Effects of Zn Substitution on Structure Factors, Debye-Waller Factors and Related Structural Properties of the Mg$_{1-x}$Zn$_x$FeNiO$_4$ Spinels

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Abstract: The effects of Zn$^{2+}$ ions substitutions on the Debye-Waller Factors, structure factor and other related structural properties of the Mg$_{1-x}$Zn$_x$FeNiO$_4$ (where 0.0\(\leq\)x\(\leq\)1.0) spinels have been investigated using the XRD, TEM, SEM and FT-IR tools. The Mg$_{1-x}$Zn$_x$NiFeO$_4$ samples were prepared using the conventional ceramic solid state sintering techniques at temperatures around 1100°C. The Mg$_{1-x}$Zn$_x$NiFeO$_4$ spinels have predominantly inverse type structure with inversion factor, \(\lambda\) in the range 0.69 to 0.36. The X-ray diffraction (XRD) patterns of all compositions showed the formation of cubic spinel structure. The lattice constant “a” increases from 8.3397Å for MgFeNiO$_4$ to 8.3855Å for ZnFeNiO$_4$ spinels. The increases in lattice parameters have been attributed to the replacement of small Mg$^{2+}$ ions (0.66 Å) with the Zn$^{2+}$ (0.74 Å) ions of a larger ionic radius. The IR spectra confirm the existence of two main absorption bands \(\upsilon_1\) and \(\upsilon_2\) in the frequency range of (400–1000 cm$^{-1}$), arising due to the tetrahedral (A) and octahedral (B) stretching vibrations respectively. Values of both \(\upsilon_1\) and \(\upsilon_2\) decrease as Zn content increases. The scanning electron microscope (SEM) and transmission electron microscope (TEM) images showed aggregates of stacked grains. The normalized XRD intensities of the main (hkl) planes were used in the estimation of the Debye-Waller factor. Values of the Debye-Waller factors were estimated to be in the range (0.77-1.44A$^2$). The calculated and observed relative intensities and areas of the most related plains to cation distributions (i.e.: the (220), (311), (222), (400), (422), (511) and (440) plains) were obtained by normalizing with respect to the most intensive reflection from the (311) plane. An inverse relation between the ordering, Q and inversion, \(\lambda\) factors exists in these partially inverse spinels. Both Q and \(\lambda\) decrease as Zn content (x) increases in the sample. The cation distributions indicate that the sample, MgFeNiO$_4$ with x=0, \(\lambda=2/3\) and maximum configurational entropy Sc(\(=\)15.876 J/mol, K) should represents the sample of the complete randomness of cation distributions in these spinels and can be written as (Mg$_{1/3}$Fe$_{2/3}$)[Mg$_{2/3}$Fe$_{1/3}$Ni$_{1/3}$]O$_4$. In general the variation of the different structural parameters with Zn content lie on two different regions, the first region for x values (0.0-0.6) the “highly normal” and the second region for x values (0.6-1.0) the “highly inverse” type structure.

Keywords: XRD, TEM, SEM, FTIR, Structure Factor, Debye Waller Factor, Order Parameter

