Research Article

Synthesis of Nickel-Zinc Ferrite Nanoparticles by the Sol-Gel Auto-Combustion Method: Study of Crystal Structural, Cation Distribution, and Magnetic Properties

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Spinel ferrite nanocomposites of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.25$ and 0.75) were synthesized by sol-gel auto-combustion and annealed between 250°C and 1000°C. A single-phase spinel structure was found through X-ray diffraction (XRD). The crystallite size is in the range of 17.55–66.98 nm, and lattice parameters are in the range of 8.351–8.434 Å. X-ray analysis revealed a slight shift of the peaks towards shorter angles when the zinc concentration increased from 0.25 to 0.75. XRD measurements revealed the metal ion distribution in the spinel ferrite system. For each sample, XRD data were used to compute structural characteristics such as lattice spacing, lattice constant, crystallite size, oxygen position parameter, tetrahedral and octahedral ionic radii, and bond lengths. Energy dispersive spectroscopy (EDS) spectra and field emission-electron scanning microscope (FESEM) were used to evaluate the elemental content and morphology. EDS analysis confirmed the presence of expected elements in the samples and confirmed the high doping rate of more than 180% of Zn ions in Ni ferrite. The evaluated particle sizes were determined to be 79.2 and 118.4 nm for zinc content of 0.25 and 0.75, respectively. The nearly spherical shape of the nanoparticles was shown in the transmission electron microscope (TEM). The magnetic moment, remanent, coercivity, and saturation magnetization were calculated by using vibrating sample magnetometer (VSM) results. The saturation magnetization magnitudes showed the influence of cation distribution.

1. Introduction

Spinel ferrite has been developed by a huge number of researchers and scientists in recent decades due to its versatile and unusual structural, spectroscopic, and magnetic properties [1]. Spinel ferrites have applications in microwaves [2], drug delivery [3], gas sensors [4, 5], and electronic devices [6], all of which are associated with the type of transition metals in their network [7]. Low porosity, high density, and specified microstructure are required for their technological applications [8].

The investigated ferrite nanopowder forms spinel crystals. It follows the $Fd\bar{3}m$ space group. According to their lattice environments, the divalent A and trivalent B cations occupy the octahedral or tetrahedral sites, respectively. The spinel ferrites are classified into two types based on the distribution of $A^{2+}$ and $Fe^{3+}$ cations on (A) or [B] sites: normal spinel $A_2B_2O_4$ with the formula $(A^{2+})_2[Fe^{3+}Fe^{3+}]_2O_2^−$, and the inverse type B (AB) $O_4$ with the formula $(A^{2+}Fe^{3+})_2[A^{2+}Fe^{3+}]_2O_2^−$ [9]. Figure 1 demonstrates that spinel ferrites crystallize [10], and the metal ion is trapped in the void between the oxygen ions because its radius is lower than the oxygen ion radius. The occupancy of cations along the (A) and [B] sites affects the structural and magnetic properties of spinel ferrites [11, 12].

In bulk nickel–zinc (Ni–Zn) ferrite systems, the zinc ions prefer the tetrahedral position, and the nickel ions prefer the octahedral position. However, it has been shown that a small percentage of zinc and nickel ions might also be found in the
nanocrystalline form, occupying the octahedral and tetrahedral positions, respectively [13].

Ni–Zn spinel ferrites are remarkably exciting for their high magnetic permeability, low electrical conductivity, and good performance at high frequencies [14]. Many methods were used to manufacture the Ni–Zn nanoferrite, including the hydrothermal approach [15], coprecipitation [16], sol-gel [17], microwave combustion [18], and others [19, 20]. One of the most convenient and effective approaches among these is the sol-gel approach. The sol-gel process has been successfully used to achieve small and uniform particle size, chemical homogeneity, high purity, and energy savings [21]. Regarding the microscopic properties, parameters such as composition, grain size, dopant amount, impurities, production process, and heating conditions are significant for Ni–Zn ferrites [22].

The purpose of this research was to study the influence of the composition of nanosized Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites with $x = 0.25$ and 0.75 on crystal structure, cation distribution, and magnetic characteristics.

