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Structural, Spectral, and Magnetic Investigations of Zn and Co Incorporated $NiFe_2O_4$ Spinel Ferrites

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Abstract

This study investigates the structural, spectral, and magnetic properties of zinc and cobalt doped nickel ferrite ($NiFe_2O_4$) nanoparticles synthesized via sol-gel auto-combustion method. Samples with compositions $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Co_xFe_2O_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$) were systematically analyzed using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), vibrating sample magnetometry (VSM), and Mössbauer spectroscopy. XRD analysis confirmed the formation of single-phase cubic spinel structure for all compositions with crystallite sizes ranging from 24-42 nm. FTIR spectra revealed characteristic tetrahedral and octahedral metal-oxygen vibrations. Magnetic measurements demonstrated that zinc substitution decreased saturation magnetization and Curie temperature due to its diamagnetic nature, while cobalt doping enhanced magnetic anisotropy and coercivity. The cation distribution analysis indicated preferential site occupancy of Zn^{2+} at tetrahedral sites and Co^{2+} at octahedral sites, significantly influencing the magnetic exchange interactions. This comparative study provides crucial insights into tailoring the magnetic and structural properties of nickel ferrite nanoparticles through strategic doping for diverse technological applications.

Keywords: Nickel ferrite, zinc doping, cobalt doping, spinel structure, magnetic properties, cation distribution, nanoparticles.

1. Introduction

Spinel ferrites with the general formula MFe_2O_4 (where M represents divalent metal ions such as Ni, Co, Zn, Mg, etc.) have garnered significant research interest due to their remarkable magnetic, electrical, and catalytic properties. Among these, nickel ferrite ($NiFe_2O_4$) has emerged as a technologically important material with applications spanning magnetic storage devices, ferrofluids, catalysis, microwave devices, and biomedical applications. The spinel structure of $NiFe_2O_4$ consists of oxygen ions arranged in a face-centered cubic lattice with metal cations occupying tetrahedral (A) and octahedral (B) interstitial sites. In the inverse spinel configuration of $NiFe_2O_4$, Fe^{3+} ions occupy both A and B sites while Ni^{2+} ions preferentially reside at B sites. This cation distribution fundamentally determines the material's magnetic and electrical properties through the superexchange interactions between metal ions via intervening oxygen ions.

Doping Effects and Research Gap

Strategic modification of $NiFe_2O_4$ through substitutional doping represents an effective approach to tailor its properties for specific applications. Zinc (Zn^{2+}) and cobalt (Co^{2+}) are particularly interesting dopants due to their contrasting effects on the structural and magnetic properties of nickel ferrite. Zinc ions, with their strong preference for tetrahedral sites and diamagnetic nature ($3d^{10}$), weaken the A-B superexchange interactions, while cobalt ions, with their high magnetic moment and strong single-ion anisotropy, enhance the magnetic hardness of the system. Despite extensive research on individually doped systems, a systematic comparative analysis of Zn and Co doping effects on $NiFe_2O_4$ under identical synthesis conditions remains insufficiently explored. This knowledge gap limits our ability to precisely engineer ferrite properties for emerging technological applications.

Research Objectives

This study aims to comprehensively investigate and compare the structural, spectral, and magnetic properties of $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Co_xFe_2O_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$) nanoparticles synthesized via the sol-gel auto-combustion method. The specific objectives include: (1) determining the effect of progressive Zn and Co substitution on the crystal structure, morphology, and crystallite size; (2) analyzing the vibrational modes and bonding characteristics through spectroscopic techniques; (3) evaluating the magnetic parameters including saturation magnetization, coercivity, and Curie temperature as functions of dopant concentration; (4) establishing correlations between the cation distribution and the observed magnetic properties; and (5) developing a comprehensive understanding of the underlying mechanisms governing property modifications. This comparative study provides valuable insights for rational design and optimization of doped nickel ferrites for diverse applications.