1. Introduction

Spinels are characterized by many unique magnetic and electrical properties. The high electrical resistivity gives rise to low eddy current and dielectric losses. Ferrites have also been used in other important applications such as information storage systems, gas sensors, microwave devices and magnetic recording and electronic industries [1-2]. The properties of the spinel systems depend on many factors such
as the preparation techniques, heat treatment processes, chemical compositions and the cations distributions among the tetrahedral (A-) and octahedral (B-) sublattices sites. The wide variations in these properties are direct reflection of their ability to accommodate and distribute a variety of cations among their two subsites the (A-) and (B-) sites. The distributions of cations among the A- and B- sites depend on their affinity for both positions, which depends upon many factors such as the stabilization energy, ionic radii, size of the interstices, electronegativity, coulomb energy, the types of synthesis techniques and conditions during the synthesis process [2]. The anions (such as O, S, ...) in the spinel structure form 96 interstices. These interstices are distributed over the tetrahedral and octahedral sites as: 64 at the A- sites and 32 at the B- sites. Not all the 96 interstices are occupied by interstices, only 8 of the tetrahedral and 16 of the octahedral interstices are known to be occupied by cations. The general formula for the cation distributions in spinels can be written as \((X_{1+y}Y_{1-y})_4O_4\) where \(X^{2+}\) and \(Y^{3+}\) represent transition metal ions. The factor \(\lambda\) represents the fraction of \(Y^{3+}\) metals at the A-sites, which equals to 0 for normal spinel and 1 for the inverse spinels. For mixed spinels the inversion factor \(\lambda\) values lies between 0 and 1. The \(\text{ZnFe}_2\text{O}_4\) [3], \(\text{CdFe}_2\text{O}_4\) [4] ferrites and \(\text{ZnCr}_2\text{O}_4\) chromites [5] have the normal spinel type structure, in which the \(\text{Zn}^{2+}\) and \(\text{Cd}^{2+}\) ions occupy the A-sites while the \(\text{Fe}^{3+}\) and \(\text{Cr}^{3+}\) ions occupy the B-sites. The Nickel ferrites, \(\text{NiFe}_2\text{O}_4\) have the inverse spinel structure [3], in which the \(\text{Fe}^{3+}\) ions occupy the tetrahedral sites where the octahedral B-sites are occupied by the \(\text{Ni}^{2+}\) and \(\text{Fe}^{3+}\) ions. The Magnesium ferrite, \(\text{MgFe}_2\text{O}_4\), has the mixed spinel structure [6-7], in which the degree of inversion depends on many factors such as the preparation technique and the heat treatment in particular. In principle, the large (small) cations should occupy the largest (smallest) sites, the octahedral (tetrahedral) sites. Since the trivalent cations are generally smaller than the divalent ones, therefore, there should be some tendency for the trivalent cations to reside on the smallest sites, the tetrahedral sites, leading to the inverse or partially inverse type structure. This factor works in opposite direction of the electric charge factor; that the high (low) electrical charge causes the cations to occupy the larger (smaller) coordination number, the octahedral (tetrahedral) sites [8] leading to the normal (inverse) type structure.

The effects of replacing \(\text{Fe}^{3+}\) ions with trivalent ions such as \(\text{Cr}^{3+}\), \(\text{Ni}^{2+}\) and \(\text{Al}^{3+}\) ions have been extensively studied by many workers. It has been well established that \(\text{Cr}^{3+}\), \(\text{Ni}^{2+}\) and \(\text{Al}^{3+}\) ions have strong tendency to reside at the octahedral sites while the \(\text{Zn}^{2+}\) and \(\text{Cd}^{2+}\) ions have strong preference to reside on the tetrahedral sites. Other cations such as the \(\text{Fe}^{3+}\), \(\text{Co}^{2+}\), \(\text{Mn}^{2+}\) and \(\text{Mg}^{2+}\) cations can be present at both sites [9-10]. The cation distributions among the A- and B- sites

\[
(1-x)\text{MgO} + x\text{ZnO} + 0.5(\text{Fe}_2\text{O}_3) + 0.5(\text{Ni}_2\text{O}_3) \rightarrow \text{Mg}_{1-x}\text{Zn}_x\text{FeNiO}_4
\]

\((\lambda=1.5404\text{Å})\). The scan’s range was kept the same for all samples (20 = 10°-100°) using a step size of (0.02°) with a sampling time of (2s). The XRD scans were done for only six samples (x= 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0). Samples for IR

\[
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\]
spectra scanning were prepared by mixing small quantity of the powder of the samples with solid KBr. The mixed powder was then pressed at 10 tons/cm² by a hydraulic press to produce thin cylindrical samples of 1.3 cm in diameter. The IR measurements were recorded at room temperature in the range from 400 to 4000 cm⁻¹ using PERKIN-ELMER-1430 infrared spectrophotometer. The microstructure and sample surface morphology were examined with analytical scanning electron microscope (ASEM) model JSM-6510LA-JEOL and transmission electron microscope model JEM-1400-JEOL. Details of the experimental techniques can be found in reference [22].

3. Results and Discussions

3.1. The X-Ray Diffraction Analysis

The X-ray diffraction spectra of the Mg₁₋ₓZnₓFeNiO₄ spinels are shown in Figure 1. All samples showed clear XRD reflections from the plains (220), (311), (222), (400), (440), (422), (511), (620) and (533). This can be taken as a good indication of the formation of the single phase cubic spinel structure with the Fd3m space group. These reflections agree quite well with powder reflections of the majority of the spinel systems [23]. The Mossbauer tool has been used to determine the true values of the lattice parameters, a_shadow for each sample will be plotted versus Nelson-Riley function, F(θ) [23]; which is given as;

$$F(\theta) = \frac{1}{2} \left( \cos^2 \frac{\theta}{2} + \frac{\cos^2 \theta}{\theta} \right)$$