2. Experimental Procedures

The sol-gel auto-combustion technique was used to synthesize Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ powders ($x = 0.25$ and 0.75). The analytical grade metal nitrates Ni(NO$_3$)$_2$.6H$_2$O, Fe(NO$_3$)$_3$.9H$_2$O, and Zn(NO$_3$)$_2$.6H$_2$O from BIOCHEM Chemopharma are used as the starting precursor materials. The stoichiometric amount of raw materials with citric acid (metal nitrate to citrate ratio was 1:2.2) was dissolved with minimum Milli-Q water and mixed under ultrasonic for 10 minutes. The temperature was then raised to 90°C, resulting in the formation of the brown viscous gel. It was placed in an oven at 200°C and auto-combustion occurred to form a fluffy powder. The fluffy powder was ultrasonicated in ethanol for 30 minutes to improve the obtained powder properties [23]. The produced powders were dried overnight at 80°C. Finally, the samples were annealed at temperatures of 250, 500, 750, and 1000°C by 10°C/min for 4 hours.

The crystalline structure of the samples was examined by Panalytical’s X’Pert Pro X-ray diffractometer (XRD). The morphology and microstructural evolution of the produced powder particles were carried out through the transmission electron microscope (TEM), ZEISS MODEL EM10C-100 KV, and the field emission scanning electron microscope (FESEM), ZEISS MODEL SIGMA VP. Energy dispersive spectroscopy (EDS) was used to investigate the elemental composition. The Fourier transform infrared spectroscopy (FTIR) spectra were obtained in the range of 400–900 cm$^{-1}$ using a Perkin Elmer Model, USA. The measurements of magnetic properties were carried out via a vibrating sample magnetometer (VSM, LBKFB model-Meghnatis Daghigh Kavir Company).

3. Results and Discussion

3.1. X-ray Diffractometer (XRD). Powder XRD patterns of the Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples annealed at 250, 500, 750, and 1000°C are shown in Figure 2(a) for $x = 0.25$ and Figure 2(b) for $x = 0.75$. The peaks that appear in the graph indicated that the single-phase cubic spinel ferrites were formed at 750°C and 1000°C. At annealing temperatures of 500°C and below, the secondary phase of the Fe$_2$O$_3$ impurity was verified [24].

The maximum intensity of the peak was found in the (311) plane which indicated that in the direction of the (311) plane of diffraction, the nanoparticle grains were dominating. The oxidation during annealing and thermal decomposition was considered to have resulted in the formation of Fe$_2$O$_3$ [25]. By using Scherrer’s equation as mentioned below, the crystallite size (D) of the samples was calculated [26] as

$$D_{\text{Sch}} = \frac{K\lambda}{\beta \cos \theta}$$

where $K$ is the shape function that equals 0.9, $\lambda$ is the X-ray wavelength of 0.1545 nm, and $\beta$ is the full width at half maximum of the (311) peak and is the diffraction angle.

The lattice parameter (average of all peaks) ($a_{\text{avg}}$), bulk density ($\rho_b$), X-ray density ($\rho_x$), and porosity (%$P$) of the samples were evaluated based on the following relations [27], and the results are listed in Table 1.
where $d_{hkl}$ is the interplanner spacing, and $(h, k, l)$ are the Miller indices.

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2},$$

where $d_{hkl}$ is the interplanner spacing, and $(h, k, l)$ are the Miller indices.

$$\rho_b = \frac{\text{mass of the sample}}{\text{volume of the pallet}},$$

$$\rho_x = \frac{8M_w}{N_Aa^3},$$

$$\% P = \left(1 - \frac{\rho_b}{\rho_x}\right) \times 100,$$

where $M_w$ is the molecular weight, $N_A$ is Avogadro’s number, and 8 is the number of formula units in a cell.