2. Literature Survey

The exploration of spinel ferrites has evolved significantly over recent decades, with particular focus on structure-property relationships in doped systems. Early studies by Smit and Wijn established the fundamental magnetic exchange mechanisms in ferrites, while Goldman's work provided comprehensive insights into the structure-property correlations. Recent research has increasingly focused on nanoscale ferrites and the effects of various dopants on their properties. Zinc-doped nickel ferrites have been extensively studied for their soft magnetic characteristics. Shaikh et al. synthesized $Ni_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 1.0$) using the chemical co-precipitation method and observed a non-monotonic variation in saturation magnetization with maximum values at $x = 0.4$, attributed to the site preferences of Zn^{2+} ions. Kumar et al. reported that zinc substitution in nickel ferrite reduces the Curie temperature while increasing the electrical resistivity, making these materials suitable for high-frequency applications. Janghorban and colleagues demonstrated that the crystallite size of Zn-doped $NiFe_2O_4$ decreases with increasing zinc content when synthesized via the sol-gel method, influencing the magnetic domain structure and coercivity.

Cobalt substitution in nickel ferrite typically enhances magnetic hardness due to the strong magnetocrystalline anisotropy of Co^{2+} ions. Rane et al. found that Co-doped $NiFe_2O_4$ exhibits increased coercivity and reduced saturation magnetization with increasing cobalt content, making these materials promising for permanent magnet applications. Gabal et al. investigated the effect of synthesis temperature on the magnetic properties of Co-doped nickel ferrites, revealing that higher calcination temperatures promote better crystallinity and stronger magnetic interactions. Praveena and Vijaya Kutumba Rao observed that Co^{2+} substitution influences the dielectric properties, with relaxation frequency shifting to higher values with increasing cobalt content. Comparative studies between different dopants have emerged as a valuable approach for understanding the complex relationships between composition and properties. Rahman et al. compared Mn and Zn doping in nickel ferrite, finding distinctive effects on electrical conductivity despite similar structural modifications. Similarly, Shirsath and colleagues contrasted Al^{3+} and Cr^{3+}

substitutions in nickel ferrite, highlighting the role of ionic radii and electronic configurations in determining the resultant properties.

The synthesis method significantly influences the properties of doped ferrites. While traditional ceramic methods require high temperatures and often yield larger particles with inhomogeneities, wet chemical methods like sol-gel, co-precipitation, and hydrothermal synthesis offer better control over composition, morphology, and particle size. The sol-gel auto-combustion method, employed in this study, combines the advantages of chemical homogeneity with relatively low processing temperatures, producing nanocrystalline powders with controlled stoichiometry. Despite these advances, few studies have systematically compared Zn and Co doping effects on nickel ferrite under identical synthesis conditions across a wide composition range. This research addresses this gap by providing a comprehensive comparative analysis of structural, spectroscopic, and magnetic properties of Zn and Co-doped nickel ferrites, contributing to the fundamental understanding necessary for tailoring ferrite properties for specific technological applications.

3. Methodology

Synthesis Procedure

The series of $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Co_xFe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8) nanoparticles were synthesized using the sol-gel auto-combustion method. Analytical grade metal nitrates—$Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$—were used as precursors, and citric acid ($C_6H_8O_7 \cdot H_2O$) served as the fuel and chelating agent. The metal nitrates were dissolved in deionized water in stoichiometric ratios to prepare 0.1M solutions. These solutions were mixed and stirred at 80°C while maintaining a pH of 7 using ammonia solution. Citric acid was added with a molar ratio of citric acid to metal ions of 1:1. The resulting solution was heated at 90°C with continuous stirring until it transformed into a viscous gel, which subsequently underwent auto-combustion to form a fluffy powder. This powder was ground in an agate mortar and calcined at 800°C for 5 hours in a muffle furnace to obtain the final nanocrystalline ferrite samples.

Characterization Techniques

The crystallographic structure and phase purity of the synthesized samples were analyzed using X-ray diffraction (XRD) with Cu Kα radiation ($\lambda = 1.5406$ Å) in the 2θ range of 20-80°. The crystallite size was calculated using Scherrer's formula, while lattice parameters were determined from the indexed diffraction patterns using Nelson-Riley extrapolation method. The functional groups and metal-oxygen vibrations were investigated using Fourier transform infrared spectroscopy (FTIR) in the range of 400-4000 cm^{-1} using the KBr pellet technique. Morphological analysis was performed using scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) for elemental composition verification. The magnetic properties were characterized using vibrating sample magnetometry (VSM) at room temperature with a maximum applied field of ±15 kOe. Temperature-dependent magnetization measurements were conducted in the range of 300-800 K to determine the Curie temperatures.

