

EFFECT OF Zn^{2+} SUBSTITUTION IN TAILORING THE STRUCTURAL, ELECTRONIC AND MAGNETIC PROPERTIES OF $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$

 D.P.T. Tien^{1*},  N.T. Nguyen^{1,2},  N. Truong-Tho²,  T.T. Thanh-Thao²,
 T.P. Hoang^{3,4},  L.V. Truong-Son⁵,  T.N. Dat⁵,  D.T. Khan⁵,
 Lien Phan⁵,  N.N. Hashimova⁶,  M.E. Aliyev⁷,  T.A. Tran⁸

¹Institute of Oceanography, Vietnam Academy of Science and Technology, Nha Trang, Vietnam

²Faculty of Electronics, Electrical Engineering and Material Technology, University of Sciences, Hue University, Hue, Vietnam

³Institute of Research and Development, Duy Tan University, Danang, Vietnam

⁴Faculty of Environmental and Natural Sciences, Duy Tan University, Danang, Vietnam

⁵The University of Danang - University of Science and Education, Danang, Vietnam

⁶Azerbaijan State Oil and Industry University, Baku, Azerbaijan

⁷Nakhchivan State University, Nakhchivan, Azerbaijan

⁸Ho Chi Minh City University of Technology and Engineering (HCM-UTE), Ho Chi Minh City, Vietnam

Abstract. This study systematically investigates the structural, vibrational, and magnetic properties of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0 - 0.5$) spinel ferrites synthesized by a conventional solid-state reaction method. The properties were investigated using a combination of X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman scattering spectroscopy, X-ray photoelectron spectroscopy (XPS), and magnetic measurements. Rietveld refinement of the XRD data confirmed that all samples were single-phase and crystallized in the cubic spinel structure with the $Fd\bar{3}m$ space group. Raman spectroscopy and XPS analyses further revealed the redistribution of cations between the tetrahedral (A) and octahedral (B) sites, with Zn^{2+} preferentially occupying the A sites and promoting the redistribution of Fe^{3+} ions to the B sites. Magnetic measurements revealed ferrimagnetic behavior for all compositions. The saturation magnetization increased with increasing Zn content up to $x = 0.3$; this increase can be attributed to the enhanced net magnetic moment of the B sublattice. At higher Zn concentrations, the saturation magnetization then decreased slightly due to the weakening of the A-B superexchange interaction. Overall, the results show that Zn-induced cation redistribution between the A and B sites governs the ferrimagnetic response of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, with the competition between the enhanced B-sublattice moment and the weakened A-B superexchange interaction setting the composition dependence of the saturation magnetization.

Keywords: Cation distribution, Ferrite spinel, Magnetic properties, Crystal structure.

Corresponding author: D.P.T. Tien, Institute of Oceanography, Vietnam Academy of Science and Technology, 650000 Nha Trang, Vietnam, e-mail: doantien@io.vast.vn

Received: 21 May 2026; Revised: 30 July 2026; Accepted: 10 September 2026; Published: 12 October 2026.

1 Introduction

Spinel ferrites with the general formula AFe_2O_4 ($A = \text{Co}, \text{Zn}, \text{Mn}$, etc.) have attracted considerable attention because of their rich physical properties and wide range of technological applications, including magnetic storage, sensing, catalysis, and spintronic devices (Aslam et

al., 2014; Bashir et al., 2017; Chen & Zhang, 1998; Kefeni et al., 2017; Materón et al., 2021). Among them, cobalt ferrite (CoFe_2O_4) is of particular interest owing to its high magnetocrystalline anisotropy, moderate saturation magnetization, excellent chemical stability, and mechanical hardness (Cernea et al., 2016; Kotnala, & Shah, 2015). Bulk CoFe_2O_4 generally exhibits an inverse spinel structure, in which Co^{2+} ions preferentially occupy the octahedral (B) sites, while Fe^{3+} ions are distributed between the tetrahedral (A) and octahedral (B) sites (Jauhar et al., 2016; Narayanaswamy et al., 2021). In spinel ferrites, the distribution of M^{2+} and Fe^{3+} ions between the A and B sublattices can vary depending on the synthesis conditions, particle size, composition, and thermal history. Therefore, the cation distribution of a spinel ferrite can be expressed as $(\text{M}_{1-\delta}\text{Fe}_\delta)[\text{M}_\delta\text{Fe}_{2-\delta}]\text{O}_4$, where the parentheses and square brackets denote the tetrahedral (A) and octahedral (B) sites, respectively, and δ represents the degree of inversion (Thi Ngoc et al., 2024). Cation redistribution is one of the most effective approaches for tailoring the physical properties of spinel ferrites (Kmječ et al., 2025). Changes in cation distribution can significantly modify the magnetic exchange interactions within the A and B sublattices, namely the A–A (J_{AA}) and B–B (J_{BB}) interactions, as well as the A–B (J_{AB}) interaction between the two sublattices (Sanchez-Marcos et al., 2018). The A–A and B–B interactions are generally weaker than the A–B superexchange interaction. Consequently, the stronger antiferromagnetic A–B interaction between the A and B sublattices results in a ferrimagnetic spin arrangement, with the magnetic moments of the two sublattices oriented antiparallel to each other (Sanchez-Marcos et al., 2018). The net magnetization of CoFe_2O_4 is therefore determined primarily by the difference between the magnetic moments of the A and B sublattices. In addition, CoFe_2O_4 exhibits a large magnetocrystalline anisotropy, which is mainly associated with Co^{2+} ions occupying the octahedral B sites (Peddis et al., 2011). Therefore, changes in the cation distribution between the A and B sites can modify the balance of magnetic exchange interactions and the net sublattice magnetization, thereby affecting the spin arrangement and overall magnetic properties of the ferrite.

The incorporation of non-magnetic Zn^{2+} ions can induce significant cation redistribution, thereby altering the balance between the magnetic moments of the A and B sublattices and modifying the strength of the A–B superexchange interaction Choi et al. (2017); Mamelí et al. (2016). In particular, Zn^{2+} ions preferentially occupy tetrahedral A sites, displacing Fe^{3+} ions toward the octahedral B sites. This redistribution can substantially modify the magnetic interactions and magnetocrystalline anisotropy of CoFe_2O_4 (Barrera et al., 2018). Aftabi et al. (2025) reported a transition from ferrimagnetic (FIM) behavior at low Zn concentrations ($x = 0.2$) to superparamagnetic behavior at higher Zn concentrations ($x = 0.5$), with the highest saturation magnetization observed at $x = 0.2$, accompanied by a gradual decrease in coercivity. In another study, the magnetic susceptibility of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ prepared by the sol–gel method increased with increasing Zn concentration up to $x = 0.4$ and then decreased sharply at higher Zn contents (Atif et al., 2018). The increase in magnetization was attributed to the preferential occupation of Zn^{2+} ions at the A sites, which modifies the cation distribution and enhances the net magnetic moment of the ferrite (Atif et al., 2018). However, at higher Zn concentrations, the progressive dilution of magnetic ions at the A sites weakens the A–B superexchange interaction, resulting in a reduction in the net magnetization (Atif et al., 2018). These findings indicate that the magnetic properties of spinel ferrites are strongly influenced by particle size, cation distribution, and Zn substitution level.