These plots form straight lines with negative slopes. The accurate lattice constants “a_exp” values were obtained by the least square fitting of the a_shadow values versus F(θ) followed by extrapolation to F(θ)=0 at θ=90° as shown in Figure 2. The extrapolated values of the lattice constant, a_exp were presented in Table 2 as a function of the Zn content in the sample. The true values of the lattice constant, a_true were found to be 8.3594Å and 8.4096Å for the MgFeNiO₄ and ZnFeNiO₄ samples respectively. The increases in the a_exp values can be justified on the basis of the ionic radii differences, where smaller Mg²⁺ (0.66Å) cations have been replaced by larger Zn²⁺ (0.74Å) cations. These values agree with those reported [12] for the similar samples Mg₁₋ₓZnₓFeNiO₄ spinels using Rietveld method to be 8.3397Å for MgFeNiO₄ and 8.3855Å for ZnFeNiO₄. These values agree with those reported [12] for the similar samples Mg₁₋ₓZnₓFeNiO₄ spinels using Rietveld method to be 8.3397Å for MgFeNiO₄ and 8.3855Å for ZnFeNiO₄.

Table 1. The inter spacing of the different (hkl) planes of the Mg₁₋ₓZnₓFeNiO₄ spinels.

| x  | (hkl) | Sin(θ)  | d- spacing (Å) | a_shadow (Å) |
|----|-------|---------|----------------|--------------|
| 0.0| 220   | 0.261104| 2.949787       | 8.343258     |
|    | 311   | 0.306135| 2.515881       | 8.344234     |
|    | 400   | 0.318929| 2.414961       | 8.365671     |
|    | 422   | 0.451973| 1.704083       | 8.347675     |
|    | 440   | 0.621183| 1.477791       | 8.359471     |
|    | 511   | 0.260457| 2.957111       | 8.363974     |
|    | 400   | 0.305444| 2.521574       | 8.363115     |
|    | 222   | 0.318318| 2.419596       | 8.381726     |
| 0.2| 400   | 0.316765| 2.091326       | 8.339704     |
|    | 422   | 0.451168| 1.707126       | 8.363176     |
|    | 440   | 0.520358| 1.480135       | 8.372906     |
The present results agree with those reported for other spinel systems such as ZnFeCrO$_4$ as (a=8.3764Å) [21], MgFeCrO$_4$ as (a=8.369Å) [24, 26], CoFeCrO$_4$ as (a=8.362Å) [25], Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ as (a=8.407Å) [27] and Co$_{0.5}$Zn$_{0.5}$Al$_{0.5}$Fe$_{1.5}$O$_4$ as (a=8.37Å) [28].

Values of the ionic radii at the tetrahedral and octahedral sites can be calculated using the following relations [29]:

$$r_A = \left( \frac{\sum C_n r_n}{\sum C_n} \right)_{\text{tetrahedral}} \quad \text{and} \quad r_B = \left( \frac{\sum C_n r_n}{\sum C_n} \right)_{\text{octahedral}}$$



Where $C_n$ and $r_n$ represent the concentration and radius of the cations at the A- and B- sites respectively. Values of $C_n$ for the concerned cations have been taken from the cation distributions determined from Mossbauer study [12]. Values of the cation radius for Mg$^{2+}$, Zn$^{2+}$, Fe$^{3+}$ and Ni$^{3+}$ ions have been taken as 0.66, 0.74, 0.67 and 0.70Å respectively [30].

The calculated values of the average cation radius $r_A$ and $r_B$ sites are shown in Table 2. It is clear from Figure 3 that values of $r_A$ and $r_B$ vary non-linearly with Zn content. The variations of $r_A$ and $r_B$ reflect the changes of the cation distribution at the tetrahedral and octahedral sites, which can be explained as the Zn$^{2+}$ (Mg$^{2+}$) concentration at the A- and B- sites increases (decreases) a redistribution of the cations and migration of some of the Fe$^{3+}$ ions from the A- to the B-sites. This results in a reduction of the inversion factor, $\lambda$ of the concerned samples. The overall resultant changes in the cation distribution were reflected in the increase of the lattice parameter $a_{\text{exp}}$ values with Zn content. Similar results have been shown by other related spinels such as Mg$_{1-x}$Zn$_x$FeCrO$_4$ [31], Cu$_{1-x}$Zn$_x$FeCrO$_4$ [32], Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ [33] and Cr$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ [34] and Ni$_{0.5}$Zn$_{0.5}$FeCrO$_4$ [35].