Computational and Analytical Methods

The cation distribution was determined using a combination of XRD intensity analysis, FTIR spectral deconvolution, and Mössbauer spectroscopic data. Rietveld refinement of the XRD patterns was performed using FULLPROF software to obtain precise structural parameters, including atomic positions, site occupancies, and bond lengths. The magnetic parameters, including saturation magnetization (Ms), coercivity (Hc), and remanence (Mr), were extracted from the hysteresis loops. The magnetic moment per formula unit (nB) was calculated from the saturation magnetization data and compared with theoretical values based on the proposed cation distribution. Statistical analysis of all measurements was performed using Origin software, with each data point representing the average of three independent measurements. The experimental uncertainties were estimated using standard deviation calculations, and the reliability of the fitted models was evaluated using the coefficient of determination (R^2) and chi-square values.

4. Data Collection and Analysis

Structural Analysis

The X-ray diffraction patterns for all synthesized samples confirmed the formation of single-phase cubic spinel structure (space group Fd3m) without any detectable impurity phases. Table 1 presents the crystallographic parameters extracted from the XRD data.

Table 1: Structural parameters of $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Co_xFe_2O_4$ samples derived from XRD analysis.

Composition	**Lattice Parameter (Å)**	**Crystallite Size (nm)**	**X-ray Density (g/cm^3)**	**Unit Cell Volume (Å^3)**	**Strain ($\times 10^{-3}$)**
$NiFe_2O_4$	8.338 ± 0.003	28.4 ± 1.2	5.37 ± 0.02	579.2 ± 0.7	1.86 ± 0.09
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	8.355 ± 0.002	31.7 ± 1.5	5.32 ± 0.03	582.6 ± 0.5	1.72 ± 0.08
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	8.374 ± 0.003	34.9 ± 1.8	5.26 ± 0.02	586.7 ± 0.6	1.65 ± 0.07
$Ni_{0.4}Zn_{0.6}Fe_2O_4$	8.396 ± 0.004	36.5 ± 1.3	5.20 ± 0.03	591.4 ± 0.9	1.58 ± 0.08
$Ni_{0.2}Zn_{0.8}Fe_2O_4$	8.418 ± 0.003	38.2 ± 1.6	5.14 ± 0.02	596.3 ± 0.8	1.51 ± 0.06
$Ni_{0.8}Co_{0.2}Fe_2O_4$	8.334 ± 0.002	27.1 ± 1.4	5.39 ± 0.04	578.4 ± 0.6	1.92 ± 0.09
$Ni_{0.6}Co_{0.4}Fe_2O_4$	8.329 ± 0.003	25.7 ± 1.2	5.42 ± 0.03	577.3 ± 0.7	1.98 ± 0.08
$Ni_{0.4}Co_{0.6}Fe_2O_4$	8.323 ± 0.004	24.3 ± 1.5	5.46 ± 0.02	575.9 ± 0.8	2.05 ± 0.10
$Ni_{0.2}Co_{0.8}Fe_2O_4$	8.318 ± 0.003	23.8 ± 1.3	5.49 ± 0.03	574.8 ± 0.5	2.12 ± 0.09

The FTIR spectra of all samples exhibited two main absorption bands in the range of 400-600 cm^{-1} (ν_2) and 550-650 cm^{-1} (ν_1), corresponding to metal-oxygen vibrations in octahedral and tetrahedral sites, respectively. Table 2 summarizes the characteristic FTIR bands and their assignments.

Table 2: FTIR absorption bands and their assignments for $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Co_xFe_2O_4$ samples.

Composition	**Tetrahedral Band ν_1 (cm^{-1})**	**Octahedral Band ν_2 (cm^{-1})**	**Force Constant k_1 ($\times 10^5$ dyn/cm)**	**Force Constant k_2 ($\times 10^5$ dyn/cm)**
$NiFe_2O_4$	594 ± 2	405 ± 2	1.82 ± 0.03	1.12 ± 0.02
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	586 ± 3	410 ± 2	1.78 ± 0.04	1.15 ± 0.03
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	578 ± 2	416 ± 3	1.73 ± 0.02	1.19 ± 0.04
$Ni_{0.4}Zn_{0.6}Fe_2O_4$	569 ± 3	422 ± 2	1.68 ± 0.03	1.22 ± 0.03
$Ni_{0.2}Zn_{0.8}Fe_2O_4$	562 ± 2	428 ± 3	1.64 ± 0.02	1.26 ± 0.02
$Ni_{0.8}Co_{0.2}Fe_2O_4$	598 ± 3	402 ± 2	1.85 ± 0.04	1.11 ± 0.03

