gel auto-combustion method with copper concentration varies from 0.0 to 0.0. Structural studies are taken by XRD, it was confirmed that the sample has pure cubic spinel phase structure and the crystallite size decreases from 25nm to 15nm as the Zn content increases. Raman spectroscopy confirming the spinel structure and in the case of Co1-xZnxFe2O4, the Raman bands show a shoulder-like feature at the lower wavenumber which are Raman active bands in Fe3O4 all the tetrahedral and octahedral sites are occupied by Fe ions. From FTIR Analysis, the peak observed at 433 cm−1 and around 580 cm−1 it confirms the metal oxygen vibration at octahedral and tetrahedral site. Morphological analysis shows that the spherical sized particles with pores due to the evolution of gases during the annealing process at higher temperature. The magnetic studies reveals that as the ratio of metal nitrates increases, the coercivity and remanence decreases following a hysteresis path. By the above characterization technique we were successfully able to confirm the substitution of Zinc in the octahedral sites of cobalt ferrite.

1. Introduction
Nanomaterial-based on ferrites have shown superparamagnetism, enhanced anisotropy and spin canting which leads to the applications such as photocatalysis, adsorption technologies, gas sensor, microwave devices, biomedical application and others [1]. Ferrites are ferrimagnetic materials, having magnetic and electrical properties [2]. Cobalt ferrite, an inverse spinel ferrite has remarkable mechanical hardness, moderate saturation magnetization, large magnetic anisotropy and high coercivity [3]. The magnetic property of ferrites can be altered by changing its compositions and by doping. The saturation magnetization and coercivity of these materials can be altered by the cation redistribution among the tetrahedral and octahedral sites during doping. The substituted cobalt ferrite is studied in order to find the applications in high-density storage, sensors, and high-frequency applications. [4-7]. Zinc ferrite has got normal spinel structure; also it is a soft ferrite. Therefore, when doped with ZnFe2O4, CoFe2O4 transforms to a distorted spinel structure. The degree of distortion depends on the concentration of precursor solutions. The Zn2+ ions have a preference for tetrahedral site whereas Co3+ for the octahedral site [8, 9]. The properties of ferrites highly depend on the synthesis methods, synthesis parameters, nature of substitutions and their Compositions. The Zn doped Cobalt ferrite can be prepared by standard ceramic method [10] sol-gel [11] co-precipitation [12] Metallo-organic decomposition technique[13] solid-state reaction , combustion synthesis [15], the
electrochemical method [16], micro-emulsions [17], the sol-gel process [18], ball milling [19], microwave processing [20]. For developing technologically important material, the control over the magnetic parameters is necessary. Substitution of nonmagnetic material (Zn\(^{2+}\)) with the magnetic material (Co\(^{2+}\)) induce changes in the structural, elastic, optical, and magnetic properties of the material which are attributed to the cations redistribution between the available A (tetrahedral) and B (octahedral) sites.

2. Experimental

2.1. Nanoparticle Synthesis

Co\((\text{NO}_3)_2\cdot 6\text{H}_2\text{O}\) (Cobalt (II) Nitrate hexahydrate), Fe\((\text{NO}_3)_3\cdot 9\text{H}_2\text{O}\) (Iron (III) nitrate), Zn\((\text{NO}_3)_2\cdot 6\text{H}_2\text{O}\) (Zinc (II) nitrate hexahydrate), C\(_6\)H\(_8\)O\(_7\). H\(_2\)O (Citric Acid), purchased from NICE chemicals, are used without further purification. In the present work, Zinc substituted Cobalt Ferrite nanoparticles are synthesized by auto-combustion sol-gel route. In the present work Co\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\) (x=0.03, 0.04 and 0.05) are prepared by auto combustion sol-gel method. The pH of the solution is kept at 7 by adding liquid ammonia. The solution is stirred for 3 hours and the final puffy brown gel is heated to 800°C for three hours and crushed to get the Zinc substituted cobalt ferrite nanopowder.

