

Article

Effects of Zinc Substitution on the Microstructural and Magnetic Characteristics of Cubic Symmetry Nickel Ferrite System

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Abstract: The preparation of $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0$ and 0.3) nanoparticles using glycine-mediated combustion route was successfully completed depending on the zwitterion and combustion characteristics of glycine. Using a variety of methods, including XRD, FTIR, SEM/EDX, and TEM, the investigated ferrites were characterized. XRD and FTIR analyses confirm that $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ and NiFe_2O_4 nanoparticles crystallize in the cubic symmetry in the space group $Fd3m$. An increase in the lattice parameters and a subsequent decrease in crystallite size were caused by the process of replacing Ni ions with Zn ions. In accordance with Waldron's hypothesis, FTIR spectra demonstrate that the ferrites have a spinel-type structure as they are produced. The substitution process by Zn led to different changes in the half band widths with subsequent in splitting in the absorption band around 400 cm^{-1} . The examined ferrites' cation distribution showed that Zn^{2+} and Ni^{2+} ions favored the tetrahedral (A) and octahedral (B) sites, respectively, while Fe^{3+} ions occupied both A- and B-sites, providing mixed spinel ferrite. TEM analysis indicates the formation of spinel nanocrystalline particles with low agglomerations. The particle size of the as-synthesized ferrites did not exceed 16 nm. By applying the VSM approach at room temperature, the magnetic characteristics of the ferrites under investigation were established. The magnetization of $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ nanoparticles was found to be higher than that of NiFe_2O_4 nanoparticles according to the magnetic data. Increasing the magnetization and the experimental magnetic moment of $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ were accompanied by a decreasing of its coercivity. The net magnetization is oriented along different high symmetry directions. On the other hand, the anisotropy of the nickel ferrite increases by substituting Ni with a Zn ion.

Keywords: XRD; FTIR; squareness; coercivity; magnetization; ferrites



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1. Introduction

Nickel ferrite (NiFe_2O_4) has attracted the attention of many scientists because of its multiple applications, including magnetic storage systems, photo magnetic materials, microwave devices, catalysts, gas sensors, Ferro fluids, magnetic storage systems, and photo magnetic materials [1,2]. Its uses also included high frequency circuits, the cores of radiofrequency (RF) transformers, inductors, antennas, and radar absorption materials. This might be explained by the material's strong resistivity and low degradation at high frequencies [3]. Generally, the significant contributions of nickel ferrite in many applied fields are primarily due to unusual structural, spectroscopic, electrical, electrochemical, and magnetic properties [4]. Directing or controlling these properties occurs through the standardized planning of their preparation processes. It is important to have a good selection and control of the ferrite preparation process, the main objective of which is to

control the structural properties, including the cation distribution in both tetrahedral and octahedral sites. The structural–property relationships in different materials are connected with the symmetry in the crystal structure. Therefore, the cation distribution can shed light on the symmetry conditions in materials. The physical characteristics of a material are mainly determined based on its structure. The ferrite type structure can be viewed as a combination of rotations, rotations inversion, and translational symmetries.

Different preparation techniques, such as the hydrothermal, wet chemical, auto combustion, and spray drying methods, have been studied for the fabrication of nanoscale mixed ferrite particles [5–10]. The Deraz group, as a group specialized in the preparation and characterization of nano magnetic materials with various applications, sought to reach one pot preparation methods that are environmentally friendly and less expensive, especially by not relying on high temperatures that may be necessary to prepare different ferrites [10–15]. This research group focused on the method of preparing nanomaterials, including ferrites, with self-combustion based on different fuels, such as glycine and egg white. In addition, this group found that the difference in fuel and its concentration greatly affects the structural, morphological, surface, magnetic, and catalytic properties of the prepared ferrites.

On improving the properties of nickel ferrites that were present in our previous works, it was necessary to change the amount of fuel used because of resorting to the process of replacing nickel ions with other non-magnetic ions, such as Zn ions. In our previous works, we found that the magnetism of nickel ferrite (NiFe_2O_4) prepared using 0 and 8 mol glycine were 0.838 emu/g and 57 emu/g, respectively [16]. Moreover, the magnetism of zinc-substituted nickel ferrite ($\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$) prepared using glycine-assisted auto combustion was 57 emu/g [15]. In bulk zinc-substituted nickel 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 nano crystalline form, occupying the octahedral and tetrahedral positions, respectively [15,17]. Finally, we can say that microscopic properties, such as composition, grain size, dopant content, impurities, precursors, and preparation conditions, clearly affect all properties of Ni-Zn ferrite system [18].

Therefore, the purpose of this project was to study the influence of the composition of nano-sized $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites with $x = 0.00$ and 0.30 on the crystal structure and morphological and magnetic characteristics.

2. Materials and Methods

2.1. Materials

Glycine, ferric nitrate hydrate, zinc (II) nitrate, and nickel (II) nitrate all have linear formulas. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{NH}_2\text{CH}_2\text{COOH}$ were the chemical components used, respectively. The Sigma-Aldrich Company provided the materials for this project (Darmstadt, Taufkirchen, Germany). No additional processing was necessary for these reagents, which were used quantitatively.

2.2. Preparation Method

Using the glycine-assisted auto combustion technique, two samples of NiFe_2O_4 and $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ were produced. The samples under investigation were created by thoroughly mixing an equimolar mixture of nickel and ferric nitrates hydrate with 3 mol glycine in a crucible, taking the stoichiometric ratio of $\text{Fe}/\text{Ni} = 2$ into consideration. To increase the viscosity of the materials under study, the obtained materials were first swirled at $80\text{ }^\circ\text{C}$ to allow the water to vaporize. By increasing the temperature to $120\text{ }^\circ\text{C}$, the mixture was afterwards transformed into a gel. The produced precursor gel was then heated to a crucible temperature by being calcined at $300\text{ }^\circ\text{C}$ for 15 min. When a spark appeared in one corner and quickly spread throughout the mass, it seemed to indicate that the mass was combusting in an incandescent manner, producing a large volume of dense, fluffy material. Foam had already started forming in this region.