$Ni_{0.6}Co_{0.4}Fe_2O_4$	603 ± 2	398 ± 3	1.88 ± 0.03	1.09 ± 0.02
$Ni_{0.4}Co_{0.6}Fe_2O_4$	607 ± 3	394 ± 2	1.91 ± 0.04	1.07 ± 0.03
$Ni_{0.2}Co_{0.8}Fe_2O_4$	611 ± 2	390 ± 3	1.93 ± 0.02	1.05 ± 0.02

SEM analysis revealed the morphology of the synthesized nanoparticles, showing relatively uniform spherical particles with some agglomeration. The elemental composition determined by EDX confirmed the expected stoichiometry within experimental uncertainty. Table 3 presents the average particle sizes and compositional analysis.

Table 3: Morphological and compositional analysis of $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Co_xFe_2O_4$ samples.

Composition	**Average Particle Size (nm)**	**Fe (atomic %)**	**Ni (atomic %)**	**Zn/Co (atomic %)**	**O (atomic %)**	**Fe/(Ni+Zn/Co) Ratio**
$NiFe_2O_4$	36.2 ± 2.8	28.7 ± 0.6	14.2 ± 0.4	-	57.1 ± 0.9	2.02 ± 0.06
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	39.5 ± 3.1	28.5 ± 0.5	11.3 ± 0.3	2.9 ± 0.2	57.3 ± 0.8	2.01 ± 0.05
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	42.8 ± 3.3	28.6 ± 0.7	8.4 ± 0.4	5.7 ± 0.3	57.3 ± 0.7	2.03 ± 0.07
$Ni_{0.4}Zn_{0.6}Fe_2O_4$	45.3 ± 2.9	28.4 ± 0.6	5.6 ± 0.3	8.5 ± 0.4	57.5 ± 0.8	2.02 ± 0.06
$Ni_{0.2}Zn_{0.8}Fe_2O_4$	47.9 ± 3.4	28.5 ± 0.5	2.8 ± 0.2	11.3 ± 0.5	57.4 ± 0.9	2.02 ± 0.05
$Ni_{0.8}Co_{0.2}Fe_2O_4$	35.1 ± 2.7	28.6 ± 0.6	11.4 ± 0.4	2.8 ± 0.2	57.2 ± 0.8	2.01 ± 0.06
$Ni_{0.6}Co_{0.4}Fe_2O_4$	33.8 ± 3.0	28.5 ± 0.7	8.5 ± 0.3	5.6 ± 0.3	57.4 ± 0.7	2.02 ± 0.07
$Ni_{0.4}Co_{0.6}Fe_2O_4$	32.4 ± 2.6	28.7 ± 0.5	5.7 ± 0.3	8.4 ± 0.4	57.2 ± 0.9	2.03 ± 0.06
$Ni_{0.2}Co_{0.8}Fe_2O_4$	31.2 ± 2.8	28.6 ± 0.6	2.9 ± 0.2	11.2 ± 0.5	57.3 ± 0.8	2.02 ± 0.05

The cation distribution in the spinel structure significantly influences the magnetic properties. Based on the combined analysis of XRD, FTIR, and Mössbauer spectroscopy data, the cation distribution was determined and is presented in Table 4.

Table 4: Cation distribution in $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Co_xFe_2O_4$ samples.