While Zn substitution is known to alter the structural and magnetic properties of CoFe_2O_4 , as summarized above, site-specific evidence linking cation redistribution to the accompanying structural distortion - combining diffraction, vibrational, and electronic-structure probes together with a quantitative analysis of the saturation magnetization - remains less frequently reported for solid-state-synthesized samples. It is well known that studying the surface and crystal structures of materials makes it possible to elucidate the structural aspects of many of their physical properties (Aliyev et al., 2026; Rutkauskas et al., 2026; Guliyeva et al., 2023;

Amiraslanov et al., 2016). In this study, we investigate the effects of Zn substitution on the structural, vibrational, and magnetic properties of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) by combining X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and magnetic measurements.

2 Experimental details

$\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples with $x = 0, 0.1, 0.2, 0.3, 0.4$, and 0.5 were synthesized by a conventional solid-state reaction method. High-purity ZnO , Fe_2O_3 , and Co_3O_4 precursor powders were first weighed according to the corresponding stoichiometric ratios. The precursor powders were then thoroughly mixed and ground in methanol using an agate mortar and pestle, followed by pre-calcination at 1000°C for 12 h. The resulting powders were subsequently re-ground, pressed into pellets, and sintered at 1200°C for 24 h. After the first sintering step, the samples were re-ground, pelletized, and sintered again at 1300°C for 24 h, followed by natural cooling to room temperature.

The crystal structures of the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples were characterized by XRD using a D8 Advance ECO X-ray diffractometer (Bruker) equipped with a $\text{Cu } K\alpha$ radiation source ($\lambda_1 = 1.5406\text{\AA}$ and $\lambda_2 = 1.5444\text{\AA}$, with an intensity ratio of $I_2/I_1 = 0.48$). The XRD data were analyzed by the Rietveld refinement method using the FullProf software package (Rodríguez-Carvajal, 1993). The surface morphology of the samples was examined using SEM. Raman spectra were recorded using an XploRA PLUS Raman spectrometer (Horiba) with a 785 nm laser excitation wavelength. XPS measurements were performed using a Thermo Fisher K-Alpha spectrometer equipped with a monochromatic $\text{Al } K\alpha$ X-ray source (1486.6 eV). The magnetic hysteresis curves, $M(H)$, were measured at room temperature using a conventional vibrating sample magnetometer (VSM) under an applied magnetic field of $-3.1 \leq \mu_0 H \leq 3.1\text{ T}$. Unless otherwise specified, all measurements were performed at room temperature.

3 Results and discussion

The XRD patterns collected at room temperature are shown in Figure 1. The XRD patterns of all $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples exhibit the characteristic diffraction peaks of a cubic spinel structure, indexed to the (111), (220), (311), (222), (400), (422), (511), and (440) planes. All samples crystallize in the cubic spinel structure with the $\text{Fd}\bar{3}m$ space group, in good agreement with the standard diffraction patterns of CoFe_2O_4 (JCPDS No. 22-1086) and ZnFe_2O_4 (JCPDS No. 22-1012). No additional diffraction peaks associated with secondary or impurity phases were detected, indicating that all samples were obtained as single-phase spinel ferrites within the detection limit of the XRD technique. With increasing Zn content, the diffraction peaks gradually shift toward lower 2θ values, indicating an expansion of the lattice. This behavior can be attributed to the substitution of Co^{2+} ions by the larger Zn^{2+} ions, whose ionic radius ($0.82\text{\AA}$) is larger than that of Co^{2+} ($0.78\text{\AA}$) (Anantharamaiah et al., 2021; Barrera et al., 2018). Rietveld refinement of the XRD patterns shows good agreement between the experimental data and the calculated structural models, confirming the cubic spinel structure of the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples.

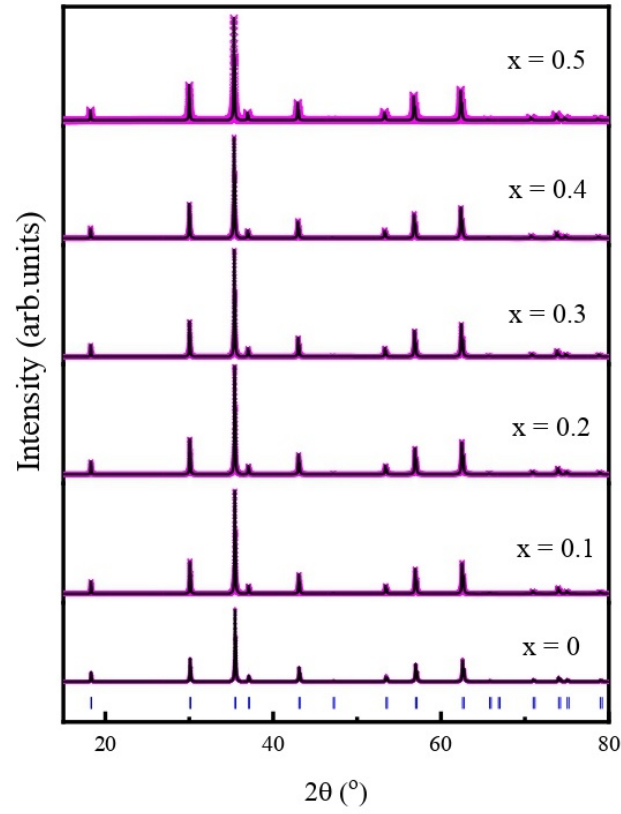


Figure 1: Room-temperature XRD patterns of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples refined by the Rietveld method. Symbols and solid lines represent the experimental data and calculated profiles, respectively. Bottom ticks indicate nuclear Bragg peak positions of the $\text{Fd}\bar{3}m$ phase.

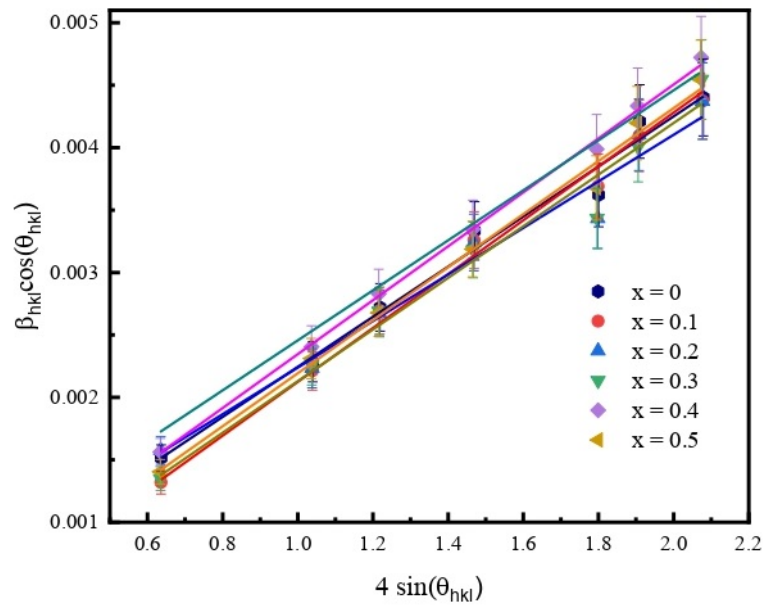


Figure 2: The dependence of $\beta_{hkl}\cos(\theta_{hkl})$ on $4\sin(\theta_{hkl})$ for the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5) samples.