2.3. Characterization Systems

X-ray diffraction and a BRUKER D8 advance diffractometer (Karlsruhe, Germany) were used to measure the structural properties of several nanoparticles. Cu K α radiation was used to run the patterns at 40 kV, 40 mA, and a scanning speed of 2° per minute. Based on X-ray diffraction line broadening of plane (311) and Scherrer equation calculations, Equation (1) through (10) have been utilized to determine the different lattice parameters of pure and substituted nickel ferrite represented in the examined product [19]:

$$d = B \lambda / \beta \cos \theta \quad (1)$$

$$\delta = 1/d^2 \quad (2)$$

$$\varepsilon = \beta \cos \theta / 4 \quad (3)$$

$$D_x = 8 M_w / N a^3 \quad (4)$$

$$L_A = (\sqrt{3}/4)a \quad (5)$$

$$L_B = (\sqrt{2}/4)a \quad (6)$$

$$r_A = (u - 1/4)a\sqrt{3} - r(O^{2-}) \quad (7)$$

$$r_B = (5/8 - u)a - r(O^{2-}) \quad (8)$$

$$A-O = (u - 1/4)a\sqrt{3} \quad (9)$$

$$B-O = (5/8 - u)a \quad (10)$$

where d is the mean crystallite size of the phasing being investigated, B is the Scherrer parameter (0.89), λ is the wavelength of the X-ray beam being used, β is the full-width half maximum (FWHM) of diffraction, δ is dislocation density, ε is the strain of the powder, and θ is the Bragg's angle, D_x is density based on XRD results, M_w is the molecular weight, N is the Avogadro's number, a is the lattice parameter, $r(O^{2-})$ is radius of oxygen ion, and u is the oxygen ion parameter. The distance between the magnetic ions (L_A , L_B), bond lengths ($A-O$, $B-O$), and ionic radii (r_A , r_B) was on tetrahedral and octahedral sites.

A PerkinElmer Spectrophotometer (type 1430) was used to measure the Fourier-transmission infrared (FTIR) spectra of several materials. An amount of 200 mg of vacuum-dried IR-grade KBr was combined with two milligrams of each solid sample. The FTIR spectra were measured in the 1000–4000 cm^{-1} range. After being processed for three minutes in a vibrating ball mill, the mixture was dispersed using a steel die with a 13 mm diameter. The FTIR spectrophotometer's double grating spectrophotometer container was filled with the identical disks.

The JEOL JAX-840A and JEOL Model 1230 (both from JEOL, Tokyo, Japan) were used to capture TEM images, respectively. The materials were dispersed in ethanol and then subjected to a short ultrasonic treatment in order to disperse individual particles over mount setup and copper grids.

The magnetic characteristics of the undetected ferrites were examined using a vibrating sample magnetometer (VSM—Model 9600-1, LDJ Electronics, Troy, MI, USA) with a 20 kG maximum applied field.

3. Results

3.1. Structural Properties of the as Synthesized Ferrites

Figure 1 shows XRD diagrams of the manufactured $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0$ and 0.3). The variations between the values of two thetas observed and computed for the S1 and S2 sample, as well as the miller indices, are reported in Table 1. These diagrams demonstrate the production of NiFe_2O_4 (PDF no; 44-1485) in the S1 sample with presence of ZnFe_2O_4 (PDF no; 10-325) in the S2 sample. The majority of the observed peaks were also robust and distinct, supporting the materials' crystalline nature as manufactured. In addition to computing the lattice parameters, the Fullprof program [20] was used to determine the crystal system, space group, and other crystallographic properties that are illustrated in Table 2. These findings confirm the combination between both NiFe_2O_4 and ZnFe_2O_4 to form the solid solution of pure $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ with an absence of any second phase.

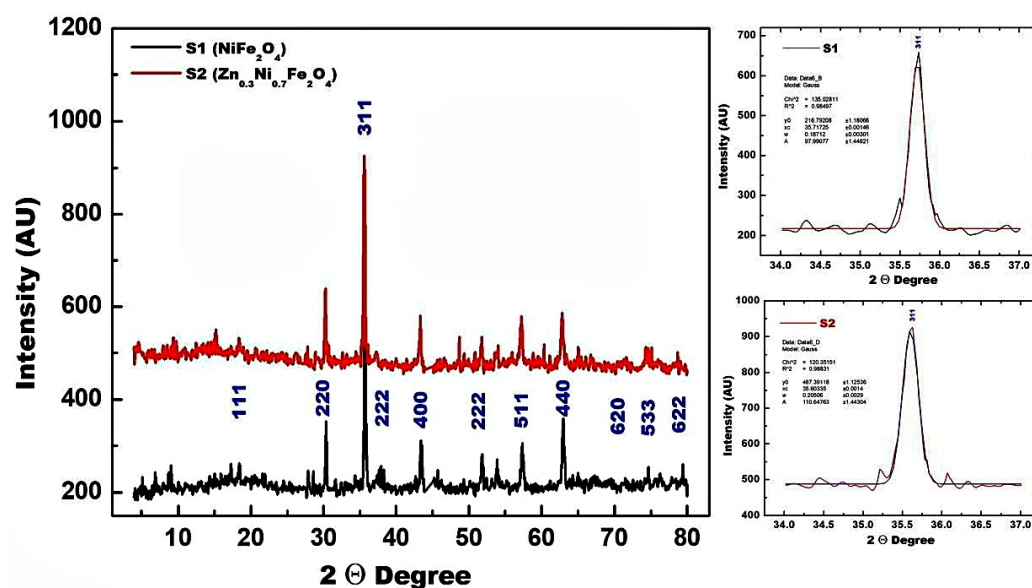


Figure 1. XRD patterns of the S1 (NiFe_2O_4) and S2 ($\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$) samples.