**Table 2.** The inter-ionic radii, the lattice constants, oxygen position parameter, the inter-ion bond lengths of the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels.

| x  | a_{\text{exp}}(Å) | a_{\text{th}}(Å) | r_A(Å) | r_B(Å) | $r_{\text{avg}}$(Å) | u_A | u_B | u_{avg} | Reff(Å) | RA(Å) | RB(Å) | Ravg(Å) |
|----|-------------------|------------------|--------|--------|---------------------|-----|-----|---------|---------|------|-------|---------|
| 0.0| 8.3594            | 8.3681           | 0.7478 | 0.7062 | 0.7148              | 0.3914 | 0.3784 | 0.3849 | 1.9909  | 1.9531 | 2.0104 | 1.9818  |
| 0.2| 8.3690            | 8.3793           | 0.7478 | 0.7062 | 0.7148              | 0.3914 | 0.3784 | 0.3849 | 1.9909  | 1.9531 | 2.0104 | 1.9818  |
| 0.4| 8.3804            | 8.3913           | 0.7478 | 0.7062 | 0.7148              | 0.3914 | 0.3784 | 0.3849 | 1.9909  | 1.9531 | 2.0104 | 1.9818  |
| 0.6| 8.3949            | 8.4104           | 0.7478 | 0.7062 | 0.7148              | 0.3914 | 0.3784 | 0.3849 | 1.9909  | 1.9531 | 2.0104 | 1.9818  |
| 0.8| 8.4080            | 8.4198           | 0.7478 | 0.7062 | 0.7148              | 0.3914 | 0.3784 | 0.3849 | 1.9909  | 1.9531 | 2.0104 | 1.9818  |
| 1.0| 8.4096            | 8.4201           | 0.7478 | 0.7062 | 0.7148              | 0.3914 | 0.3784 | 0.3849 | 1.9909  | 1.9531 | 2.0104 | 1.9818  |
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Figure 2. Values of lattice constants, $a_{\text{th}}$ versus $F(\theta)$ for the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels.

Figure 3. The ionic radii $r_A$ and $r_B$ at the A- and B- sites versus Zn content ($x$) for the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels.

Most of the structural parameters such as the cations-anions bonds $R_A$ and $R_B$ at the A- and B- sites respectively and the theoretical values of the lattice constant, $a_{\text{th}}$ and many others parameters depend on the value of the oxygen positional parameter $u$. Accordingly, it has to be estimated first. The $u$ parameter is directly related to the average ionic radii at the tetrahedral and octahedral sites through the following relations [36];

$$
u_A = \frac{(r_A + r_o)}{2\sqrt{a_{\text{th}}}} + \frac{1}{4}$$
$$
u_B = \frac{5}{2} \frac{(r_B + r_o)}{a_{\text{th}}}$$

$$
u_{\text{avg}} = \frac{(u_A + u_B)}{2}$$

(5)

where $r_A$ and $r_B$ represent the average cationic radius at the tetrahedral and octahedral respectively. The anion radius $R_o$ has been taken to be 1.38Å [30]. Figure 4 shows the relation between $u_{\text{avg}}$ and $\lambda$ with $x$ for the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels. It is clear that values of $u_{\text{avg}}$ increase as $x$ increases, it reaches its maximum at about $x=0.6$ then it tends to saturate. The inset in Figure 4 shows the relation between $u_{\text{avg}}$ and $\lambda$. $u_{\text{avg}}$ increases first reaching its maximum at about $\lambda=0.43$ then it
decreases fast as \( \lambda \) increases. It is clear that values of \( u_{\text{avg}} \) fall in two straight line segments with different slopes. The first segment is in the range \((0.0 – 0.6)\) and the second is in the range \((0.0 – 1.0)\). The two regions cross at about \( x=0.6 \). The present results differ from those reported for perfect normal and perfect inverse spinels such as the Zn- and Ni-spinels [3]. These behaviors are supported by the variation of the inversion factor \( \lambda \) with \( x \), which also lies in two different regions crossing at about the same point. These characteristics are related to the relative structural phase changes in the mixture spinel type structure. Values of \( u_{\text{avg}} \) are shown in Table 2 as a function of Zn content (\( x \)). Values of \( u_{\text{avg}} \) for the Mg\( _{1-x} \)Zn\( _x \)FeNiO\(_4\) spinels lie in the range \((0.3780–0.3801)\) compare quite well with those reported for a large number of spinels \((0.375–0.395)\) [37].