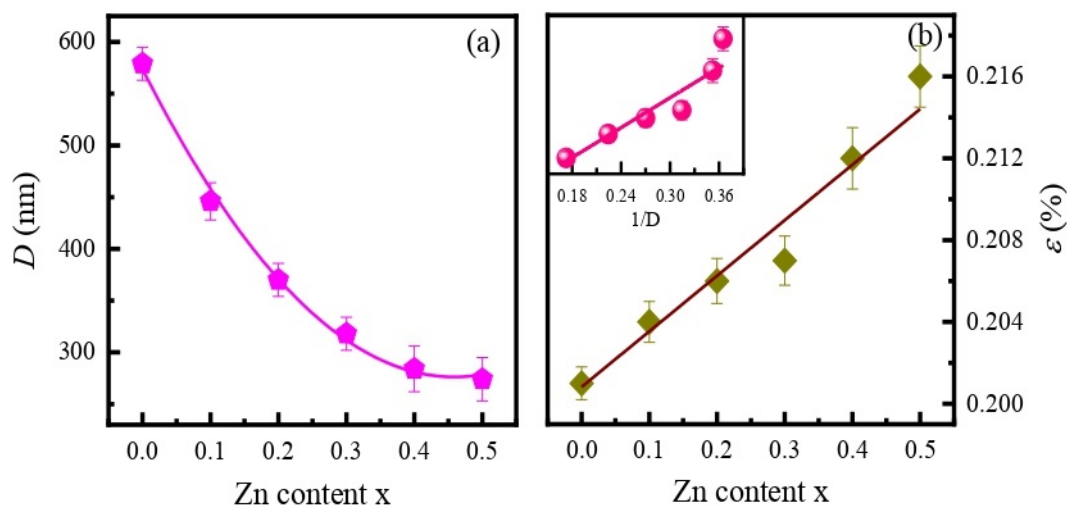


Figure 3: Crystallite size and microstrain of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ as a function of Zn content x . Inset: linear correlation between ε and D^{-1} along with its linear fit.

The lattice parameter increases from 8.386 Å to 8.412 Å with increasing Zn content, consistent with the ionic-radius mismatch noted above, and the unit-cell volume increases correspondingly. The crystallite size (D) and microstrain (ε) were estimated from the broadening of the XRD diffraction peaks using the Williamson–Hall (W–H) method (Biju et al., 2008; Mittemeijer & Welzel, 2008). Within this framework, the peak broadening, β_{hkl} , at the diffraction angle $2\theta_{hkl}$ is considered to arise from the combined contributions of finite crystallite size (D) and microstrain (ε), which can be expressed as $\beta_D = \frac{K\lambda}{D\cos(\theta_{hkl})}$ and $\beta_\varepsilon = 4\varepsilon\tan(\theta_{hkl})$ respectively, where K is the shape factor, λ is the X-ray wavelength, and θ_{hkl} is the Bragg angle (Biju et al., 2008; Mittemeijer & Welzel, 2008). A linear fit of $\beta_{hkl}\cos(\theta_{hkl})$ as a function of $4\sin(\theta_{hkl})$ allows ε to be determined from the slope, while D is calculated from the intercept on the y-axis (Figure 2). As shown in Figures 3(a) and 3(b), D decreases significantly from approximately 579 nm to 274 nm with increasing Zn content, whereas the microstrain increases. This behavior differs from that reported in previous studies (Siva et al., 2022). The increase in microstrain can be associated with the substitution of Co^{2+} by Zn^{2+} ions and the resulting redistribution of cations between the tetrahedral (A) and octahedral (B) sites. The difference in ionic radii between Zn^{2+} and Co^{2+} , together with the accompanying local structural distortion, can introduce additional lattice strain into the spinel structure.

The surface morphology of the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples was examined by SEM, and the corresponding SEM images are presented in Figure 4. The undoped sample ($x = 0$) exhibits relatively well-defined polyhedral grains with smooth surfaces and distinct grain boundaries. Zn substitution induces noticeable changes in both the grain size and surface morphology of the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples. At higher Zn concentrations ($x = 0.3$ and 0.4), the microstructure becomes more heterogeneous, with irregular and fragmented grains accompanied by pronounced agglomeration. The observed reduction in grain size may reflect Zn-induced changes in grain-growth kinetics during sintering, consistent with modification of the local crystal structure. This behavior is consistent with the decrease in crystallite size and the increase in microstrain determined from the XRD analysis.

On the other hand, Raman spectroscopy was employed to further investigate the cation distribution between A and B sites in the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ system. In spinel ferrites, the Raman-active modes are generally described by five fundamental modes, namely A_{1g} , E_g and $3T_{2g}$ modes, which are associated primarily with the vibrational motions of oxygen atoms within

the AO_4 tetrahedral and BO_6 octahedral structural units (D'Ippolito et al., 2015; Graves et al., 1988). The A_{1g} mode is particularly sensitive to the local structural environment of the tetrahedral A sites, and changes in its position and spectral components can provide information about the cation distribution and local bonding environment (Nekvapil et al., 2020).

As shown in Figure 5, the Raman spectra of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ exhibit more than the five fundamental Raman-active modes expected for an ideal spinel structure, with distinct bands located at approximately 172, 192, 228, 258, 306, 362, 476, 567, 616, and 695 cm^{-1} , together with an additional band near 651 cm^{-1} whose intensity and position vary with Zn content. The appearance of these additional Raman components can be associated with the local structural disorder and the coexistence of different cation–oxygen configurations resulting from the redistribution of Co^{2+} , Zn^{2+} , and Fe^{3+} ions between the A and B sites. Similar spectral features have been reported for substituted spinel ferrites (Chandramohan et al., 2011; Kim & Park, 2019).

To gain insight into the cation distribution, the Raman modes associated with the local environments of Co, Zn, and Fe ions at the tetrahedral and octahedral sites were considered. According to previous studies (Chandramohan et al., 2011; Kim & Park, 2019; Shafaay & Ramadan, 2023; Yadav et al., 2017), the three low-frequency bands located at approximately 172, 192, and 228 cm^{-1} can be assigned to the $\text{T}_{2g}(1)$ mode, which is mainly associated with translational or rotational vibrations involving the tetrahedral structural units. The bands observed at approximately 258, 306, and 362 cm^{-1} can be attributed to vibrational modes involving oxygen motion within the tetrahedral AO_4 units. The T_{2g} modes observed near 476 and 567 cm^{-1} are associated mainly with oxygen-related bending and stretching vibrations within the spinel lattice and are sensitive to the local bonding environments of the tetrahedral and octahedral sites.