Table 1. Structural data of the as-synthesized S1 (NiFe_2O_4) and S2 ($\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$).

Fd3m (227) Space Group			S1 (NiFe_2O_4)			S2 ($\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$)	
h	k	l	2θ (Cal)	2θ (Obs)	Dif.	2θ (Obs)	Dif.
1	1	1	18.6	18.6096	−0.0096	18.593	0.007
2	2	0	30.7	30.619	0.081	30.5913	0.1087
3	1	1	36.17	36.071	0.099	36.0381	0.1319
2	2	2	37.64	37.7341	−0.0941	37.6995	−0.0595
4	0	0	43.94	43.8508	0.0892	43.8101	0.1299
3	1	3	48.1	48.0208	0.0792	47.9757	0.2043
2	2	4	54.08	54.4285	−0.3485	54.3765	0.0135
3	3	3	58.16	58.0328	0.1272	57.9767	−0.0067
4	4	0	63.59	63.7498	−0.1598	63.6869	−0.0969
3	1	5	67.049	67.0451	0.0039	66.9781	0.0709
2	4	4	68.129	68.1253	0.0037	68.0569	0.0721
6	2	0	72.375	72.3703	0.0047	72.2963	0.0787
5	3	3	75.493	75.4882	0.0048	75.4099	−0.3199
6	2	2	76.522	76.5173	0.0047	76.4376	0.0844

Table 2. Some structural properties of the as-synthesized S1 (NiFe₂O₄) and S2 (Zn_{0.3}Ni_{0.7}Fe₂O₄).

Properties	S1	S2
a, nm	0.82587	0.82660
b, nm	0.82587	0.82660
c, nm	0.82587	0.82660
α	90	90
β	90	90
γ	90	90
Volume, nm ³	0.5633	0.5647
d, nm	89.155976	81.363253
δ , Lines/nm	1.26×10^{-4}	1.51×10^{-4}
ϵ	3.89×10^{-4}	4.26×10^{-4}
D_x , g/cm ³	5.3320	5.3380
L_A , nm	0.3576	0.3579
L_B , nm	0.2918	0.2921
A-O, nm	0.1888	0.1889
B-O, nm	0.2130	0.2133
r_A , nm	0.0583	0.0587
r_B , nm	0.0826	0.0830

By shedding light on the peak height for the (220) and (440) planes, which could be an indicator of the cation distribution at sub-lattice (namely, the tetrahedral (A-) and octahedral (B-) sites, respectively) involved in the spinel type ferrite, we found that [16] (i) in the S1 sample, the intensity of (440) plane is higher than that of the (220) plane depending on fabrication of inverse spinel type nickel ferrite. Counter behavior was displayed in the case of the S2 sample depending on the manufacturing of mixed spinel Zn-Ni ferrite. (ii) The peak height of the (2 2 0) plane is greater than that of the (440) plane, indicating the incorporation of Zn ions in A-site. It is clear from this table that the values of δ , ϵ , a , D_x , L_A , L_B , r_A , r_B , A-O, and B-O for Zn-substituted nickel ferrite are higher than that of unsubstituted Ni ferrite.

3.2. FTIR Analysis

The spectra of FTIR for the manufactured samples are given in Figure 2. This figure displays modifications in the absorption bands of the as-prepared materials due to the substitution process by Zn ions. However, this figure shows two major absorption bands (i.e., ν_1 and ν_2) in the range of 537–410 cm^{−1} related to A- and B-sites at higher and lower frequencies, respectively. These bands confirm the formation of the as-prepared materials with a cubic spinel phase structure according to report of Waldron [21]. The major absorption band for two samples at 537 cm^{−1} is relatively narrow and strong in its intensity; however, it is due to the metal–oxygen (M–O) intrinsic vibrations for tetrahedral complexes. Two minor absorption bands for the S2 sample at 422 cm^{−1} and 410 cm^{−1} are narrow and weak in their intensities; however, they are due to the octahedral M–O intrinsic vibrations. A similar narrow and weak absorption band for the S1 sample was observed at 419 cm^{−1}. An additional two broad absorption bands at 1410 cm^{−1} and 1125–1075 cm^{−1} are due to the stretching vibrations of both hydrogen and hydroxyl carbon (C–H and C–OH).

3.3. Morphological Characteristics of the Investigated Ferrites

The microstructure properties of Zn-substituted and unsubstituted nickel ferrites were determined using the transmission electron microscopy (TEM) technique. Figures 3 and 4 display TEM, or high resolution (RT)-TEM, images of the selected area electron diffraction (SAED) and histograms of the crystallite size statistical distribution (CSD) of the manufactured samples. Figures 3a and 4a show a progressive change in the morphology characteristics of nickel ferrite nanoparticles with the substitution of some Ni ions with Zn ions, yielding particles with average size of 5 nm. One cannot ignore presence of some agglomerations. Figures 3b and 4b display CSD histograms of the investigated samples, confirming that these samples consisted entirely of different particles in Nano scale in the range from 2 nm to

≥ 40 nm. In fact, the crystallite size calculated from XRD was larger than the particle size determined from TEM. This difference may be due to the fact that TEM gives a complete picture of all crystallized and amorphous granules while the X-ray gives this picture of crystallized granules only. In this study, the majority of the granules prepared in the S1 and S2 samples had an average size of 15 and 5 nm, respectively. While Figures 3c and 4c show a fast Fourier transform (FFT) of the manufactured solids, which confirmed the formation of a spinel type structure. In addition, the particles of the manufactured samples have a polycrystalline nature, as shown in Figures 3d and 4d, which display the selected area electron diffraction (SAED) images with regular rings containing light spots of different sizes.