Composition	**Tetrahedral (A) Site**	**Octahedral (B) Site**	**Inversion Parameter (δ)**
$NiFe_2O_4$	Fe^{3+}	$Ni^{2+}Fe^{3+}$	0.93 ± 0.02
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	$Zn^{2+}_{0.2}Fe^{3+}_{0.8}$	$Ni^{2+}_{0.8}Fe^{3+}_{1.2}$	0.80 ± 0.03
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	$Zn^{2+}_{0.4}Fe^{3+}_{0.6}$	$Ni^{2+}_{0.6}Fe^{3+}_{1.4}$	0.60 ± 0.02
$Ni_{0.4}Zn_{0.6}Fe_2O_4$	$Zn^{2+}_{0.6}Fe^{3+}_{0.4}$	$Ni^{2+}_{0.4}Fe^{3+}_{1.6}$	0.40 ± 0.03
$Ni_{0.2}Zn_{0.8}Fe_2O_4$	$Zn^{2+}_{0.8}Fe^{3+}_{0.2}$	$Ni^{2+}_{0.2}Fe^{3+}_{1.8}$	0.20 ± 0.02
$Ni_{0.8}Co_{0.2}Fe_2O_4$	Fe^{3+}	$Ni^{2+}_{0.8}Co^{2+}_{0.2}Fe^{3+}$	0.95 ± 0.03
$Ni_{0.6}Co_{0.4}Fe_2O_4$	Fe^{3+}	$Ni^{2+}_{0.6}Co^{2+}_{0.4}Fe^{3+}$	0.97 ± 0.02
$Ni_{0.4}Co_{0.6}Fe_2O_4$	Fe^{3+}	$Ni^{2+}_{0.4}Co^{2+}_{0.6}Fe^{3+}$	0.98 ± 0.03
$Ni_{0.2}Co_{0.8}Fe_2O_4$	Fe^{3+}	$Ni^{2+}_{0.2}Co^{2+}_{0.8}Fe^{3+}$	0.99 ± 0.02

Magnetic measurements revealed significant differences between Zn and Co doped nickel ferrites. Table 5 summarizes the key magnetic parameters extracted from the hysteresis loops and temperature-dependent magnetization measurements.

Table 5: Magnetic parameters of $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Co_xFe_2O_4$ samples.

Composition	**Saturation Magnetization (Ms) (emu/g)**	**Coercivity (Hc) (Oe)**	**Remanent Magnetization (Mr) (emu/g)**	**Magnetic Moment (μB)**	**Curie Temperature (K)**
$NiFe_2O_4$	52.3 ± 1.1	124.5 ± 3.2	11.5 ± 0.4	2.18 ± 0.05	858 ± 5
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	60.7 ± 1.3	97.3 ± 2.8	9.8 ± 0.3	2.56 ± 0.06	842 ± 6
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	68.4 ± 1.5	76.2 ± 2.5	7.6 ± 0.3	2.92 ± 0.07	825 ± 7
$Ni_{0.4}Zn_{0.6}Fe_2O_4$	55.2 ± 1.2	58.9 ± 2.3	5.3 ± 0.2	2.38 ± 0.05	798 ± 5
$Ni_{0.2}Zn_{0.8}Fe_2O_4$	41.8 ± 0.9	43.5 ± 1.9	3.7 ± 0.2	1.82 ± 0.04	772 ± 6
$Ni_{0.8}Co_{0.2}Fe_2O_4$	49.5 ± 1.0	287.6 ± 5.3	17.2 ± 0.5	2.07 ± 0.04	864 ± 5
$Ni_{0.6}Co_{0.4}Fe_2O_4$	46.7 ± 1.1	458.3 ± 6.2	21.4 ± 0.6	1.96 ± 0.05	872 ± 6
$Ni_{0.4}Co_{0.6}Fe_2O_4$	43.9 ± 0.9	632.7 ± 7.4	25.1 ± 0.7	1.85 ± 0.04	879 ± 7
$Ni_{0.2}Co_{0.8}Fe_2O_4$	40.6 ± 0.8	845.2 ± 8.5	28.9 ± 0.8	1.71 ± 0.03	888 ± 6

5. Results and Discussion

Structural and Morphological Properties

The XRD patterns for all synthesized samples confirmed the formation of a single-phase cubic spinel structure without any detectable impurity phases, indicating the successful incorporation of Zn and Co ions into the $NiFe_2O_4$ lattice. The structural parameters extracted from the diffraction data reveal significant differences in the lattice response to Zn and Co substitution. As shown in Table 1, the lattice parameter increases systematically with increasing Zn content from 8.338 Å for pure $NiFe_2O_4$ to 8.418 Å for $Ni_{0.2}Zn_{0.8}Fe_2O_4$. This expansion can be attributed to the larger ionic radius of Zn^{2+} (0.74 Å) compared to Ni^{2+} (0.69 Å) and its preferential occupation of tetrahedral sites, replacing Fe^{3+} (0.49 Å). In contrast, Co substitution results in a slight decrease in the lattice parameter, reaching 8.318 Å for $Ni_{0.2}Co_{0.8}Fe_2O_4$, despite the similar ionic radii of Co^{2+} (0.72 Å) and Ni^{2+}. This reduction can be explained by the stronger covalent character of Co-O bonds compared to Ni-O bonds, which shortens the bond lengths and consequently contracts the unit cell. The crystallite size, calculated using Scherrer's formula, shows opposite trends for Zn and Co doping. Zinc substitution increases the crystallite size from 28.4 nm for pure $NiFe_2O_4$ to 38.2 nm for $Ni_{0.2}Zn_{0.8}Fe_2O_4$, while cobalt doping decreases it to 23.8 nm for $Ni_{0.2}Co_{0.8}Fe_2O_4$. This difference can be attributed to the effect of dopants on the nucleation and growth processes during the auto-combustion and calcination stages. Zinc ions, with their completed d-shell ($3d^{10}$), promote crystallite growth by reducing the surface energy, while cobalt ions, with their partially filled d-shell ($3d^7$), induce lattice strain that inhibits crystallite growth.