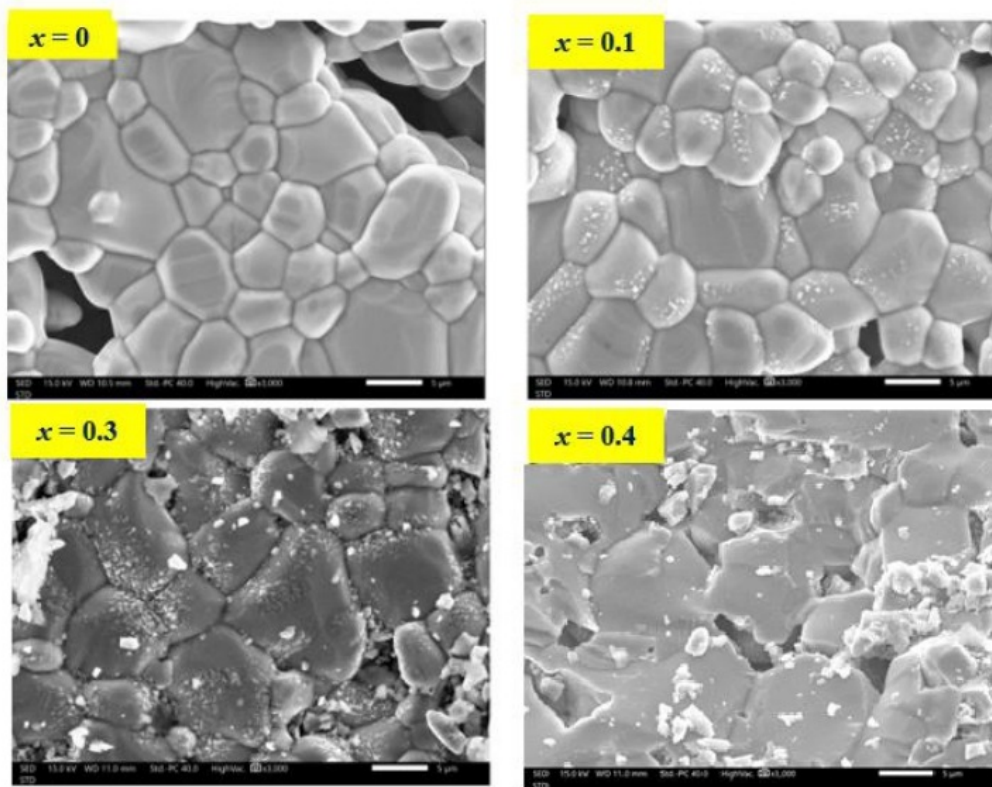


Figure 4: Representative SEM images of the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples.

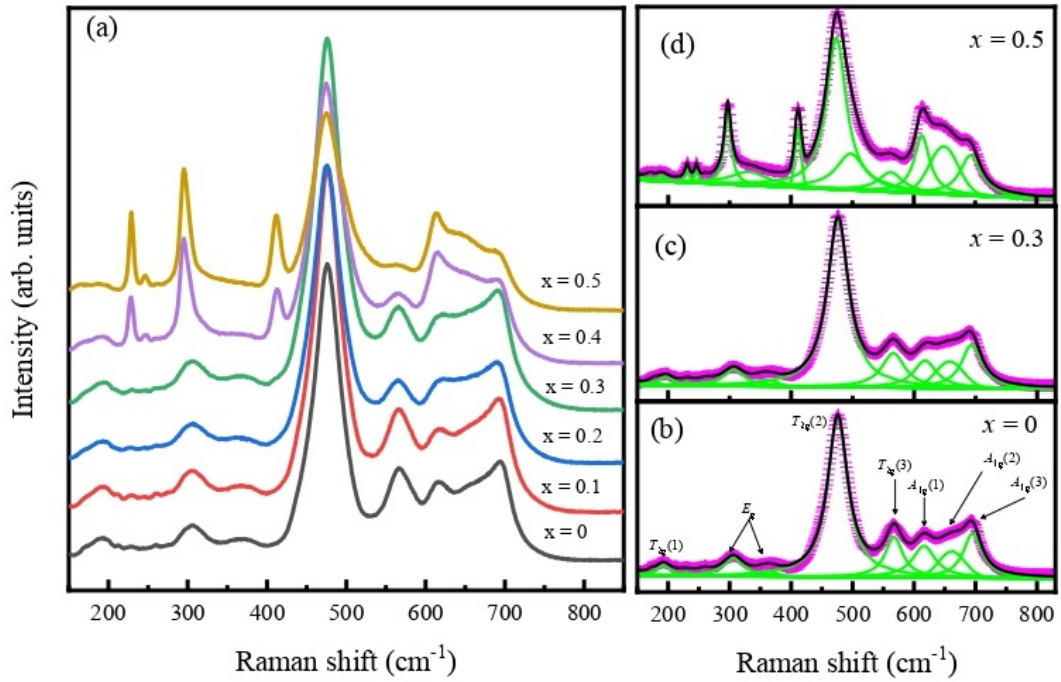


Figure 5: (a) Raman spectra of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ compounds ($x = 0-0.5$). The deconvolution of Raman spectra of the compounds with $x = 0$ (b), 0.3 (c) and 0.5 (d).

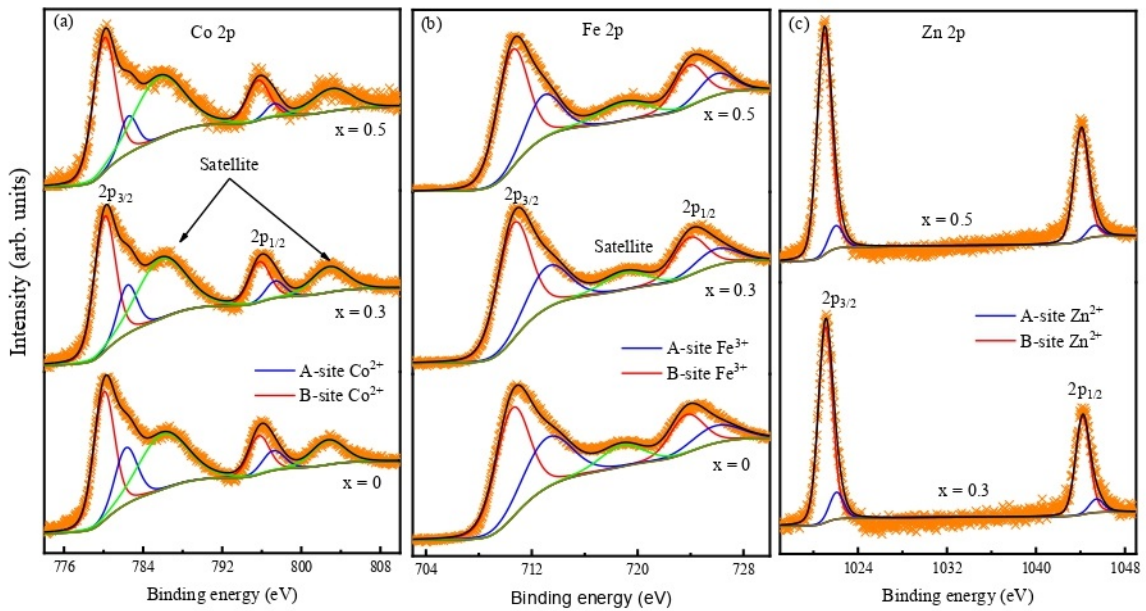


Figure 6: XPS spectra of (a) Co 2p, (b) Fe 2p, and (c) Zn 2p of the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples.