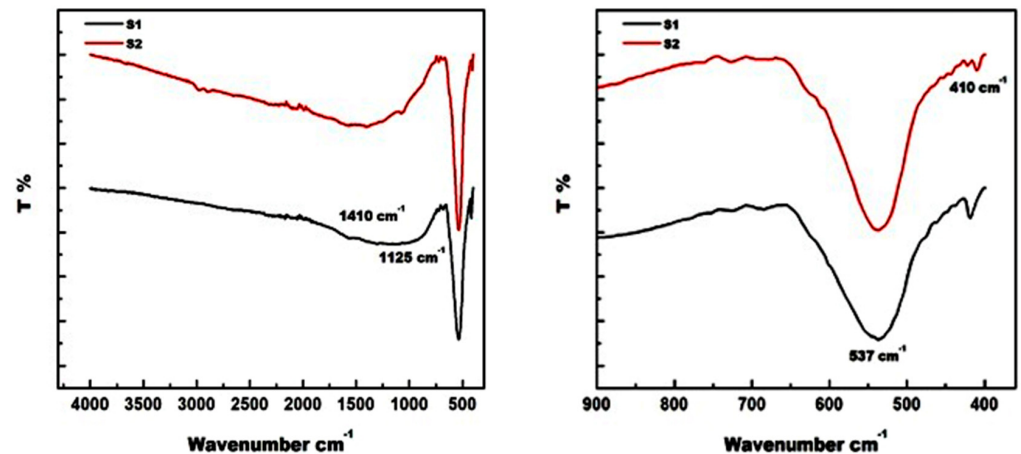


Figure 2. FTIR of the S1 (NiFe_2O_4) and S2 ($\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$) samples.

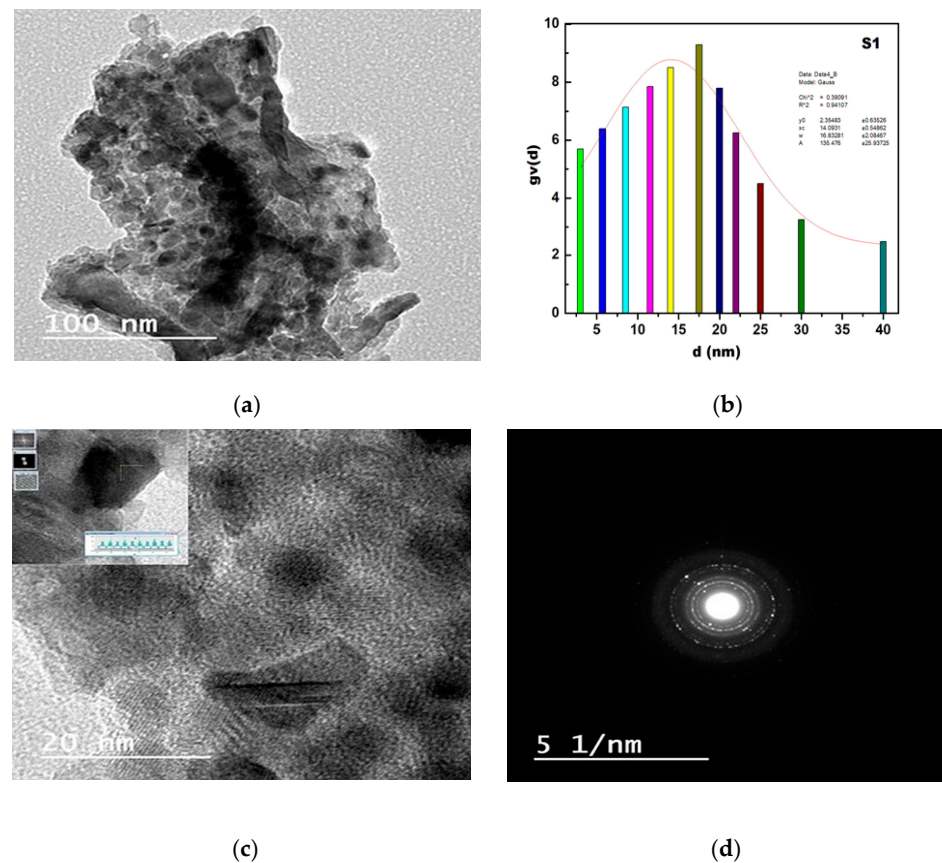


Figure 3. TEM analysis of the S1 sample: (a) TEM; (b) particle size distribution; (c) FFT; and (d) SAED.

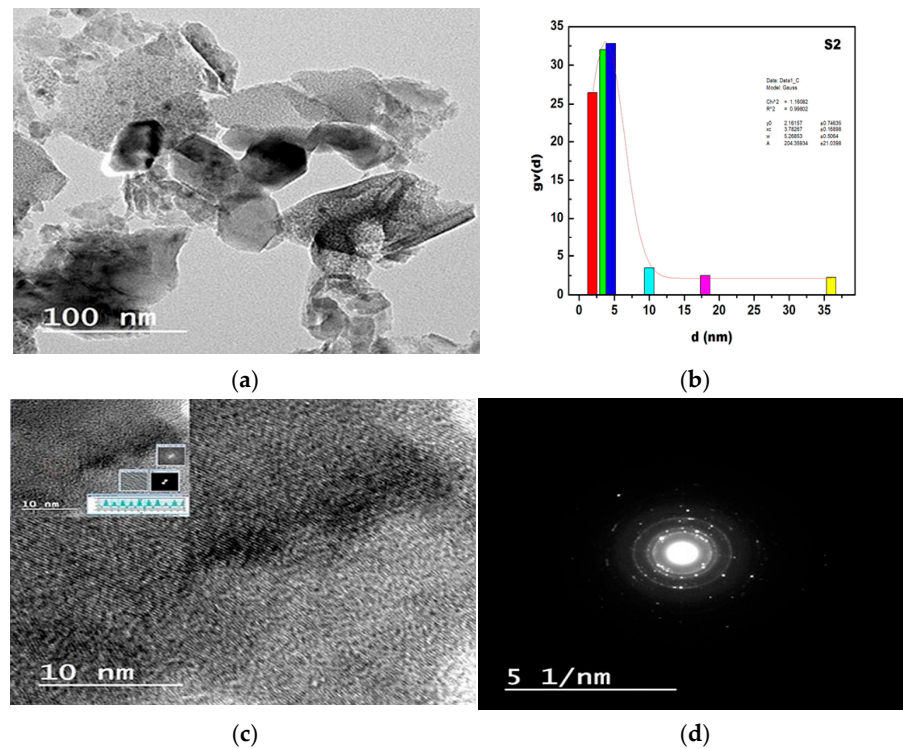


Figure 4. TEM analysis of the S2 sample: (a) TEM; (b) particle size distribution; (c) FFT; and (d) SAED.