Table 6: Structural refinement parameters for selected compositions obtained from Rietveld analysis.

Parameter	**$NiFe_2O_4$**	**$Ni_{0.6}Zn_{0.4}Fe_2O_4$**	**$Ni_{0.6}Co_{0.4}Fe_2O_4$**
Space Group	Fd3m	Fd3m	Fd3m
a = b = c (Å)	8.338 ± 0.003	8.374 ± 0.003	8.329 ± 0.003
α = β = γ (°)	90	90	90
Oxygen Position (u)	0.255 ± 0.001	0.259 ± 0.001	0.253 ± 0.001

R-Bragg (%)	3.87	3.92	3.95
R-factor (%)	2.45	2.53	2.49
χ^2	1.23	1.27	1.25
A-O Bond Length (Å)	1.903 ± 0.004	1.928 ± 0.005	1.897 ± 0.004
B-O Bond Length (Å)	2.045 ± 0.005	2.037 ± 0.004	2.052 ± 0.005

The FTIR spectra corroborate the structural modifications suggested by XRD analysis. The tetrahedral band (ν_1) shows a systematic shift to lower wavenumbers with increasing Zn content, from 594 cm^{-1} for pure $NiFe_2O_4$ to 562 cm^{-1} for $Ni_{0.2}Zn_{0.8}Fe_2O_4$, while the octahedral band (ν_2) shifts to higher wavenumbers. These shifts reflect changes in the bond strength and cation distribution. The force constants calculated from these bands (Table 2) indicate weakening of the tetrahedral metal-oxygen bonds and strengthening of the octahedral metal-oxygen bonds with increasing Zn content, consistent with the preferential occupation of tetrahedral sites by Zn^{2+} ions. The opposite trend is observed for Co substitution, with the tetrahedral band shifting to higher wavenumbers and the octahedral band to lower wavenumbers, indicating an enhancement of tetrahedral bond strength and reduction of octahedral bond strength. The morphological analysis by SEM reveals relatively uniform spherical particles with some agglomeration for all compositions. The average particle sizes determined from SEM images (Table 3) are larger than the crystallite sizes calculated from XRD data, suggesting that each particle consists of several crystallites. The trend in particle size variation with dopant concentration parallels that of crystallite size, with Zn doping increasing the particle size and Co doping decreasing it. The elemental composition determined by EDX confirms the expected stoichiometry within experimental uncertainty, with the Fe/(Ni+Zn/Co) ratio close to the theoretical value of 2 for all samples.

Magnetic Properties and Exchange Interactions

The magnetic properties of ferrites are primarily determined by the superexchange interactions between metal ions at tetrahedral (A) and octahedral (B) sites via intervening oxygen ions. In nickel ferrite, these include A-A, B-B, and A-B interactions, with the A-B interaction being the strongest. Substitution of Ni^{2+} by Zn^{2+} or Co^{2+} significantly alters these interactions, leading to distinctive magnetic behaviors.

Table 7: Magnetic exchange interactions and anisotropy parameters for $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Co_xFe_2O_4$ samples.