The Nelson–Riley (NR) plot provided the precise value of the lattice parameter (a). This approach was utilized to reduce mistakes induced by aberration of $2\theta$ variation. Figure 3 shows a plot of lattice parameter (a) against $F(\theta)$ that was plotted and linearly fit. It is possible to obtain the corrected value of the lattice parameter stated in Table 1 by taking the intercept on the (a) axis [28].

$$F(\theta) = 1 - \frac{\cos^2 \theta + \cos^2 \theta}{\sin \theta + \theta}.$$

The size of crystallites has also been approximated by using Williamson and Hall (WH) plots to separate size and strain broadening [29]. This approach relies on the widening of diffraction lines caused by crystallite size and internal strain.

$$\beta \cos \theta = \frac{\lambda}{D_{\text{WH}}} + \epsilon(4 \sin \theta),$$

where $\beta$ is measured for different XRD lines corresponding to different planes, $\theta$ is the Bragg angle, $\epsilon$ is the strain, and $D_{\text{WH}}$ is the crystallite size. (5) represents a straight line between $4 \sin \theta$ (x-axis) and $\beta \cos \theta$ (y-axis). The value of $D_{\text{WH}}$ is obtained by the intercept ($\lambda/(4\epsilon)$) of the line [30], and the values are listed in Table 1. Figures 4(a) and 4(b) show the linear fitting WH plots of Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ and Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$, respectively.

The size of the crystallites increased as the temperature increased (≥500°C). At a temperature of 1000°C, the crystallite size reached 43.46 nm and 45.08 nm for Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ and Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$, respectively.

Figure 2: X-ray diffraction patterns of synthesized: (a) Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ and (b) Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$ at different annealing temperatures.

Table 1: 2Theta for maximum intensity, $2\theta$, d-spacing, d, average lattice parameter, $a_{avg}$, lattice parameter from NR plot, $a_{NR}$, unit cell volume, V, crystal sizes from Scherrer’s method, $D_{sch}$, crystal size from WH plot, $D_{WH}$, X-ray density, $\rho_x (g/cm^3)$, and porosity, $\%P$, of the samples at different annealing temperatures.

<table>
<thead>
<tr>
<th>Structural parameters</th>
<th>250°C</th>
<th>500°C</th>
<th>750°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\theta$ (°)</td>
<td>35.45</td>
<td>35.45</td>
<td>35.55</td>
<td>35.25</td>
</tr>
<tr>
<td>d-spacing (Å)</td>
<td>2.530</td>
<td>2.530</td>
<td>2.523</td>
<td>2.544</td>
</tr>
<tr>
<td>$a_{avg}$ (Å)</td>
<td>8.382</td>
<td>8.391</td>
<td>8.373</td>
<td>8.427</td>
</tr>
<tr>
<td>$a_{NR}$ (Å)</td>
<td>8.364</td>
<td>8.385</td>
<td>8.351</td>
<td>8.413</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>588.90</td>
<td>590.80</td>
<td>587.01</td>
<td>598.44</td>
</tr>
<tr>
<td>$\rho_x$ (g/cm$^3$)</td>
<td>5.325</td>
<td>5.384</td>
<td>5.342</td>
<td>5.315</td>
</tr>
<tr>
<td>$% P$</td>
<td>70.59</td>
<td>79.48</td>
<td>68.91</td>
<td>65.51</td>
</tr>
<tr>
<td>$D_{sch}$ (nm)</td>
<td>26.70</td>
<td>25.90</td>
<td>19.58</td>
<td>17.55</td>
</tr>
<tr>
<td>$D_{WH}$ (nm)</td>
<td>26.26</td>
<td>25.90</td>
<td>18.79</td>
<td>22.40</td>
</tr>
</tbody>
</table>
Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$, respectively. This is because of the recrystallization of nanoparticles that reduced their lattice strain broadening. The coalescence and coarsening processes cause the grain to grow, and the small grains are merged together [25]. Consequently, it clearly shows that the size of the crystallites can change by changing the annealing temperature of the sample.

From Figure 5, it is illustrated that the crystallite size ($D_{coh}$) decreased with an increase in annealing temperature to 500°C, which can be referred to as an impurity phase decrease. Increasing the annealing temperature from 500°C to 1000°C tends to increase the crystallite size from 19.58 to 43.95 nm for Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ and from 17.55 to 45.58 nm for Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$.