3.4. Magnetic Properties

Under an applied magnetic field, different information on the changes in magnetization for Zn substituted and unsubstituted NiFe_2O_4 powders can be obtained from the hysteresis illustrated in Figure 5. These curves were constructed using a VSM technique at room temperature and an applied magnetic field in the range of -20 to 20 kG. An examination of the measured hysteresis loops confirms the formation of typical soft magnetic ferrites depending upon the narrow loop area of the magnetization curves. In addition, the resulted ferrites have ferromagnetic characteristics depending on the typical shape of the hysteresis loop, which has an S-type. The magnetic properties, including the coercive field (H_c), remanent magnetization (M_r), saturation magnetization (M_s), squareness (M_r/M_s), anisotropy constant (K_a), initial permeability (μ_i), and magnetic moment (μ_m) per unit formula in Bohr magneton of the fabricated samples, can be calculated according to the next expression [19]:

$$\mu_m = M_w M_s / 5588 \quad (11)$$

$$\mu_i = M_s^2 d / K \quad (12)$$

$$K_a = H_c M_s / 0.96 \quad (13)$$

Where M_w is the molecular weight. All calculated data are presented in Table 3. This table shows that the values of M_r/M_s and H_c decrease in the presence of Zn ions. Counter behavior was observed for the values of K_a , M_r , M_s , μ_i , and μ_m in presence of previous zinc ions.

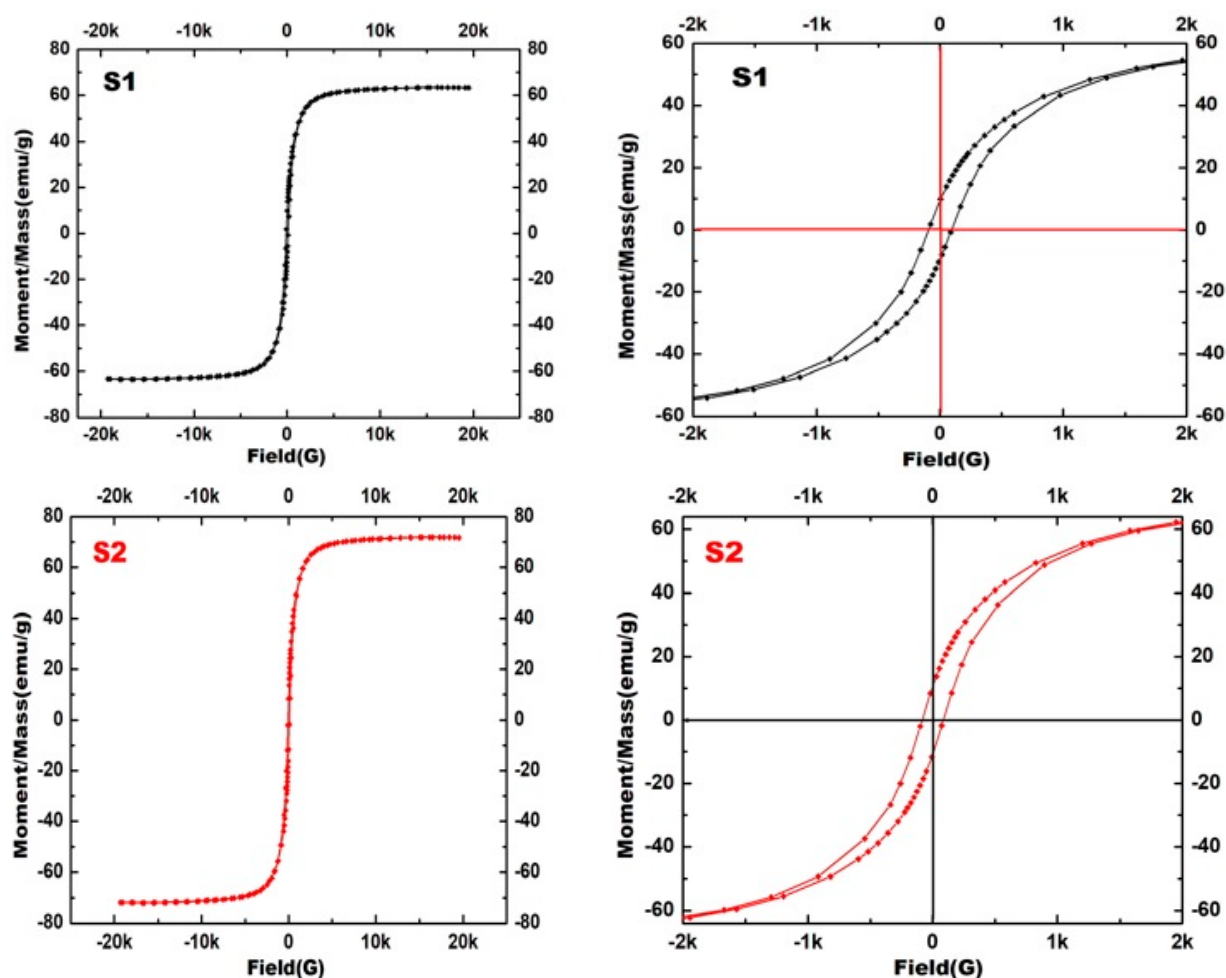


Figure 5. The magnetic hysteresis loops of the S1 (NiFe_2O_4) and S2 ($\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$) samples at room temperature.

Table 3. The magnetic properties of S1 and S2 samples.