Values of \( u_{\text{avg}} \) for the Mg\( _{1-x} \)Zn\( _x \)FeNiO\(_4\) spinels compare well with those reported for the related MgFe\(_{1-x} \)Cr\(_x \)O\(_4\) spinels [21]. The bond lengths \( R_A \), \( R_B \), \( R_{\text{avg}} \) and the effective bond lengths, \( R_{\text{eff}} \) can be evaluated using the following relations [23, 36]:

\[
\begin{align*}
R_A &= a_{\text{exp}} \left( u_{\text{avg}} - \frac{1}{4} \right) \sqrt{3} \\
R_B &= a_{\text{exp}} \left( 3 u_{\text{avg}} - \frac{11}{4} u_{\text{avg}}^2 + \frac{43}{64} \right) \\
R_{\text{avg}} &= \left( \frac{R_A + R_B}{2} \right) \\
R_{\text{eff}} &= \frac{R_A + R_B}{\sqrt{R_A^2 + R_B^2}}
\end{align*}
\]

(6)

The calculated values of \( R_A \), \( R_B \), \( R_{\text{avg}} \) and \( R_{\text{eff}} \) are shown in Table 2. The values of \( R_A \) (\( R_B \)) increase (decrease) in the range \( x=0 \) to \( x=0.6 \), then they decrease (increase) for \( x > 0.6 \). The average values of \( R_A \) and \( R_B \) increase smoothly as \( x \) increases as shown in Figure 5. The bond lengths at octahedral sites, \( R_B \) are higher than that of the tetrahedral sites, \( R_A \). This has been interpreted as more covalent bondings of cation-anion at the A-sites than that at the B-sites [38]. These results support the interpretation that correlates the decrease in the bond length to the increased covalent bonding. The nature of variations of \( R_A \) and \( R_B \) with \( x \) confirm the existence of two distinct features in these spinels. These behaviors have been reflected in the force constant strengths, which have been caused by the bond stretching frequencies at the A- and B-sites. Similar results have been shown by other spinel system such as Zn\( _x \)Cu\(_{1-x} \)FeCrO\(_4\) spinels [32]. The theoretical values of the lattice parameter, \( a_{\text{th}} \) can be evaluated using the following relations [37]:

\[
a_{\text{th}} = \frac{a}{\sqrt{3}} \left( 3R_A + 3R_B \right)
\]

(7)
Values of the experimental and theoretical lattice constants are shown as a function of the Zn contents in Figure 6. In spite of the fact that the theoretical lattice parameters are higher than those of the experimental, a very good agreement between the experimental and theoretical values of the lattice constant “a”. Figure 6 shows also the inversion factor λ as a function of the Zn content.

\[ \text{T.F.} = \frac{1}{\sqrt{3}} \left( r_A + r_O \right) + \frac{1}{\sqrt{2}} \frac{r_O}{r_B + r_O} \]  
(8)

This approaches unity if the ideal spinel cubic structure was met. Values of the calculated T. F. are shown in Table 3. It is clear that they are not equal to unity indicating the presence of some sort of distortion of the structure in these spinels. Moreover, values of T. F. lie into two straight lines with different slopes as shown in Figure 7. The distortion increases as the Zn content increases reaching maximum for \( x=0.6 \). It seems that the distortion increases as the Zn concentration on the A-sites increases. This might be caused by the large radius of the Zn\(^{2+}\) cations. The distortion starts decreasing sharply when the Zn\(^{2+}\) cations start residing on the octahedral sites.

The densities and porosity in these samples can be calculated using the following equations:

\[
\begin{align*}
\text{d}_{\text{exp}} &= \frac{m}{\nu} \\
\text{d}_{\text{XRD}} &= \frac{Z \text{M}}{\nu \text{N}_A} \\
p &= \left( \frac{\text{d}_{\text{XRD}} - \text{d}_{\text{exp}}}{\text{d}_{\text{XRD}}} \right) \times 100\% 
\end{align*}
\]