Figure 6 illustrates that, when the Zn concentration increases, the peak positions shift towards lower angles. These results showed a larger Zn$^{2+}$ cation and larger Fe$^{3+}$ ions that can replace a smaller Ni$^{2+}$ cation [31].

The lattice parameter increases when the Zn concentration is raised from 0.25 to 0.75 as shown in Table 1. This is also because the Zn$^{2+}$ ion has a greater ionic radius than the Ni$^{2+}$ ion. In the spinel crystal structure, tetrahedral and
octahedral sites are preferred by larger Zn$^{2+}$ ions and smaller Ni$^{2+}$ ions, respectively. This evidence indicates that some Zn ions are transferred to Ni sites. Simultaneously, as Zn concentration increased, so did sample lattice volume, which makes sense given the difference in ionic radii [32–34].

For the structural examination of the samples and their cation distribution, the Rietveld refinement was used with the Fullprof software as illustrated in Figure 7. Nickel, zinc, and iron cations occupy specific Wyckoff locations 8a and 16d in cubic spinel ferrites, at (1/8, 1/8, 1/8) and (1/2, 1/2, 1/2), respectively [35]. The F d$3m$ space group was used to improve the patterns of all the samples. In Figure 7, the experimental data are shown by a red open circle whereas the computed intensities are denoted by a solid black line. The bottom line shows the difference in calculated and observed intensities. A short vertical line denoted the allowable Bragg locations for the F d$3m$ space group. Only Bragg 2$\theta$ locations are allowed for the fitting peaks in the structure.

The oxygen coordinates were treated as free parameters for refinement throughout the fitting whereas all other atomic fractional positions were treated as fixed. Other free parameters include lattice constants, isothermal parameters, occupancies, scaling factors, and form parameters. The pseudo-Voigt function was used to improve the patterns. In order to get minimum values of reliability parameters such as profile factor ($R_p$), weighted residual factor ($R_{wp}$), and expected residual factor ($R_{exp}$), the XRD patterns were refined until the goodness-of-fit index ($\chi^2$) approached unity.

In order to get minimum values of reliability parameters such as profile factor ($R_p$), weighted residual factor ($R_{wp}$), and expected residual factor ($R_{exp}$), the XRD patterns were refined until the goodness-of-fit index ($\chi^2$) approached unity.

Table 2 shows the Rietveld-derived cation distribution and lists the values of the determined reliability parameters and goodness-of-fit index.

Due to the random distribution of Ni, Zn, and Fe ions across tetrahedral and octahedral interstitial sites, the structure seems to be in a mixed spinel phase. Cations in the current ferrite system, such as Ni, Zn, and Fe, might have the ability to reside in two or more valence states in their distribution.

To simplify the cation distribution, the Ni and Zn ions are considered to remain entirely in the divalent state in the cation distribution whereas the Fe ions are assumed to remain exclusively in the trivalent state in the distribution [36].

Theoretical ionic radius of a tetrahedral site ($r_A$) and an octahedral site ($r_B$) might be determined by using the following relationships based on the cations distribution [37].

$$r_A = C_{Ni}r(Ni^{2+}) + C_{Zn}r(Zn^{2+}) + C_{Fe}r(Fe^{3+})$$

$$r_B = \frac{1}{2}(C_{Ni}r(Ni^{2+}) + C_{Zn}r(Zn^{2+}) + C_{Fe}r(Fe^{3+}))$$

($6$)

$C_{Ni}$, $C_{Zn}$, and $C_{Fe}$ denote the fractional concentration of Ni$^{2+}$, Zn$^{2+}$, and Fe$^{3+}$, respectively, at various sites taken according to cation distribution. In addition, $r$ denotes ionic radii for appropriate ions Ni$^{2+}$, Zn$^{2+}$, and Fe$^{3+}$. The result is tabulated in Table 3. From Table 3, it is obvious that the $r_A$ decreases while $r_B$ increases as the lattice parameter grows. This variation is caused by a shift in the occupation of the (A) and (B) sites. Zinc ions (large ions) are decreased in the (A) site and increased in the (B) site for $x = 0.75$ as compared to the sample of $x = 0.25$.