2.2. Characterization Techniques

The samples were subjected to Powder X-ray diffraction analysis using Shimadzu XRD 6000 diffractometer with CuK\(_\alpha\) radiation of wavelength 1.541 Å. The functional group was analyzed by FTIR using Perkin-Elmer spectrometer by KBr pellet technique in the range of 4000-400 cm\(^{-1}\). The structure and its corresponding vibrational modes were confirmed using Micro-Raman Spectroscopy (Renishaw Raman Microscope (RE04)). The morphology analysis of the prepared samples was assessed by Scanning Electron microscopy using JEOL (JSM 6390). Magnetic properties of the samples were analyzed by VSM (Lakeshore VSM 7410) equipped with electromagnet at room temperature with the maximum applied field of 15kOe

3. Results and Discussion

3.1. Structural Analysis

The observed diffraction planes (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 3 3) confirms the pure cubic mixed spinel structure with Fd3m space group, matches with JCPDS data (82 - 1049 - ZnFe\(_2\)O\(_4\) and 22 -1086 - CoFe\(_2\)O\(_4\)) no secondary phases were observed. The substitution of Zn leads to the migration of Fe\(^{3+}\) ion from A site to the B site causing the change in the lattice structure. The shift in the peaks positions is due to the substitution of Zn in the cobalt ferrite lattice and the formation of Zn-Co ferrite nanoparticle as shown in the figure 1.

The average crystallite size (D) is calculated for the prominent peak (311) by the Scherrer formula [21]

\[
D = \frac{0.89 \lambda}{\beta \cos\theta}
\]

\(\lambda\), the wavelength of the Cu K\(_\alpha\) radiation( 1.514Å) and \(\beta\), full width at half maximum value, \(\theta\) is the angle of diffraction.

The average crystallite size decreases with the Zn concentration is attributed to the lower bond energy of Zn\(^{2+}\) - O\(^{2-}\) as compared to Co\(^{2+}\) - O\(^{2-}\).

The lattice constant is calculated by the equation [22]

\[
a = \frac{d_{hkl}}{(h^2 + k^2 + l^2)^{\frac{1}{2}}}
\]

h, k, and l are Miller indices of the crystal planes. The lattice constant increases from 8.139 to 8.271Å. The observed lattice expansion in Co\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\) with x=0.03, 0.04 and 0.05 without affecting the lattice symmetry is due to the size of Zn\(^{2+}\) ion radius (0.74Å) is larger than Co\(^{2+}\) ion radius(0.70 Å). A
similar type of observations was noted for Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles synthesized by the co-
precipitation method [23]

The X-ray density ($\rho_x$) is calculated by (table 1)

$$\rho_x = \frac{6M}{N_\text{A}a^3}$$  \hspace{1cm} (3)

Where $M$ the molecular mass of the compound, $N$ the Avogadro number ($6.0225 \times 10^{23}$ particles/mole) and $a^3$ volume of the cell. The observed decrease in the X-ray density with increase in the Zn concentration is due to the atomic weight of Co which is lower than Fe. Similar type of observations is noted by Pandit et. Al. for Mg-Zn ferrite system prepared at different molar concentrations. Also, X-ray density is found to be higher than their bulk counterpart is due to the formation of pores during the synthesis process and also due to the ionic radii [24].

The ionic radii ($r_A$, $r_B$) bond length (A-O, B-O) and hopping length ($L_A, L_B$) at tetrahedral (A) and octahedral (B) sites are calculated by [25] (table 2)

$$r_B = \left(\frac{5}{8} - u\right)a - r(O^{-2}) \quad \text{Å}$$  \hspace{1cm} (5)

$$A-O = (u-\frac{1}{4})a\sqrt{3} \quad \text{Å}$$  \hspace{1cm} (6)

$$B-O = (\frac{5}{8} - u) a \quad \text{Å}$$  \hspace{1cm} (7)

$$L_A = a(\sqrt{\frac{3}{4}}) \quad \text{Å}$$  \hspace{1cm} (8)

$$L_B = a(\sqrt{\frac{2}{4}}) \quad \text{Å}$$  \hspace{1cm} (9)

$r(O^{-2})$ is the radius of oxygen ion (1.35 Å), $u$ is the oxygen ion parameter ($u=3/8$). It is noted that the value of $r_A$ increases gradually compare to $r_B$. The increase in A-O and B-O is due to the increase in the lattice constant. The value of $L_A$ and $L_B$ increases with the increase in the lattice constant shows the electron hopping between A and B sites are less than between B-B sites. It may be also due to the cation redistribution when the zinc content is increased.