The Raman bands above 600 cm^{-1} are mainly associated with A_{1g} symmetric stretching vibrations of oxygen atoms within the AO_4 tetrahedral units. The bands near 616 and 695 cm^{-1} assigned to the A_{1g} modes, are consistent with reported assignments for CoFe_2O_4 and can be tentatively associated with local CoO_4 and FeO_4 related tetrahedral environments, respectively (Iliev et al., 2011; Ivanov et al., 2010). The additional component near 651 cm^{-1} , denoted $A_{1g}(2)$,

can be attributed to the coexistence of ZnO_4 and FeO_4 related tetrahedral environments. The appearance of multiple Al_g components in the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples therefore reflects the increased complexity of the local structural environment at the tetrahedral A sites resulting from the heterogeneous distribution of Co^{2+} , Zn^{2+} , and Fe^{3+} ions. In the spinel structure, the AO_4 tetrahedra and BO_6 octahedra form a three-dimensional framework through shared oxygen atoms. Consequently, changes in the local coordination environment and A–O and B–O bond strengths can modify the vibrational frequencies and intensities of the Raman modes. The evolution of the Raman bands with Zn substitution therefore provides complementary evidence for changes in the local cation distribution and structural distortion.

Because the cation distribution and valence states of Co and Fe ions are closely related to the magnetic properties of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, with XPS measurements performed on selected samples to further investigate their chemical states and local electronic environments (Figure 6). The XPS survey spectra show the characteristic signals of Fe, Co, Zn, and O, together with a weak C 1s signal arising from adventitious carbon contamination. The C 1s peak was used as a reference for binding-energy calibration to compensate for surface charging effects.

The high-resolution Co 2p spectra exhibit two spin–orbit components corresponding to $\text{Co}2p_{3/2}$ and $\text{Co}2p_{1/2}$, located at approximately 780.3 and 795.9 eV, respectively, together with their corresponding shake-up satellite features at approximately 785.8 and 802.7 eV (Dhivya Bharathi & Rajan Babu, 2025; Kmječ et al., 2025; Sanchez-Lievanos et al., 2021; Šutka et al., 2013). The binding energies and satellite structure are consistent with the presence of Co^{2+} ions in the studied samples. Thus, the XPS results indicate that Co predominantly exists in the +2 oxidation state in the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples. As shown in Figure 6(a), the high-resolution Co 2p spectrum can be deconvoluted into the $\text{Co}2p_{3/2}$ and $\text{Co}2p_{1/2}$ spin–orbit components together with their corresponding shake-up satellite features. The $\text{Co}2p_{3/2}$ component can be further fitted with two contributions associated with Co^{2+} ions in different local coordination environments, corresponding to A and B sites Dhivya Bharathi & Rajan Babu (2025); Kmječ et al. (2025); Sanchez-Lievanos et al. (2021); Šutka et al. (2013). As shown in Figure 6(b), the high-resolution Fe 2p spectra of the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples exhibit similar spectral features, with two main spin–orbit components centered at approximately 710.3 and 723.9 eV, corresponding to $\text{Fe}2p_{3/2}$ and $\text{Fe}2p_{1/2}$, respectively. A weaker feature at approximately 719.2 eV can be assigned to the shake-up satellite associated with the $\text{Fe}2p_{3/2}$ component. The binding energies and spectral features are consistent with Fe predominantly existing in the +3 oxidation state in all $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples (Dhivya Bharathi & Rajan Babu, 2025; Kmječ et al., 2025; Sanchez-Lievanos et al., 2021; Šutka et al., 2013). The asymmetric line shape of the $\text{Fe}2p_{3/2}$ component can be related to the coexistence of Fe^{3+} ions in different local coordination environments, including the tetrahedral A and octahedral B sites. Accordingly, the $\text{Fe}2p_{3/2}$ component was deconvoluted into two contributions associated with Fe^{3+} ions at the A and B sites, respectively. For $x > 0$, the high-resolution Zn 2p spectrum exhibits two spin–orbit components centered at approximately 1021.1 and 1044.2 eV, corresponding to $\text{Zn}2p_{3/2}$ and $\text{Zn}2p_{1/2}$, respectively, as shown in Figure 6(c). These binding energies are characteristic of Zn^{2+} ions in the spinel ferrite structure. The $\text{Zn}2p_{3/2}$ component can also be deconvoluted into contributions associated with Zn^{2+} ions occupying different local coordination environments, which may be related to the tetrahedral A and octahedral B sites (Sarkar et al., 2020; Šutka et al., 2013). Furthermore, the distribution of Co^{2+} , Fe^{3+} , and Zn^{2+} ions between A and B sites was qualitatively assessed from the relative integrated areas of the corresponding $2p_{3/2}$ components. The results indicate that Co^{2+} ions occupy both A and B sites, while Zn^{2+} ions are distributed between the two sites upon substitution into CoFe_2O_4 , with a preferential tendency toward the A sites. Among the selected compositions, the Co^{2+} concentration decreases more markedly at the A sites than at the B sites, whereas Fe^{3+} ions preferentially occupy the B sites in the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ system. These results are consistent with the cation redistribution inferred from the Raman analysis.

The $M(H)$ curves measured at room temperature confirm FIM character of all $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples, as shown in Figure 7. The magnetization increases rapidly at low magnetic fields but does not reach complete saturation even at $\mu_0 H \approx 3\text{T}$ (inset), suggesting contributions from magnetic anisotropy, cation disorder, and/or magnetic inhomogeneity in the samples (Limaye et al., 2009; Siva et al., 2022). Furthermore, the Raman and XPS results suggest that CoFe_2O_4 does not exhibit a perfectly inverse spinel cation distribution, but rather a partial degree of inversion, with a fraction of Fe^{3+} ions occupying the A site. Such a cation distribution allows strong A–B superexchange interactions mediated by Fe–O–Co and Fe–O–Fe pathways, thereby contributing to the ferrimagnetic ordering at room temperature Limaye et al. (2009); Siva et al. (2022).