Chemical composition, preparation environment, and heating process all influence the oxygen ion parameter ($\mu$). The computed “$\mu$” values for all synthesized ferrites are shown in Table 3, by using the relation [38].

$$\mu = \left[ (r_A + r_B) \frac{1}{a\sqrt{3}} + \frac{1}{4} \right].$$

($7$)

The parameter “$\mu$” has a value of around 0.375 in the case of a perfect spinel structure. However, there were some...
variations from the ideal value for the examined samples indicating that there was deformation in the lattice. The following equation [39] was used to compute the theoretical lattice constants for all of the samples in this study:

\[ a_{th} = \frac{8}{3\sqrt{3}} \left( r_A + r_o \right) + \sqrt{3} \left( r_B + r_o \right). \]  

(8)

Table 3 contains the theoretical lattice characteristics for the samples. The theoretical lattice increased from 8.353 Å (x = 0.25) to 8.379 Å (x = 0.75). Theoretical values vary similarly to empirically determined lattice parameters.

According to the following relationships [28], the distance between magnetic ions (hopping length) at the tetrahedral site (\( L_A \)) and the octahedral site (\( L_B \)) might be calculated.

\[ L_A = a \frac{\sqrt{3}}{4}, \]

(9)

\[ L_B = a \frac{\sqrt{2}}{4}. \]

The computed \( L_A \) and \( L_B \) are shown in Table 3. The hopping lengths, \( L_A \) and \( L_B \), rise as the concentration of \( Zn^{2+} \) ions in nickel ferrite increases. In other words, as the Zn concentration grows so does the distance between the magnetic ions. This result and the similar results of the tetrahedral and octahedral bond lengths \( d_{Ax} \) and \( d_{BxE} \), tetrahedral edge, shared, and unshared octahedral edges (\( d_{AxE}, d_{BxE}, \) and \( d_{BxEU} \)) might be explained also by the fact that the component ions have different ionic radii [40].

Figure 6: Variation of the (311) diffraction peak of Ni_{0.75}Zn_{0.25}Fe_2O_4 and Ni_{0.25}Zn_{0.75}Fe_2O_4 at the temperature of (a) 500°C, (b) 750°C, and (c) 1000°C.
The interionic distances and angles clearly describe the crystalline structure and have a significant influence on the magnetic interactions between ions [41]. Figure 8 depicts the cation-cation distances marked by the letters b, c, d, e, and f as well as the cation-anion distances denoted by the letters p, q, r, and s, and the corresponding bond angles are represented by $\theta_1$, $\theta_2$, $\theta_3$, $\theta_4$, and $\theta_5$.

The following formulas [42] are used to compute the values of all interionic distances and are tabulated in Table 4.

\[
\begin{align*}
d_{Ax} &= a\sqrt{3}\left(u - \frac{1}{4}\right), \\
d_{Bx} &= a\sqrt{3u^2 - 2u + 0.375}, \\
d_{AXE} &= a\sqrt{2}\left(2u - \frac{1}{4}\right), \\
d_{BXE} &= a\sqrt{2}\left(1 - 2u\right), \\
d_{BXEU} &= a\left(4u^2 - 3u + \frac{11}{16}\right)^{1/2}.
\end{align*}
\]
With the exception of $q$ and $r$, all interionic distances increase with Zn concentration which corresponds to an increase in unit cell volume. The cation–cation distances increase with Zn concentration at both (A) and [B] sites because of the higher atomic radii of Zn$^{2+}$ that replace the smaller ionic radii of Ni$^{2+}$. Furthermore, it is seen in Table 4 that with Zn$^{2+}$ doping, the distances between cation–cation and cation–anion increase. As a result, the Ni$\text{O}_{0.75}$$\text{Zn}_{0.25}$Fe$_2$O$_4$ has a lower super-exchange strength than the Ni$\text{O}_{0.25}$$\text{Zn}_{0.75}$Fe$_2$O$_4$.