Parameters	S1	S2
M_s , emu/g	54.3	62.19
M_r , emu/g	9.28	9.45
M_r/M_s	0.1709	0.1520
H_c , Oe	96.28	86.19
μ_m	2.279	2.610
μ_i	27.13	19.77
K_a , erg/cm ³	5503.16	5642.26

4. Discussion

The substituted and unsubstituted nickel ferrite nanoparticles were prepared using different methods, the most important of which was the self-combustion method since it is an effective, low-cost, and fast method for preparing highly pure and homogeneous nanocrystalline materials. Indeed, the combustion method depends entirely on a heat-initiated, self-sustained reaction between both the metal nitrate as an oxidizer and the fuel, which promotes the reaction by heating at a low temperature (≥ 200 °C) so it can be called a self-propagating high temperature preparation. Different factors have a direct effect on the various properties of the combusted product. These factors include the heat content of the reactants, the flame-temperature generated during combustion, fuel nature, and the effectiveness of the fuel-to-oxidizer ratio [10–15].

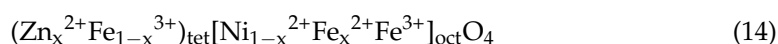
Among the important and influential fuel materials, we find glycine, which acts as a gelation agent as well as fuel, through a redox reaction. Glycine (3 mol) acts as a gelation agent because it has zwitterion properties [22]. The zwitterion characteristics of glycine resulted in the formation of a colloidal gel of Zn and/or Ni-Fe metal oxide nanoparticles depending on two distinct end groups, namely carboxylic ($-\text{COOH}$) and amino ($-\text{NH}_2$), which can be used to create complexes with the relevant metal ions [23]. The gel is formed with the following steps: (i) the formation of metal hydroxides due to the initial reactions during the formation of the combustion mixture, (ii) the formation of polymeric or cluster-like polyoxometallates due to the polycondensation previous mixture after heating at $80\text{ }^\circ\text{C}$, and (iii) the structural and temporal evolution of these clusters, resulting in the investigated gel. Regarding the role of glycine as fuel, it supplies the energy required for combustion of the gel after heating it at $300\text{ }^\circ\text{C}$ for 15 min, yielding a fine burned powder containing NiFe_2O_4 or $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ nanoparticles.

The results of XRD revealed that (i) Zn-substituted and unsubstituted nickel ferrites had the same characteristics of Bragg reflection that confirm the fabrication of a single spinel type structure of $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ and NiFe_2O_4 structure, respectively. (ii) The crystallinity of $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ are smaller than that of NiFe_2O_4 except that the crystal plane reflection corresponds to (220). This exception confirms the preference of Zn^{2+} ions to occupy A-site in the spinel ferrite [8,15]. The incorporation of Zn^{2+} ions at A-site could be stimulated by the migration of Fe^{3+} ions from A-site to B-site with its reduction to Fe^{2+} ions in order to compensate the deficiency in Ni^{2+} ions at B-site. (iii) Because the ionic radius of both Zn^{2+} ions (0.074 nm) and Fe^{2+} ions (0.076 nm) is higher than that of Fe^{3+} ions (0.064 nm), the augmentation in the crystal parameters of the substituted nickel ferrite compared to that of the unsubstituted Ni ferrite indicates the lack of Fe^{3+} ions. Indeed, the substitution process of nickel ferrite by Zn ions resulted in an augment in the values of δ , ϵ , a , L_A , L_B , r_A , r_B , A-O, and B-O parameters, indicating a lattice expansion of $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ nanoparticles. In addition, this treatment displays an increase in the value of D_x depending on the higher atomic weight of Zn. (iv) On the contrary, the crystallite size of $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ is smaller than that of NiFe_2O_4 nanoparticles. A lattice expansion of $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ occurs with a decreasing crystallite size due to a decrease in intra-crystalline pressure resulting from the electrostatic interaction of ions and electrons in the metal lattice [24,25] or vacancy super saturation [26,27].

An FTIR analysis of the manufactured solids in the range of $1000\text{--}400\text{ cm}^{-1}$ can provide us with intrinsic vibrations of the metal ions in the lattice structure. The absorption bands corresponding to ν_1 (tetrahedral site) and ν_2 (octahedral site) for the crystalline lattice of M-O are located in the range of $600\text{ to }400\text{ cm}^{-1}$ [19]. The difference in bond lengths for the M-O ions in tetrahedral and octahedral sites led to the different frequencies of distinctive vibrations for these sites. The cation distribution is associated with the position of cations in the sub-lattice (A- and B-sites) of ferrite. This cation distribution is considered the key factor or the influencing parameter in the different properties of ferrites [10]. An inspection of FTIR spectra of the fabricated samples revealed that (i) these samples have cubic spinel structure depending upon the appearance of two main characteristic absorption bands at 537 cm^{-1} and $422\text{--}410\text{ cm}^{-1}$ according to the assumption of Waldron [27]. Based on the results of FTIR and XRD, the S1 and S2 samples consisted entirely of $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0$ and 0.3) with a cubic spinel type structure. (ii) The substitution process by Zn brought about a rise in the intensity of the absorption band at 537 cm^{-1} with subsequent splitting of the absorption band around 400 cm^{-1} to obtain two narrow and weak absorption bands at 422 cm^{-1} and 410 cm^{-1} . The increase in the intensity of the absorption band at 537 cm^{-1} could be attributed to an incorporation of zinc ions in the tetrahedral site depending on the preference of these ions for this site. The splitting of the absorption band, which was observed in the FTIR spectra of the S1 specimen at 419 cm^{-1} , to two narrow and weak bands at 422 cm^{-1} and 410 cm^{-1} is due to a decrease in the concentration of Ni ions at B-site with a presence of both Ni^{2+} and Fe cations at this site. With the incorporation of Zn^{2+} cations, Fe^{3+} cations in the A-site will migrate to the B-site with subsequent conversion to Fe^{2+}

cations. (iii) $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ has a mixed or random spinel structure if the bulk ZnFe_2O_4 and NiFe_2O_4 are normal and inverse spinel ferrites, respectively [3,5,6,15,17,28]. However, the formation of a solid solution of $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ depends on a certain combination between both ZnFe_2O_4 and NiFe_2O_4 nano-particles [15,17]. (iv) The presence of a carbon trace, which originated from an internal combustion process of glycine, resulted in an appearance of two broad absorption bands at 1410 cm^{-1} and $1125\text{--}1075\text{ cm}^{-1}$ due to the stretching vibrations of both C-H and C-OH [10].