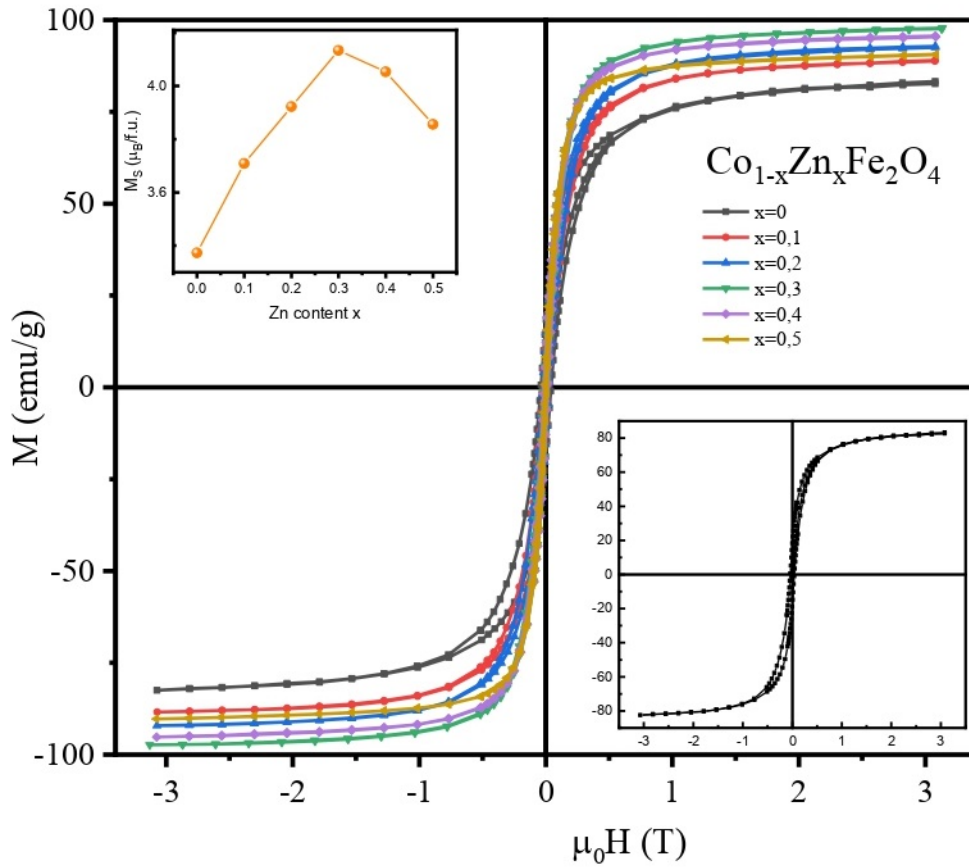


Figure 7: Room-temperature $M(H)$ curves of the $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ samples. Lower inset: An enlarged view of the $M(H)$ curve of the undoped sample. Upper inset: The variation of the saturation magnetization as a function of the Zn content x .

Upon Zn substitution, the magnetization increases significantly, reaching a maximum at $x = 0.3$. Because the magnetization curves remain unsaturated even at fields as high as $\mu_0 H = 3\text{T}$, the saturation magnetization (M_S) was estimated using the law of approach to saturation (LAS) Aftabi et al. (2025); Islam et al. (2024):

$$M = M_s \left(1 - \frac{a}{H} - \frac{b}{H^2} \right) + \chi H \quad (1)$$

where a and b are the inhomogeneity-related and anisotropy-related coefficients, respectively, and χ is the high-field susceptibility. The saturation magnetization, M_S , estimated from the high-field region, increases from approximately $3.37\mu_B/\text{f.u.}$ for $x = 0$ to $4.13\mu_B/\text{f.u.}$ for $x = 0.3$, as shown in the inset of Figure 7. This increase can be attributed primarily to the preferential

occupation of the tetrahedral A sites by non-magnetic Zn^{2+} ions ($0 \mu_B$), which promotes the redistribution of Fe^{3+} ions ($5 \mu_B$) from the A sites toward the B sites. Consequently, the magnetic moment of the B sublattice increases, leading to an increase in the net ferrimagnetic moment. At higher Zn concentrations ($x = 0.4$ and 0.5), however, M_s shows a slight decrease. This behavior reflects the competition between two effects: the increase in the B-sublattice magnetic moment caused by cation redistribution and the progressive weakening of the A–B superexchange interaction resulting from magnetic dilution of the A sublattice by non-magnetic Zn^{2+} ions. At sufficiently high Zn concentrations, the weakening of the A–B exchange interaction becomes dominant, leading to a reduction in the net magnetization.

4 Conclusions

In summary, $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ spinel ferrites were successfully synthesized by a conventional solid-state reaction method, and their structural, vibrational, and magnetic properties were systematically investigated. XRD analysis confirmed the formation of a single-phase cubic spinel structure with the $Fd\bar{3}m$ space group for all compositions. The systematic increase in the lattice parameter with increasing Zn content was attributed to the substitution of Co^{2+} by the larger Zn^{2+} ions. Raman and XPS analyses revealed significant cation redistribution, with Zn^{2+} ions preferentially occupying the A-site and promoting the redistribution of Fe^{3+} ions toward the B-site. The microstructural analysis showed a decrease in the XRD-derived crystallite size, a corresponding refinement of the SEM-observed grain morphology, and an increase in lattice microstrain with increasing Zn content, indicating enhanced structural disorder. Magnetic measurements confirmed ferrimagnetic behavior for all samples at room temperature. The saturation magnetization increased with Zn substitution up to $x = 0.3$, mainly due to the enhanced net magnetic moment of the B sublattice resulting from cation redistribution, and then decreased slightly at higher Zn concentrations because of the progressive weakening of the A–B superexchange interaction and magnetic dilution of the A sublattice by non-magnetic Zn^{2+} ions. Overall, these results demonstrate the important role of Zn substitution in tailoring the interplay among crystal structure, cation distribution, lattice strain, and magnetic properties in CoFe_2O_4 -based spinel ferrites, providing useful insights into the design of spinel ferrites with tunable structural and magnetic properties.

Acknowledgments

This work was supported by the Vietnam Academy of Science and Technology under Grant No. VAST03.07/25-26.