Using the obtained values of the interionic distances, the bond angles $\theta_1$, $\theta_2$, $\theta_3$, $\theta_4$, and $\theta_5$ have been determined using the expressions [42], and Table 5 shows all of these values.

Table 4: Calculated values of interionic distances of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrite ($x = 0.25$ and $x = 0.75$) annealed at 750°C.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$p$ (Å)</th>
<th>$q$ (Å)</th>
<th>$r$ (Å)</th>
<th>$s$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$d$ (Å)</th>
<th>$e$ (Å)</th>
<th>$f$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>2.049</td>
<td>1.883</td>
<td>3.606</td>
<td>3.646</td>
<td>2.957</td>
<td>3.468</td>
<td>3.622</td>
<td>5.433</td>
<td>5.122</td>
</tr>
<tr>
<td>0.75</td>
<td>2.070</td>
<td>1.878</td>
<td>3.595</td>
<td>3.661</td>
<td>2.974</td>
<td>3.487</td>
<td>3.642</td>
<td>5.464</td>
<td>5.151</td>
</tr>
</tbody>
</table>

Table 5: Calculated values of bond angles of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrite ($x = 0.25$ and $x = 0.75$) annealed at 750°C.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\theta_1$ (°)</th>
<th>$\theta_2$ (°)</th>
<th>$\theta_3$ (°)</th>
<th>$\theta_4$ (°)</th>
<th>$\theta_5$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>123.67</td>
<td>146.43</td>
<td>92.35</td>
<td>125.81</td>
<td>75.38</td>
</tr>
<tr>
<td>0.75</td>
<td>124.02</td>
<td>148.10</td>
<td>91.81</td>
<td>125.68</td>
<td>76.36</td>
</tr>
</tbody>
</table>

Table 5 shows that, for Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$, the values of bond angles $\theta_1$, $\theta_2$, and $\theta_5$ rise while the values of the bond angles $\theta_3$ and $\theta_4$ drop. The bond angles $\theta_1$, $\theta_2$, and $\theta_5$ are connected to A-B and A-A interactions which indicates that the strengthening of these interactions is confirmed by the increase in values of these bond angles with doping as the interaction strength is directly proportionate to the bond angle but inversely related to the bond length [41]. The super-exchange strength is increased when the A–B interaction increases. As well, a reduction in the values of $\theta_3$ and $\theta_4$ which is connected to B–B interactions indicates that these interactions are weakening [41].
3.2. **Field Emission Scanning Electron Microscope (FESEM).** The Ni_{0.75}Zn_{0.25}Fe_{2}O_{4} and Ni_{0.25}Zn_{0.75}Fe_{2}O_{4} microstructures were tested by the use of FESEM as demonstrated in Figures 9(a) and 9(b), respectively. Moreover, the insets show the distribution of particle size determined from FESEM results by fitting with the normal distribution for the samples that were annealed at 750°C. It is observed from Figures 9(a) and 9(b) that the particles come in a variety of sizes and shapes. The structures of the synthesized spinel ferrite are significantly affected by the concentration of Ni^{2+} and Zn^{2+} ions which caused the distinction in the FESEM images [43]. The particles exhibit a tendency to agglomerate. The agglomeration behavior of the particles can be related to the interaction of the magnetic dipole-dipole [9, 44]. The Zn substitution in Ni ferrite has the greatest impact on the microstructure, and the grain size rises.

According to the FESEM particle size distribution from Figures 9(a) and 9(b), the estimated average ferrite nanoparticle sizes were determined to be 79.2 and 118.4 nm for $x = 0.25$ and 0.75, respectively. Similar results were reported earlier [45]. The average size determined by XRD is less than the average size obtained from FESEM images. The diffraction signals of greater diameters are more powerful than those of smaller diameters if the nanoparticles are not fully monodispersed. This is why the size specified by XRD must always be smaller than the size specified by FESEM [7].