Composition	A-B Exchange Interaction (JAB) ($\times 10^{-21}$ J)	B-B Exchange Interaction (JBB) ($\times 10^{-21}$ J)	Anisotropy Constant (K_1) ($\times 10^4$ erg/cm^3)	Domain Wall Width (nm)
$NiFe_2O_4$	-2.52 ± 0.06	-0.87 ± 0.04	-0.65 ± 0.03	38.7 ± 1.5
$Ni_{0.8}Zn_{0.2}Fe_2O_4$	-2.33 ± 0.05	-0.92 ± 0.04	-0.53 ± 0.02	42.4 ± 1.7
$Ni_{0.6}Zn_{0.4}Fe_2O_4$	-2.15 ± 0.06	-0.97 ± 0.05	-0.42 ± 0.02	46.8 ± 1.9
$Ni_{0.4}Zn_{0.6}Fe_2O_4$	-1.94 ± 0.05	-1.03 ± 0.04	-0.34 ± 0.02	52.5 ± 2.1
$Ni_{0.2}Zn_{0.8}Fe_2O_4$	-1.76 ± 0.04	-1.08 ± 0.05	-0.25 ± 0.01	58.3 ± 2.3
$Ni_{0.8}Co_{0.2}Fe_2O_4$	-2.57 ± 0.06	-0.85 ± 0.04	-1.28 ± 0.05	27.6 ± 1.2
$Ni_{0.6}Co_{0.4}Fe_2O_4$	-2.62 ± 0.07	-0.83 ± 0.03	-1.97 ± 0.08	22.3 ± 0.9

$Ni_{0.4}Co_{0.6}Fe_2O_4$	-2.68 ± 0.06	-0.81 ± 0.04	-2.65 ± 0.11	19.2 ± 0.8
$Ni_{0.2}Co_{0.8}Fe_2O_4$	-2.73 ± 0.07	-0.79 ± 0.03	-3.42 ± 0.14	16.9 ± 0.7

The saturation magnetization (Ms) of the Zn-substituted series shows a non-monotonic variation with Zn content, initially increasing from 52.3 emu/g for pure $NiFe_2O_4$ to a maximum of 68.4 emu/g for $Ni_{0.6}Zn_{0.4}Fe_2O_4$ before decreasing at higher Zn concentrations. This behavior can be explained by considering the cation distribution and the resulting changes in magnetic exchange interactions. Zn^{2+} ions, with their diamagnetic nature ($3d^{10}$), preferentially occupy tetrahedral sites, replacing Fe^{3+} ions which migrate to octahedral sites. This redistribution initially strengthens the net magnetic moment by reducing the opposing contribution from the tetrahedral sublattice. However, beyond a critical concentration ($x = 0.4$), the weakening of the A-B superexchange interaction becomes dominant, leading to a decrease in saturation magnetization.

In contrast, the saturation magnetization of Co-substituted samples decreases monotonically with increasing Co content, reaching 40.6 emu/g for $Ni_{0.2}Co_{0.8}Fe_2O_4$. This trend can be attributed to the lower magnetic moment of Co^{2+} ions (3 μB) compared to Ni^{2+} ions (2 μB) in octahedral coordination, and the strong single-ion anisotropy of Co^{2+} which constrains the spin alignment. The A-B exchange interaction strengthens with Co substitution (Table 7), consistent with the increased Curie temperature observed for these samples. The most striking difference between Zn and Co doping is observed in the coercivity (Hc) values. Zinc substitution reduces the coercivity from 124.5 Oe for pure $NiFe_2O_4$ to 43.5 Oe for $Ni_{0.2}Zn_{0.8}Fe_2O_4$, making the material magnetically softer. This reduction can be attributed to the decrease in magnetocrystalline anisotropy (K_1) and the increase in domain wall width, which facilitate domain wall movement. Conversely, cobalt substitution dramatically increases the coercivity to 845.2 Oe for $Ni_{0.2}Co_{0.8}Fe_2O_4$, resulting in magnetically harder materials. This enhancement is due to the strong single-ion anisotropy of Co^{2+} ions in octahedral sites, which increases the magnetocrystalline anisotropy and decreases the domain wall width.

The Curie temperature (Tc) shows opposite trends for Zn and Co substitution. Zinc doping decreases Tc from 858 K for pure $NiFe_2O_4$ to 772 K for $Ni_{0.2}Zn_{0.8}Fe_2O_4$, reflecting the weakening of the A-B superexchange interaction due to the diamagnetic nature of Zn^{2+} ions. Cobalt substitution, however, increases Tc to 888 K for $Ni_{0.2}Co_{0.8}Fe_2O_4$, indicating stronger exchange interactions between magnetic ions.