References

- Aftabi, A., Babakhani, A., & Khoshlahni, R. (2025). Optimized Zn substituted CoFe_2O_4 nanoparticles for high efficiency magnetic hyperthermia in biomedical applications. *Scientific Reports*, 15(1), 10039. <https://doi.org/10.1038/s41598-025-94535-8>
- Aliyev, Y.I., Guliyeva, Kh.M., Mursakulov, N.N., Ahmadova, Kh.N., Bayramova, A.I., & Ibrahimova, L.N. (2026). Study of thermophysical properties of Cu_2NiTe_2 compound at high temperatures by DSC spectroscopy. *East European Journal of Physics*, 2, 368-372. <https://doi.org/10.26565/2312-4334-2026-2-39>
- Amiraslanov, I.R., Alieva, N.A., & Guseinov, G.G. (2016). Crystalline structure of Cu_4SSe . *Crystallography Reports*, 61(7), 1047-1050. <https://doi.org/10.1134/S1063774516070026>
- Anantharamaiah, P.N., Shashanka, H.M., Kumar, R., Chelvane, J.A., & Sahoo, B. (2021). Chemically enabling CoFe_2O_4 for magnetostrictive strain sensing applications at lower mag-

- netic fields: Effect of Zn substitution. *Materials Science and Engineering: B*, 266, 115080. <https://doi.org/10.1016/j.mseb.2021.115080>
- Aslam, A., Islam, M.U., Ali, I., Awan, M.S., Irfan, M., & Iftikhar, A. (2014). High frequency electrical transport properties of CoFe₂O₄ and Sr₂NiMnFe₁₂O₂₂ composite ferrites. *Ceramics International*, 40(1 PART A), 155-162. <https://doi.org/10.1016/j.ceramint.2013.05.116>
- Atif, M., Asghar, M.W., Nadeem, M., Khalid, W., Ali, Z., & Badshah, S. (2018). Synthesis and investigation of structural, magnetic and dielectric properties of zinc substituted cobalt ferrites. *Journal of Physics and Chemistry of Solids*, 123, 36-42. <https://doi.org/10.1016/j.jpccs.2018.07.010>
- Barrera, G., Coisson, M., Celegato, F., Raghuvanshi, S., Mazaleyrat, F., Kane, S.N., & Tiberto, P. (2018). Cation distribution effect on static and dynamic magnetic properties of Co_{1-x}Zn_xFe₂O₄ ferrite powders. *Journal of Magnetism and Magnetic Materials*, 456, 372-380. <https://doi.org/10.1016/j.jmmm.2018.02.072>
- Bashir, B., Shaheen, W., Asghar, M., Warsi, M. F., Khan, M. A., Haider, S., Shakir, I., & Shahid, M. (2017). Copper doped manganese ferrites nanoparticles anchored on graphene nano-sheets for high performance energy storage applications. *Journal of Alloys and Compounds*, 695, 881-887. <https://doi.org/10.1016/j.jallcom.2016.10.183>
- Biju, V., Sugathan, N., Vrinda, V., & Salini, S.L. (2008). Estimation of lattice strain in nanocrystalline silver from X-ray diffraction line broadening. *Journal of Materials Science*, 43(4), 1175-1179. <https://doi.org/10.1007/s10853-007-2300-8>
- Cernea, M., Galizia, P., Ciuchi, I., Aldica, G., Mihalache, V., Diamandescu, L., & Galassi, C. (2016). CoFe₂O₄ magnetic ceramic derived from gel and densified by spark plasma sintering. *Journal of Alloys and Compounds*, 656, 854-862. <https://doi.org/10.1016/j.jallcom.2015.09.271>
- Chandramohan, P., Srinivasan, M.P., Velmurugan, S., & Narasimhan, S.V. (2011). Cation distribution and particle size effect on Raman spectrum of CoFe₂O₄. *Journal of Solid State Chemistry*, 184(1), 89-96. <https://doi.org/10.1016/j.jssc.2010.10.019>
- Chen, Q., & Zhang, Z.J. (1998). Size-dependent superparamagnetic properties of MgFe₂O₄ spinel ferrite nanocrystallites. *Applied Physics Letters*, 73(21), 3156-3158. <https://doi.org/10.1063/1.122704>
- Choi, H., Lee, S., Kouh, T., Kim, S.J., Kim, C.S., & Hahn, E. (2017). Synthesis and characterization of Co-Zn ferrite nanoparticles for application to magnetic hyperthermia. *Journal of the Korean Physical Society*, 70(1). <https://doi.org/10.3938/jkps.70.89>
- Dhivya Bharathi, S., & Rajan Babu, D. (2025). Synthesis and characterization of Zn doped CoFe₂O₄ magnetic nanoparticles and their antimicrobial and wound healing assay. *Results in Physics*, 72, 108210. <https://doi.org/10.1016/J.RINP.2025.108210>
- D'Ippolito, V., Andreozzi, G.B., Bersani, D., & Lottici, P.P. (2015). Raman fingerprint of chromate, aluminate and ferrite spinels. *Journal of Raman Spectroscopy*, 46(12), 1255-1264. <https://doi.org/10.1002/jrs.4764>
- Graves, P.R., Johnston, C., & Campaniello, J.J. (1988). Raman scattering in spinel structure ferrites. *Materials Research Bulletin*, 23(11). [https://doi.org/10.1016/0025-5408\(88\)90255-3](https://doi.org/10.1016/0025-5408(88)90255-3)

- Guliyeva, Kh.M., Mursakulov, N.N., Aliyeva, N.A., & Aliyev, Y.I. (2023). Synthesis, structure and thermal properties of the Cu₂NiSeTe. *Integrated Ferroelectrics*, 237, 67-72. <https://doi.org/10.1080/10584587.2023.2227048>
- Iliev, M.N., Mazumdar, D., Ma, J.X., Gupta, A., Rigato, F., & Fontcuberta, J. (2011). Monitoring B-site ordering and strain relaxation in NiFe₂O₄ epitaxial films by polarized Raman spectroscopy. *Physical Review B - Condensed Matter and Materials Physics*, 83(1), 014108. <https://doi.org/10.1103/PhysRevB.83.014108>
- Islam, M.R., Khan, M.K.R., Hossain, M.S., Rahman, M.M., Haque, M.M., Aliuzzaman, M., Alam, M.K., & Sarker, M.S.I. (2024). Structural, thermodynamic, and magnetic properties of SrFe₁₂O₁₉ hexaferrite modified by co-substitution of Cu and Gd. *RSC Advances*, 14(11), 7314-7328. <https://doi.org/10.1039/d3ra08878b>
- Ivanov, V.G., Abrashev, M.V., Iliev, M.N., Gospodinov, M.M., Meen, J., & Aroyo, M.I. (2010). Short-range B-site ordering in the inverse spinel ferrite NiFe₂O₄. *Physical Review B - Condensed Matter and Materials Physics*, 82(2), 024104. <https://doi.org/10.1103/PhysRevB.82.024104>
- Jauhar, S., Kaur, J., Goyal, A., & Singhal, S. (2016). Tuning the properties of cobalt ferrite: A road towards diverse applications. In *RSC Advances*, 6(100), 97694-97719. <https://doi.org/10.1039/c6ra21224g>
- Kefeni, K.K., Msagati, T.A.M., & Mamba, B.B. (2017). Ferrite nanoparticles: Synthesis, characterisation and applications in electronic device. In *Materials Science and Engineering: B*, 215, 37-55. <https://doi.org/10.1016/j.mseb.2016.11.002>
- Kim, K.J., & Park, J. (2019). Spectroscopic investigation on tetrahedral Co²⁺ in thin-film CoFe₂O₄. *Journal of Sol-Gel Science and Technology*, 92(1), 40-44. <https://doi.org/10.1007/s10971-019-05099-9>
- Kmječ, T., Nghiem, N.T., Truong-Tho, N., Kozlenko, D.P., Kichanov, S.E., Rutkauskas, A.V., ... & Dang, N.T. (2025). Revealing crucial factors governing magnetic properties of high-energy ball-milled CoFe₂O₄ nanoparticles. *Ceramics International*, 51(4), 5168-5180. <https://doi.org/10.1016/J.CERAMINT.2024.11.491>
- Kotnala, R. K., & Shah, J. (2015). Ferrite Materials: Nano toSpintronics Regime. *Handbook of Magnetic Materials*, 23, 291-379. <https://doi.org/10.1016/B978-0-444-63528-0.00004-8>
- Limaye, M.V., Singh, S.B., Date, S.K., Kothari, D., Reddy, V.R., Gupta, A., ... & Kulkarni, S.K. (2009). High coercivity of oleic acid capped CoFe₂O₄ nanoparticles at room temperature. *Journal of Physical Chemistry B*, 113(27). <https://doi.org/10.1021/jp810975v>
- Mameli, V., Musinu, A., Ardu, A., Ennas, G., Peddis, D., Niznansky, D., ..., & Cannas, C. (2016). Studying the effect of Zn-substitution on the magnetic and hyperthermic properties of cobalt ferrite nanoparticles. *Nanoscale*, 8(19). <https://doi.org/10.1039/c6nr01303a>
- Materón, E.M., Miyazaki, C.M., Carr, O., Joshi, N., Picciani, P.H.S., Dalmaschio, C.J., Davis, F., & Shimizu, F.M. (2021). Magnetic nanoparticles in biomedical applications: A review. *Applied Surface Science Advances*, 6. <https://doi.org/10.1016/j.apsadv.2021.100163>
- Mitte-meijer, E. J., & Welzel, U. (2008). The “state of the art” of the diffraction analysis of crystallite size and lattice strain. *Zeitschrift Fur Kristallographie*, 223(9), 552-560. <https://doi.org/10.1524/zkri.2008.1213>