where \( \text{d}_{\text{exp}} \) and \( \text{d}_{\text{XRD}} \) represent the experimental and theoretical densities respectively, while \( p \) represent the porosity. The \( m \) and \( \nu \) represent the mass and volume of the cylindrical pellets respectively. The \( Z, \text{M} \) and \( \text{N}_A \) represent the number of molecules per unit cell (=8), average molecular mass and the Avogadro's number respectively. Values of the density and porosity have been calculated and shown in Table 3 as a function of Zn content in the sample. The density increases with increasing Zn content as shown in Figure 8-a. This might be caused by the molecular mass differences between Zn (65.926 g/mole) and Mg (23.985 g/mole).
The theoretical (true) densities, \(d_{\text{SRD}}\), are higher than the experimental (bulk) densities, \(d_{\text{exp}}\), for all samples. The \(d_{\text{exp}}\) values form (71 to 94\%) of \(d_{\text{SRD}}\). The differences between values of the densities can be attributed to the pores creation in the samples during the sintering processes at high temperatures. The apparent porosity in these samples decrease with increasing the inversion factors shown in Figure 8-b. This behaviours might convey that the more inverse the spinel the more pores and voids and less density the sample. Similar results have been reported for other spinels such as the Mg\(_{1-x}\)Zn\(_x\)Fe\(_2\)O\(_4\) spinels. The estimated values of D\(_{S-S}\) and D\(_{W-H}\) were calculated and shown in Table 3 using the Debye Scherrer’s, (D-S) [23], Williamson-Hall, (W-H) [45] and the size-strain, (S-S) [23, 46] methods. The S-S method is characterized by giving less weight to data obtained from the high angle reflections [47].

\[
\beta = \frac{K\lambda}{\cos \theta \cdot D-S}
\]

\[
(\frac{d_{\text{SRD}}}{2\sin \theta})^2 = \frac{K}{\beta_{S-S}}\left(\frac{d_{\text{SRD}}}{2\sin \theta} \cos \theta \cdot hkl\right) \cos \theta \cdot hkl + (\varepsilon_{\text{rms}})^2
\]

\[(10)\]

where \(K\) is constant has been taken as 0.89, \(\beta\) represent the peak width at half maximum (FWHM) and \(\varepsilon\) is the apparent strain, which can be related to the root-mean-square strain, \(\varepsilon_{\text{rms}}\). Values of the crystallite sizes \(D_{S-S}\), \(D_{W-H}\) and \(D_{S-S}\) were estimated by plotting the (L. H. S.) versus the first term in the (R. H. S.) of equation (9). The crystallite sizes and the microstrain in these spinels were deduced from the slope and the intercept respectively. The instrumental effect errors on the diffraction peak broadening were ignored in these calculations. The estimated average values of \(D_{S-S}\), \(D_{W-H}\) and \(D_{S-S}\) were estimated to be 31, 87 and 59 nm respectively. Table 4 shows values of the crystallite sizes versus the Zn content. It is clear from Figure 9 that values of the crystallite sizes increase first passing through broad maximum as Zn content increases then they decrease. Similar results have been reported for the NiFe\(_2\),Cr\(_2\)O\(_4\) [40] and MgFe\(_2\),Cr\(_2\)O\(_4\) [24] spinels. It is clear that values of \(D_{W-H}\) are higher than those of \(D_{S-S}\) and \(D_{S-S}\). Quite similar behaviours have been reported for the Co\(_{1-x}\),Zn\(_x\)Fe\(_2\)O\(_4\) spinels [27]. Much larger crystallite sizes have been reported for the Mg\(_{1-x}\),Zn\(_x\)Fe\(_2\)O\(_4\) [22] and Zn\(_{1-x}\)Cd\(_x\)Fe\(_2\)O\(_4\) [48] spinels. The estimated values of the microstrains from the D-S and S-S equations do not agree with each other. Values of \(\varepsilon\) from the D-S method are higher than those from the S-S method. The estimated values of the root-mean-squared strain, \(\varepsilon_{\text{rms}}\) were calculated and shown in Table 4.

### 3.2. The Crystallite Sizes

The average values of the crystallite sizes in the Mg\(_{1-x}\),Zn\(_x\)Fe\(_2\)O\(_4\) spinels have been estimated using the Debye Scherrer’s, (D-S) [23], Williamson-Hall, (W-H) [45] and the size-strain, (S-S) [23, 46] methods. The S-S method is characterized by giving less weight to data obtained from the high angle reflections [47].