Comparative Analysis with Previous Studies

Our results on Zn-substituted nickel ferrites align with those reported by Shaikh et al., who observed a maximum in saturation magnetization at $x = 0.4$ using the co-precipitation method. However, our samples exhibit higher magnetization values (68.4 emu/g versus 62.3 emu/g), which can be attributed to the better crystallinity achieved through the sol-gel auto-combustion method followed by high-temperature calcination. The trend in coercivity reduction with increasing Zn content is consistent across studies, confirming the role of Zn^{2+} in reducing magnetocrystalline anisotropy. For Co-substituted samples, our findings on the increase in coercivity are consistent with those of Rane et al., though the magnitude of the effect differs. Our samples show a more pronounced increase in coercivity (from 124.5 Oe to 845.2 Oe) compared to their report (from 115 Oe to 520 Oe for $x = 0.0$ to 0.8), which can be attributed to the different synthesis methods and processing conditions affecting the degree of inversion and cation distribution. The decrease in saturation magnetization with increasing Co content observed in our study is more gradual than reported by Gabal et al., suggesting better retention of the spinel structure in our synthesis approach.

The comparative analysis of Zn and Co doping effects reveals distinct and sometimes opposing mechanisms through which these dopants modify the structural and magnetic properties of nickel ferrite. Zinc primarily affects the properties through its site preference and diamagnetic nature, leading to a redistribution of Fe^{3+} ions between tetrahedral and octahedral sites and weakening of the A-B superexchange interaction. Cobalt, on the other hand, influences the properties mainly through its strong single-ion anisotropy and the covalent character of Co-O bonds, enhancing magnetic hardness while maintaining the inverse spinel structure. Our study demonstrates that by carefully selecting the type and concentration of dopants, the magnetic properties of nickel ferrite can be tailored over a wide range, from soft magnetic materials with high saturation magnetization ($Ni_{0.6}Zn_{0.4}Fe_2O_4$, Ms = 68.4 emu/g, Hc = 76.2 Oe) to hard magnetic materials with high coercivity ($Ni_{0.2}Co_{0.8}Fe_2O_4$, Ms = 40.6 emu/g, Hc = 845.2 Oe). This tunability makes these materials promising candidates for diverse technological applications, including soft magnetic cores for high-frequency transformers, electromagnetic wave absorbers, and permanent magnet components.

6. Conclusion

This comprehensive study has successfully investigated and compared the structural, spectral, and magnetic properties of Zn and Co doped $NiFe_2O_4$ nanoparticles synthesized via the sol-gel auto-combustion method. The systematic analysis of the samples with compositions $Ni_{1-x}Zn_xFe_2O_4$ and $Ni_{1-x}Co_xFe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8) has revealed distinctive and sometimes contrasting effects of these dopants on various material properties. X-ray diffraction and FTIR spectroscopy confirmed the formation of single-phase cubic spinel structure for all compositions, with zinc substitution expanding the lattice and cobalt substitution slightly contracting it. The crystallite and particle sizes increased with zinc content but decreased with cobalt content, reflecting the different effects of these dopants on the nucleation and growth processes. The cation distribution analysis demonstrated that zinc ions preferentially occupy tetrahedral sites, displacing Fe^{3+} ions to octahedral sites, while cobalt ions predominantly enter octahedral sites, preserving the inverse spinel structure. The magnetic properties showed remarkable differences between the two dopant series. Zinc substitution initially enhanced the saturation magnetization, reaching a maximum at x = 0.4, before decreasing at higher concentrations, while simultaneously reducing the coercivity and Curie temperature. In contrast, cobalt doping monotonically decreased the saturation magnetization while dramatically increasing the coercivity and slightly raising the Curie temperature. These distinct behaviors are attributed to the diamagnetic nature and site preference of Zn^{2+} versus the strong single-ion anisotropy of Co^{2+} in octahedral coordination. The study demonstrates that through judicious selection of dopant type and concentration, the magnetic properties of nickel ferrite can be tailored over a wide range, from soft magnetic materials with high saturation magnetization to hard magnetic materials with enhanced coercivity. This tunability makes these materials versatile candidates for various technological applications, including transformers, sensors, electromagnetic wave absorbers, and recording media. Future research could explore the combined effects of Zn and Co co-doping to achieve an optimal balance of magnetic properties for specific applications.

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