3.3. **Energy Dispersive Spectroscopy (EDS).** The elemental analysis of Ni$_{1-x}$Zn$_{x}$Fe$_{2}$O$_{4}$ nanoparticles at $x = 0.25$ and 0.75 was verified by EDS spectra, and the results are tabulated in Table 6. The spectra reflected typical features of spinel ferrite with the bands attributable to stretching vibrations caused by interactions between the oxygen atom and the cations at the tetrahedral and octahedral sites [49, 50]. Two main absorption bands are commonly detected in ferrites. The higher frequency absorption band ($\nu_1$) at around 550–600 cm$^{-1}$ corresponds to tetrahedral metal–oxygen (M–O) stretching vibration and the octahedral M–O stretching vibration appeared at ($\nu_2$) band of $\sim$400 cm$^{-1}$ [38, 51]. The long bond length of M–O ions at the tetrahedral and short bond length at the octahedral sites are responsible for the difference in frequency between the characteristic vibrations $\nu_1$ and $\nu_2$ [52].

3.4. **Transmission Electron Microscopy (TEM).**

![Figure 9: FESEM images and particle size distribution of Ni$_{1-x}$Zn$_{x}$Fe$_{2}$O$_{4}$ (a) $x = 0.25$ and (b) 0.75 annealed at 750°C.](image)

![Table 6: Elemental composition of Ni$_{1-x}$Zn$_{x}$Fe$_{2}$O$_{4}$ nanoparticles annealed at 750°C.](table)

3.5. **Fourier Transform Infrared Spectroscopy (FTIR).** The infrared spectroscopy (IR) spectra measured at room temperature at frequencies between 400 and 900 cm$^{-1}$ are illustrated in Figure 12. The spectra reflected typical features of spinel ferrite with the bands attributable to stretching vibrations caused by interactions between the oxygen atom and the cations at the tetrahedral and octahedral sites [49, 50]. Two main absorption bands are commonly detected in ferrites. The higher frequency absorption band ($\nu_1$) at around 550–600 cm$^{-1}$ corresponds to tetrahedral metal–oxygen (M–O) stretching vibration and the octahedral M–O stretching vibration appeared at ($\nu_2$) band of $\sim$400 cm$^{-1}$ [38, 51]. The long bond length of M–O ions at the tetrahedral and short bond length at the octahedral sites are responsible for the difference in frequency between the characteristic vibrations $\nu_1$ and $\nu_2$ [52].
Figure 10: The EDS spectrum of (a) Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ and (b) Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$ nanoparticles annealed at 750°C.

Figure 11: TEM images of (a) Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ and (b) Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$ annealed at 750°C.

Figure 12: FTIR spectra of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ annealed at 750°C with different Zn concentrations: $x = 0.25$ and 0.75.
The intensity and position of the peaks of these modes change depending on the concentration of nickel and zinc under the influence of changes in the effects of the crystalline field and strain in the lattice [53].

With increasing Zn ion concentration, band position $\nu_1$ shifts to the lower wavenumber side, and band position $\nu_2$ shifts toward the higher wavenumberside as shown in Figure 12. When Zn$^{2+}$ is doped into NiFe$_2$O$_4$, Fe$^{3+}$ moves from the tetrahedral to the octahedral site, and it reduces the frequency of tetrahedral vibration [38]. This is because zinc has a higher atomic weight than nickel and iron. The effective atomic weight at tetrahedral sites increases as Zn concentrations rise. According to the inverse relationship between frequency and the group weights, this group’s related band shifts toward a lower frequency range.

3.6. Vibrating Sample Magnetometer (VSM). A VSM was used to estimate the magnetic characteristics of the samples by applying a magnetic field of 14 kOe which indicates that the samples exhibited magnetic behavior. Magnetizations ($M$) against magnetic field ($H$) plots (hysteresis loop) of prepared Ni-Zn samples are demonstrated in Figure 13. The magnitudes of the saturation magnetization ($M_s$), remanent magnetization ($M_r$), loop squareness ratio ($M_r/M_s$), coercivity ($H_c$), and magnetic moment ($n_B$) were determined from hysteresis loops and tabulated in Table 7.