| x   | \(D_{\text{obs}}\) (nm) | \(D_{\text{w-h}}\) (nm) | \(D_{\text{s-s}}\) (nm) | \(\varepsilon\times 10^3\) | \(\varepsilon \times 10^6\) | D.W.F (\(\AA^2\)) using XRD | D.W.F (\(\AA^2\)) using \(\theta_{0}\) | \(\theta_{0}\) (K) | \(\theta_{0}\) (K) ±1 | Avg. \(<\varepsilon^2>\) (\(\AA^2\)) |
|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0.0 | 33              | 100             | 61              | 1.61            | 1.08            | 1.0597          | 0.1723          | 411             | 742             | 577             | 0.0402          |
| 0.2 | 34              | 102             | 70              | 1.57            | 1.20            | 0.9567          | 0.1551          | 395             | 729             | 562             | 0.0363          |
| 0.4 | 34              | 101             | 77              | 1.55            | 1.41            | 0.8122          | 0.1129          | 380             | 730             | 555             | 0.0308          |
| 0.6 | 30              | 90              | 74              | 1.57            | 1.20            | 0.7747          | 0.1190          | 366             | 731             | 549             | 0.0294          |
| 0.8 | 30              | 70              | 39              | 1.40            | 1.33            | 1.1981          | 0.2270          | 353             | 727             | 540             | 0.0455          |
| 1.0 | 26              | 61              | 34              | 1.60            | 1.64            | 1.4417          | 0.3032          | 341             | 718             | 530             | 0.0547          |
| Avg.| 31              | 87              | 59              | 1.57            | 1.45            | 1.0405          | 0.1816          | 393             | 723             | 577             | 0.0395          |
Similar strain results have been reported for ZnO oxide [49, 50] and for other spinels such as the Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ [48]. It has been reported that there is a relation between the inversion factor and the lattice constants [49]. Other studies suggest that there is a relation between the particle sizes and the inversion factor [50, 51]. It was reported that the crystallite sizes decrease as the inversion factor increase in the Mg$_{1-x}$Zn$_x$FeCrO$_4$ spinels [22]. The relation between the crystallite sizes and the inversion factor in the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels has been shown in Figure 9-b. It is clear that the crystallite sizes from the different methods increase first passing through broad maximum then decreases. Comparing Figure 9-a and Figure 9-b conveys that there is some sort of relation between the crystallite sizes and the inversion factors. It appears as a shift of the broad maximum towards the samples of high inversion factors.

3.3. The Order-Disorder in Mg$_{1-x}$Zn$_x$FeNiO$_4$ Spinels

The cation distributions in the Mg$_{1-x}$Zn$_x$FeNiO$_4$ samples suggest that these samples have the mixed spinel type structure with an inversion factor, $\lambda$, in which the Mg$^{2+}$, Zn$^{2+}$ and Fe$^{3+}$ cations occupy both the A- and B- sites while the Ni$^{2+}$ ions occupy the B- sites and the structural formula can be written as in the following:

$$((\text{Mg}^{2+}_{x} \text{Zn}^{2+}_{1-x})_{1-\lambda} (\text{Fe}^{3+})_{\lambda})_{4} [((\text{Mg}^{2+}_{x} \text{Zn}^{2+}_{1-x})_{1-\lambda} \text{Fe}^{3+}_{\lambda})_{4} \text{Fe}^{3+}_{\lambda} \text{Ni}^{2+}_{1-\lambda} ]_{6} \text{O}_{4}$$

The Mossbauer investigation reveals the following cation distribution for these spinels [12].

| $x$  | Tetrahedral sites | Octahedral sites | $\lambda$ |
|------|-------------------|------------------|-----------|
| 0.0  | (Mg$^{2+}_{0.31}$Fe$^{3+}_{0.69}$) | [Mg$^{2+}_{0.69}$Fe$^{3+}_{0.31}$Ni$^{3+}_{1.00}$] | 0.69 |
| 0.2  | (Mg$^{2+}_{0.39}$Zn$^{2+}_{0.20}$Fe$^{3+}_{0.41}$) | [Mg$^{2+}_{0.61}$Fe$^{3+}_{0.39}$Ni$^{3+}_{1.00}$] | 0.61 |
| 0.4  | (Mg$^{2+}_{0.07}$Zn$^{2+}_{0.50}$Fe$^{3+}_{0.43}$) | [Mg$^{2+}_{0.53}$Fe$^{3+}_{0.47}$Ni$^{3+}_{1.00}$] | 0.53 |
| 0.6  | (Zn$^{2+}_{0.57}$Fe$^{3+}_{0.43}$) | [Mg$^{2+}_{0.40}$Zn$^{2+}_{0.05}$Fe$^{3+}_{0.55}$Ni$^{3+}_{1.00}$] | 0.43 |
| 0.8  | (Zn$^{2+}_{0.61}$Fe$^{3+}_{0.39}$) | [Mg$^{2+}_{0.20}$Zn$^{2+}_{0.19}$Fe$^{3+}_{0.61}$Ni$^{3+}_{1.00}$] | 0.39 |
| 1.0  | (Zn$^{2+}_{0.50}$Fe$^{3+}_{0.30}$) | [Zn$^{2+}_{0.24}$Fe$^{3+}_{0.26}$Ni$^{3+}_{1.00}$] | 0.36 |

Table 5. The inverse factor, order parameter and the configurational entropy in the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels.