Variation in the population of both Zn^{2+} and Fe^{3+} cations with a subsequent conversion of some Fe^{3+} cations to Fe^{2+} cations results in numerous modes of vibration at both the A- and B-sites, resulting in changes in the different absorption bands and their widening [29]. In other words, the distribution of Fe^{3+} cations between both the tetrahedral or octahedral sites depends on the other cations in the crystal lattice of ferrite. An incorporation of Zn^{2+} cations in the lattice of NiFe_2O_4 will minimize the content of Fe^{3+} cations on the tetragonal site because the cations of Zn^{2+} have a stronger affinity for this site. These observations enabled us to speculate the following convention to an imagining of the position of the cations in the A- and B-sites of ferrite:



An investigation of Figures 3 and 4 revealed that (i) there are drastic change in the morphology of the Zn-substituted NiFe_2O_4 , or S2, sample compared to the unsubstituted nickel ferrite, or S1, sample, as shown in TEM images in Figures 3a and 4a, respectively. An analysis of the microstructure for the S1 specimen reveals that its particles are almost semi-spherical with various agglomerations having grain boundaries. Moreover, regular spherically shaped particles and some irregularly cubic particles were observed, as shown in the S2 specimen. In addition, many aggregates disappeared in the S2 solid, with a significant decrease in the size of particles yielding uniform distribution of grains. Figures 3c and 4c confirm that the fabricated samples consisted of nanoparticles having a spinel type structure. (ii) The CSD histograms of the manufactured samples revealed that the grain diameter lies in the range between 6 nm and 20 nm for the S1 sample and between 0.5 nm to 3 nm for the S2 sample with average particles sizes located at 1.5 nm and 13 nm, respectively. This variation in the diameter of grains can be attributed to different factors, such as the coefficient of the diffusion and the dissimilar ions content [10]. Indeed, a one pot synthesis of the as-synthesized samples using a glycine-assisted combustion method led to the rapid evolution of a large volume of gaseous products, which dissipates the heat of the process and limits the increase in temperature, reducing the probability of local sintering among the investigated particles with subsequent fabrication of a fine porous powder [30]. (iii) A fast Fourier transform (FFT) of the manufactured samples was determined due to the appearance of the corresponding lattice planes of these samples. The observed crystallographic values of the interplanar distance (d) are 0.2552 nm and 0.2546 nm concerning plan (311) of the samples studied as shown in Figures 3c and 4c. These results confirm the formation of the spine ferrite and coincide with those determined using the XRD analysis. Therefore, the XRD and TEM confirm the spinel phase formation. (iv) Figures 3d and 4d show the patterns of SAED, which consisted entirely of concentric rings containing many differently oriented crystallites with good crystalline quality and the clear space fringe. These figures depict a regular pattern of bright spots, indicating the formation of polycrystalline nanoparticles. Indeed, the S1 specimen is characterized by a uniform intensity distribution along the ring circumference, leading smooth rings as observed in Figure 3d. On the other hand, the S4 has a non-uniform intensity distribution along the resulting rings due to a decrease in its crystallinity as determined in Figure 4c [10].

Our previous work on the preparation of nickel ferrite using a glycine-assisted combustion method showed the following: (i) changing the glycine content brought about some progressive modifications in the magnetic characteristics of Ni ferrite. Using 0, 1, 2, 4, and 8 moles of glycine led to an increase in the magnetization of NiFe_2O_4 from 0.838 emu/g to 57 emu/g and an increase in its retentivity, squareness, and coercivity as well [16]. (ii) Zn substituted nickel ferrite ($\text{Zn}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$) has the values of 57 emu/g, 10 emu/g, and

58 G for M_s , M_r , and H_c , respectively [15]. In other words, the values of magnetism for the unsubstituted and substituted nickel ferrites in our previous studies are smaller than those of these ferrites present in this study. The opposite behavior was observed in the values of coercivity. These findings are due to the changes in the contents of the fuel (glycine) and zinc used. Because of these, the changes have different effects on the material density, structure, microstructure, defects, and cation distribution of the ferrites prepared [10,15,16]. All these effects will have different effects on the magnetic behavior of the as-synthesized ferrites, and this will be clear in the next explanation.