Table 1. Microstructural Parameters of Zinc Substituted Cobalt ferrite nanoparticles

| Zn Conc. | Lattice Constant (Å) | Crystallite Size (nm) | Microstrain | X-Ray Density (g cm$^{-3}$) | $r_A$ (Å) | $r_B$ (Å) |
|----------|----------------------|-----------------------|-------------|-----------------------------|-----------|-----------|
| 0.03     | 8.1386               | 25                    | 0.00143     | 5.78                        | 0.4466    | 0.5858    |
| 0.04     | 8.1508               | 21                    | 0.00165     | 5.75                        | 0.4494    | 0.5888    |

Figure 1. PXRD Pattern of Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x=0.0 to 0.3) samples.
### Table 2. Hopping length (dA) and (dB), tetrahedral bond length (dA×), octahedral bond length (dB×), tetrahedral edge (dA×E), shared (dB×E) and unshared octahedral edge (dB×EU) for zinc substituted cobalt ferrite nanoparticles.

| Zn Conc. | L_A (Å) | L_B (Å) | dA× (Å) | dB× (Å) | dA×E (Å) | dB×E (Å) | dB×EU (Å) |
|----------|---------|---------|---------|---------|----------|----------|-----------|
| 0.03     | 3.5241  | 2.8774  | 1.8466  | 1.9870  | 3.6932   | 2.7393   | 2.8790    |
| 0.04     | 3.5294  | 2.8817  | 1.8499  | 1.9800  | 3.6988   | 2.7434   | 2.8834    |
| 0.05     | 3.5815  | 2.9243  | 1.8768  | 2.0194  | 3.7534   | 2.7839   | 2.9260    |

3.2. Micro-Raman Analysis
The atomic structure of Co_{1-x}Zn_xFe_2O_4 nanoparticles is analyzed by Raman spectroscopy [26] (figure 2). The observed Raman bands match with the cubic spinel ferrite structure with Oh7 (Fd-3m) space group [27]. The characteristic bands are spinel ferrites observed at 480.14 cm^{-1} (E2g) and 686.45 cm^{-1} (A1g) which are assigned to octahedral and tetrahedral sites [28]. A1g and Eg mode corresponds to the symmetric stretching and bending of oxygen.

![Raman Spectra of Zinc Substituted Cobalt Ferrite Nanoparticles.](image)

3.3. Functional Group Analysis
FT-IR spectra of the prepared samples are shown in the Figure 3. The intrinsic stretching vibrations of metal oxygen bond occur in the range of 600 – 550 cm^{-1} for the tetrahedral site and 450 – 350 cm^{-1} octahedral site [29]. The prominent band around 3440 cm^{-1} and 1630 cm^{-1} corresponds to stretching and H-O-H bending vibrations of absorbed water which confirms the presence of water compound of zinc, cobalt and iron nitrate and hexahydrate in the system. The peaks observed at 2923 cm^{-1} corresponds to C-H stretching vibrations [30]. The axial deformation of the C-H bond is observed at 2851 cm^{-1} and the significant change in the CH bending is observed at 1392 cm^{-1} [30, 31].
present work, the M-O stretching band is observed at 433 cm⁻¹ is due to the vibrations at octahedral sites.

3.4. Morphological Analysis
The surface morphology of Co₁₋ₓZnₓFe₂O₄ is shown in the figure 4. The grain size was found to be 25 to 15nm. The observation shows agglomerated particles with dense structure.