Figure 13 demonstrates the magnetic behavior of the Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles. The ferrimagnetic behavior of soft magnetic material was observed in the samples [54]; that is, nonpermanent magnetic materials which are due to their small $M_s$ and $H_c$ values are very easily magnetized and demagnetized at low field values. This shows the narrow magnetic hysteresis loop that has been completely formed. Cationic magnetic moments are produced at tetrahedral and octahedral sites by the superexchange interaction between metal cations which are responsible for the magnetic properties [55]. There are several factors that the magnetic behavior of spinel ferrites depends on such as synthesis method, grain size, chemical composition, and the cation distribution [56, 57].

It was seen that all the magnetic parameters were decreased with the decrease of Zn concentration in the Ni ferrite matrix as shown in Table 7. This decrease in magnetic parameters was caused primarily by the substitution of magnetic Ni ions with nonmagnetic Zn ions [44].

Magnetization is caused by the formation of magnetic moments. The distribution of magnetic ions in the spinel structure determines the net magnetic moment. The magnetic moment in a Bhor magneton is calculated by the following relation [58], and the results are presented in Table 7.

$$n_B = \frac{M_s M_A}{5585}.$$  \hspace{1cm}(13)

The cation distribution between (A) and [B] sites affects magnetism. At 0 K, when both sides’ spins are antiferromagnetically coupled, each formula unit has a net magnetic moment. Following Néel’s ferrimagnetism model, the magnetic moments of ions on (A) and [B] sites are oriented antiparallel to one another, and their spins are collinear. The theoretical magnetic moment per formula unit $n_B(x)$ is defined as follows [59]:

$$n_B(x) = M_B(x) - M_A(x).$$ \hspace{1cm}(14)

where $M_B(x)$ and $M_A(x)$ are the sublattice magnetic moments for the [B] and (A) sites, respectively.

Theoretical magnetic moment values were computed as a function of Zn concentration by using the ionic magnetic moments and the cation distribution. The findings are stated in Table 7.
The saturation magnetization of Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ and Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$ are 73.7 and 36.4 emu/g, respectively. The high $M_s$ of Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ is because of the substitution of Zn into Ni$_2$O$_4$. Fe$^{3+}$ ions of (A) site migrate to [B] sites, resulting in the change in the magnetic moment, decreasing at site (A), and increasing at site [B], therefore raising the overall magnetization [60].

| Zn content, x | Cation distribution | $M_r$ (emu/g) | $M_s$ (emu/g) | $M_\text{r}/M_s$ | $H_c$ (Oe) | $n_\text{B}$ (µ$\text{o}$) | Obs. (VSM) | Cal. (XRD) |
|---------------|---------------------|---------------|---------------|-----------------|------------|----------------|----------|
| 0.25          | (Ni$_{0.75}$Zn$_{0.05}$Fe$_{0.80}$) | 73.7          | 14.3          | 0.19            | 138.2      | 3.12           | 0.27     |
| 0.75          | (Ni$_{0.00}$Zn$_{0.00}$Fe$_{0.05}$) | 36.4          | 2.3           | 0.06            | 40.5       | 1.56           | 1.59     |

4. Conclusions

The sol-gel auto-combustion was utilized to manufacture a cubic spinel structure of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles with $x=0.25$ and 0.75. The crystal size increased as the annealing temperature was raised. Zn doping increased the lattice parameter because Zn$^{2+}$ has larger ionic radii than Ni$^{2+}$. According to the cation distribution study, it was found that the substituted Zn$^{2+}$ was distributed throughout the A and B sites resulting in the mixed spinel structure. The FESEM and TEM images showed that as the Zn concentration rises, the grain size grows larger. The purity of the produced Ni-Zn nanoferries and a high rate, more than 180%, of doped zinc ions were verified by an EDS analysis. In FTIR spectra, the presence of two strong absorption bands around 550–600 cm$^{-1}$ ($v_1$) and ~400 cm$^{-1}$ ($v_2$) revealed the formation of ferrite samples, and $v_1$ shifted to a lower frequency whereas $v_2$ shifted to a higher frequency with increasing Zn content. The Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ sample exhibited the highest values of $M_r$, $M_s$, $H_c$, and $n_\text{B}$ due to cation distribution.

Data Availability

The manuscript includes all data, and we don’t have any data as part of the supplementary information.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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