- Narayanaswamy, V., Al-Omari, I.A., Kamzin, A.S., Issa, B., Tekin, H.O., Khourshid, H., ..., & Obaidat, I.M. (2021). Specific absorption rate dependency on the Co^{2+} distribution and magnetic properties in $\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ nanoparticles. *Nanomaterials*, 11(5). <https://doi.org/10.3390/nano11051231>
- Nekvapil, F., Bunge, A., Radu, T., Cinta Pinzaru, S., & Turcu, R. (2020). Raman spectra tell us so much more: Raman features and saturation magnetization for efficient analysis of manganese zinc ferrite nanoparticles. *Journal of Raman Spectroscopy*, 51(6), 959-968. <https://doi.org/10.1002/jrs.5852>
- Peddis, D., Yaacoub, N., Ferretti, M., Martinelli, A., Piccaluga, G., Musinu, A., ..., & Fiorani, D. (2011). Cationic distribution and spin canting in CoFe_2O_4 nanoparticles. *Journal of Physics Condensed Matter*, 23(42), 426004. <https://doi.org/10.1088/0953-8984/23/42/426004>
- Rodríguez-Carvajal, J. (1993). Recent advances in magnetic structure determination by neutron powder diffraction. *Physica B: Physics of Condensed Matter*, 192(1-2), 55-69. [https://doi.org/10.1016/0921-4526\(93\)90108-I](https://doi.org/10.1016/0921-4526(93)90108-I)
- Rutkauskas, A.V., Lis, O.N., Lukin, E.V., Kichanov, S.E., Ahmadova, Kh.N., Ibrahimova, L.N., Rymyski, G.S., & Zhaludkevich, A.L. (2026). The structural and magnetic properties of magnetite nanoparticles doped with rare earth elements Dy and Sm. *Advanced Physical Research*, 8(2), 173-182 <https://doi.org/10.62476/apr82173>
- Sanchez-Lievanos, K.R., Stair, J.L., & Knowles, K.E. (2021). Cation Distribution in Spinel Ferrite Nanocrystals: Characterization, Impact on their Physical Properties, and Opportunities for Synthetic Control. *Inorganic Chemistry*, 60(7), 4291-4305. <https://doi.org/10.1021/acs.inorgchem.1c00040>
- Sanchez-Marcos, J., Mazario, E., Rodriguez-Velamazán, J. A., Salas, E., Herrasti, P., & Menendez, N. (2018). Cation distribution of cobalt ferrite electrosynthesized nanoparticles. A methodological comparison. *Journal of Alloys and Compounds*, 739, 909-917. <https://doi.org/10.1016/j.jallcom.2017.12.342>
- Sarkar, K., Mondal, R., Dey, S., & Kumar, S. (2020). Cation vacancy and magnetic properties of ZnFe_2O_4 microspheres. *Physica B: Condensed Matter*, 583. <https://doi.org/10.1016/j.physb.2020.412015>
- Shafaay, A.S., & Ramadan, R. (2023). The Influence of Zn Doping on the Cation Distribution and Antibacterial Activity of CoFe_2O_4 . *Journal of Superconductivity and Novel Magnetism*, 36(5), 1465-1480. <https://doi.org/10.1007/s10948-023-06589-2>
- Siva, D., Sivaprakash, P., Raja, S., Muthu, S. E., Kim, I., Renuka, N., Arumugam, S., & Oh, T.H. (2022). Impact of Zn doping on the dielectric and magnetic properties of CoFe_2O_4 nanoparticles. *Ceramics International*, 48(22). <https://doi.org/10.1016/j.ceramint.2022.07.263>
- Šutka, A., Pärna, R., Zamovskis, M., Kisand, V., Mezinskis, G., Kleperis, J., Maiorov, M., & Jakovlev, D. (2013). Effect of antisite defects on the magnetic properties of ZnFe_2O_4 . *Physica Status Solidi (A) Applications and Materials Science*, 210(9), 1892-1897. <https://doi.org/10.1002/pssa.201329039>
- Thi Ngoc Nha, T., Toan, D.N., Nam, P.H., Manh, D.H., Khan, D.T., & Phong, P.T. (2024). Determine elastic parameters and nanocrystalline size of spinel ferrites MFe_2O_4 ($\text{M} = \text{Co}, \text{Fe}, \text{Mn}, \text{Zn}$) through X-ray diffraction and infrared spectrum: Comparative approach. *Journal of Alloys and Compounds*, 996, 174773. <https://doi.org/10.1016/J.JALLCOM.2024.174773>

Yadav, R.S., Kuřitka, I., Vilcakova, J., Havlica, J., Masilko, J., Kalina, L., ..., & Hajdúchová, M. (2017). Impact of grain size and structural changes on magnetic, dielectric, electrical, impedance and modulus spectroscopic characteristics of CoFe_2O_4 nanoparticles synthesized by honey mediated sol-gel combustion method. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 8(4). <https://doi.org/10.1088/2043-6254/aa853a>