3.5. Magnetic Analysis
The magnetic properties were analyzed by Vibration sample magnetometer (VSM) at room temperature with the magnetic field of 19Oke (figure 10). The substitution of nonmagnetic ion, Zinc, prefer to occupy the tetrahedral site, results in the reduced exchange interaction between the sites and by varying the amount of Zn concentration, alter the interaction between the sites and hence the magnetic properties changed. Due to this interaction, this spin of the neighbouring A and B sites antiferromagnetically coupled which increases the net magnetic moment of the crystal [32]. The observed coercivity table 3 decreases with increase in the Zn concentration. In the case of
superparamagnetic material, the magnetization will pass through the origin and the hysteresis curve shows the superparamagnetism behavior of the Zn doped cobalt ferrite nanoparticle [33]. In general, coercivity decreases with a decrease in grain size. The two possible factors identified for the increase in the coercivity are the decrease of the stress anisotropy (due to the microstructural strain); and the decrease of the density of structural defects that causes the decrease of the centres of domains wall pinning [34]. From the table 3, it is noted that the when the concentration of Zn dopant increases, the coercivity decreasing [34]. The saturation magnetization initially decreases and then increases when the concentration of Zn dopant increases is due to the non-magnetic nature of the Zn$^{2+}$ ion. The increase in the saturation magnetization is due to the migration of Fe$^{3+}$ ions from tetrahedral A site to octahedral B sites and decreases in the saturation magnetization due to the decreases of grain size with the grain size decreases the field required for the alignment of the domain is less and hence decrease the pinning sites for the spins. According to Stoner-Wohlfarth theory, the magnetic anisotropy for a single domain particle is given by [35]

$$H_c = \frac{2K}{M_s}$$  (10)

Where Ms is the saturation magnetization. The Decrease in the value of the anisotropy constant with the increase in the Zn content results in the complete crystallization and the saturation magnetization increases.

| Zn Conc. (M) | Coercivity (Oe) | Mr (emu/g) | Ms (emu/g) | Anisotropy Constant | Mr / Ms |
|--------------|----------------|-----------|------------|---------------------|---------|
| 0.03         | 71.03          | 7.572     | 3.745      | 277                 | 2.02    |
| 0.04         | 70.00          | 11.26     | 1.72       | 125.4               | 6.54    |
| 0.05         | 20.64          | 3.252     | 2.001      | 43                  | 1.62    |

4. Conclusion
Zinc Substituted Cobalt ferrite nanoparticles are prepared by sol-gel auto combustion method by increasing the zinc concentration from 0.03 to 0.05M and the characteristics of the synthesized nanoparticles is analysed. The structural analysis shows the pure phase of the prepared sample and the planes matches with the JCPDS data. The peak shift reveals that the incorporation of zinc in the cobalt ferrite lattice. Increase in the lattice constant is due to the substitution of larger zinc cation for smaller cobalt cation. From the microstructural analysis, the average crystallite size was found to decreases from 25 to 15nm when the increasing the zinc concentration. The other structural parameters such as ionic radii, bond length, hopping length at the tetrahedral and octahedral site increases which is attributed to the substitution of zinc in the place of cobalt. Raman Spectroscopy revealed that deconvolution of spectrum demonstrates that each peak can be presented like a doublet, which is a characteristic of the inverse spinel structure. The two most intense Raman bands were observed at 480.14 cm\(^{-1}\) (E\(_{g}\)) and 686.45 cm\(^{-1}\) (A\(_{1g}\)) are the characteristic modes of spinel ferrite. The low-frequency mode at 480.14 cm\(^{-1}\) is assigned to the vibrations of octahedral sublattice, and the high energy phonon mode at 686.45 cm\(^{-2}\) originates from vibrations of the tetrahedral sublattice. The observed peak at 433 cm\(^{-1}\) and around 580 cm\(^{-1}\) from FTIR confirms the metal oxygen vibration at octahedral and tetrahedral site. The morphological analysis shows the agglomerated particles and the compositional analysis shows the increase in the atomic weight (%) of zinc with increase in the zinc concentration. From VSM analysis, it is noted that the Zn substituted cobalt ferrite nanoparticle showing superparamagnetism. Coercivity decreases with increases in the zinc concentration. The saturation magnetization increases with the decrease in the crystallite size and in the present work it reflects the same.

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