In this study, the magnetism of the S2 specimen is higher than that of the S1 specimen despite the pronounced decrease in its particle size and dissolution of nonmagnetic Zn ions in its crystal lattice. In this point, Kumar and coworkers reported to prepare the same ferrites using an oxalylhydrazide-mediated combustion method followed by heating at 600 °C for 2 h [31]. These authors found that the substitution of Ni by Zn ions resulted in an increase in both the magnetization and particle size from 22.17 emu/g and 20 nm to 38.73 emu/g and 28 nm. Indeed, the difference in the magnetization of a sub-lattice (B- and A-sites) is proportional to the saturated magnetization of ferrite. In normal spinel based ZnFe_2O_4 , A-sites are occupied by Zn^{2+} cations while in reverse spinel based NiFe_2O_4 , these sites are filled by Fe^{3+} cations. The combination of Zn and Ni ferrites to fabricate a solid solution of $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ resulted in the replacement of some Fe^{3+} cations in A-sites by Zn^{2+} cations with the subsequent conversion of some Fe^{3+} cations to Fe^{2+} cations and their migration to B-sites. However, Zn^{2+} ions do not contain any unpaired electrons while Ni^{2+} , Fe^{2+} , and Fe^{3+} ions have 2, 4, and 5 unpaired electrons, respectively. The theoretical values of the magnetization for NiFe_2O_4 and $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ spinels can be calculated depending on the speculated distribution of the Zn^{2+} , Ni^{2+} , Fe^{2+} , and Fe^{3+} cations, which are shown in Equation (2). The net magnetic moment due to the number of unpaired electrons in $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0$, and 0.3) can be calculated according to the speculated cation distribution in Equation (2). The calculated net magnetic moment from this equation for the S1 and S2 samples increases from 2 to 4.1 is consistent with the experimental net magnetic moment (μ_m) 2.67 μ_B and 3.04 μ_B , shown in Table 3. These results reported that the theoretical values of the magnetization were consistent with the magnetization data, which indicates an increasing trend with the substitution of Ni by Zn. In other words, the overall magnetization of the Zn substituted nickel ferrite increases although a decrease of the magnetic moment at A- sites due to the Zn^{2+} ions occupying these sites. However, the substitution of Ni by Zn in order to synthesis of the substituted nickel ferrite using glycine-assisted combustion method resulted in presence of the Zener double exchange (ZDE) mechanism leading to enhanced hole density [31,32]. This is due to the presence of Fe^{2+} ions with Fe^{3+} cations at B-sites. Thus, these results confirm that M_s is linked to the material's structure depending on the cationic distribution of Fe/Ni ions at octahedral and tetrahedral sites. Increasing M_s can be understood in terms of highly super-exchange interaction within the inter-sub-lattice (A–B), which occurred between Fe^{3+} ions in A- and B-sites over oxygen ions. In addition, the effect of ZDE at B-sites plays an important role in detecting the M_s of different ferrites.

Regarding the squareness of the investigated ferrites, values of M_r/M_s were smaller than 0.5, indicating a presence of uniaxial anisotropy. This anisotropy (K_a) increases with the substitution of Ni with Zn, referring to the effects of the surface spin-disorder produced from the canted spin on the nanoparticles surface. Moreover, an increase in anisotropy and reduction of particle size led to a decrease in the initial permeability (μ_i), which originated from the domain wall motion. Upon the transition from a multidomain to a single-domain microstructure, the spin directions within a grain, departing from a more or less random distribution, become uniformly oriented.

Moreover, the H_c of nanoparticle-based ferrites is influenced by various factors, such as particle size, canting angle, and anisotropy. Zn ions have zero orbital magnetic moments and zero spin angular moments, yielding no anisotropy compared with Ni and Fe ions. However, the substitution of Ni by Zn ions resulted in a very slight decrease in the value

of H_c due to a reduction in particle size. These findings indicate the presence of superparamagnetic grains in the substituted nickel ferrite, which contribute to the non-saturation. A mossbauer analysis for $Zn_xNi_{1-x}Fe_2O_4$ ($x = 0$ and 0.3) carried out by Kumar and coworkers confirms presence of a super paramagnetic relaxation effect, electronic spin–spin, and spin–lattice interactions with neighboring ions. This finding confirms the validity of using ferrites prepared in high-frequency applications [31,32].

Finally, the substitution of some Ni ions by Zn ions resulted in the fabrication of mixed nickel–zinc ferrite with no-secondary phases and the crystal field distortion depending on irregular cation distribution. This finding resulted in the spatial and temporal symmetries with a subsequent trigger of the vibrational bands or magnetic characteristics change rather than a simple alternation of different cations in the interstitial sites.

5. Conclusions

$Zn_xNi_{1-x}Fe_2O_4$ ($x = 0$ and 0.3) nanoparticles were successfully synthesized using glycine-assisted combustion technique as a gentle, simple, and economical method. Through the preparation and characterization of these ferrites, we can draw the following points:

The zwitterion characteristics of glycine helped a lot in obtaining nanosized spinel $Zn_{0.3}Ni_{0.7}Fe_2O_4$ and $NiFe_2O_4$ particles in one step and a short time. The treatment of Ni ferrite using a certain amount of Zn led to an enhancement of the lattice parameters with a subsequent inhibition of the crystallite size.

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FTIR of unsubstituted and Zn substituted nickel ferrites have been analyzed in the frequency range of $4000\text{--}400\text{ cm}^{-1}$. Two prominent bands were determined in FTIR spectra of the ferrites studied, a high frequency band at 537 cm^{-1} and a low frequency band at $422\text{--}410\text{ cm}^{-1}$, were assigned to the tetrahedral and octahedral sites of the spinel type structure. The glycine-mediated combustion method led to the manufacturing of polycrystalline spinel type nickel ferrite particles and those substituted by zinc ions in nanoscale size.

An improvement of the magnetization of nickel ferrite nanoparticles was achieved by substituting Ni by Zn ions. The value of M_s for $Zn_{0.3}Ni_{0.7}Fe_2O_4$ was 62.9 emu/g while such a value for $NiFe_2O_4$ was 54.3 emu/g . This increase could be attributed to an increase in the magnetic moment for the cations at octahedral sites in the spinel Zn substituted nickel ferrite. This increase in the sum magnetic moment at B-site resulted in an increase in the super-exchange interaction within the inter-sub-lattice (A–B), which happens between Fe^{3+} ions in A- and B-sites over oxygen ions.

Not increasing the squareness value by 0.5 indicates the presence of uniaxial anisotropy. An increase of anisotropy confirms a magnetic multidomain–single-domain transition at a “critical size value”, which is a well-known phenomenon for ferromagnetic materials, such as Ni, Co, and Fe.

Increasing the magnetization of Zn substituted nickel ferrite was accompanied by a slight decrease in the coercivity due to an increase in the surface anisotropy of small grains.

The effective magnetic moment and exchange interaction in nickel ferrite increased by substituting Ni ions with Zn ions with the fabrication of a multi-element ferrite system. The ferrite is prepared in a pure phase with no secondary phases, which led us to explore the effect of symmetry-based cation distribution of different elements.

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