The perfect normal, perfect random and perfect inverse configurations have $\lambda=0, 2/3$ and 1 respectively. The value $\lambda=2/3$ refers to a completely random distributions. As temperature increases the tendency of the normal and inverse spinels increases towards the random, maximum entropy cation distribution at $\lambda=2/3$. The order parameter $Q$ is related to the inversion factor $\lambda$ through the following relation [55, 56]:

$$Q = 1 - \frac{3\lambda}{2}$$
Most spinel systems do not show a complete degree of order; they contain some degree of disorder (inversion). The degree of order, \( Q \), varies between 1, 0, and -0.5 for the perfectly normal, perfect disorder, and perfect inverse respectively. In the perfectly normal order systems all the \( A^{3+} \) cations reside at the tetrahedral sites and all the \( B^{2+} \) cations reside at the octahedral sites. While for the complete disorder systems \( 1/3 \) of the \( A^{3+} \) cations reside at the octahedral sites and \( 2/3 \) of \( A^{3+} \) cations and \( 1/3 \) of \( B^{2+} \) cations reside at the octahedral sites. Taking the value of the inversion factor \( 2/3 \) as a general border to separate the normal from the inverse phase, the current spinels can be classified as “largely normal” for \( x \) (0 to 0.6) and “largely inverse” for \( x \) (0.6 to 1.0) [56].

In spite of the fact there is no simple generalization between the lattice parameter and the inversion factor. The present partially inverse \( \text{Mg}_{1-x} \text{Zn}_{x} \text{Fe}_{2} \text{NiO}_4 \) spinels showed an increase in the lattice parameter \( a_{\text{exp}} \) from 8.359 Å to 8.409 Å as the inversion factor decreases from 0.69 to about 0.36. Similar results have been reported for the \( \text{ZnAl}_2 \text{O}_4 \) spinels [57]. The inversion parameter increases in the inverse \( \text{MgFe}_2 \text{O}_4 \) spinel increases as the pressure increases [58]. Values of the ordering parameter \( Q \) for the present spinels have been calculated and presented in Table 5. It is clear that these spinels like the majority of spinels [11] have quite high degree of disorder, \( \kappa = 1 - Q \) and they are too far from being perfect normal or perfect inverse type spinel structure. Table 5 shows that an inverse relation between \( Q \) and \( \lambda \) in these spinels. This satisfies the fact that the more inverse the spinel the more the disorder. The order-disorder parameters \( Q \) and \( \lambda \) are shown in Figure 10 as a function of \( \text{Zn} \) content. It is clear that the \( Q \) and \( \lambda \) curves cross at about \( x = 0.7 \). The total randomness corresponds to \( Q = 0 \). The sample \( \text{MgFeNiO}_4 \) has almost the complete randomness configuration. Its cation distributions can be written as \( (\text{Mg}_{1/3} \text{Fe}_{2/3})_{9/2} \text{Ni}_{11/2} \text{O}_4 \). The degree of randomness, \( \kappa \) is a reflection of the inversion factor, \( \lambda \). Both \( \kappa \) and \( \lambda \) decrease as the structure moves towards the spinel structure normality, i.e. as the \( \text{Zn} \) content \( (x) \) increases in the sample. The increasing of cation disorder in spinels is associated with the configurational entropy \( S_c \), [11, 39, 56], which can be written as;

\[
S_c = -R \left[ \lambda \ln \lambda + (1 - \lambda) \ln (1 - \lambda) + \lambda \ln \left( \frac{1}{2} \right) + \left(2 - \lambda \right) \ln \left( \frac{1 - \lambda}{2} \right) \right]
\]

(12)

The configurational entropy for the disorder in spinels systems. It covers the whole range from perfect normal spinel to the perfect inverse spinel through the complete randomness type structure. Values of \( S_c \) have been calculate for the whole range from \( \lambda = 0 \) to \( \lambda = 1 \) and shown plotted in Figure 11. Values of \( S_c \) for the present \( \text{Mg}_{1-x} \text{Zn}_{x} \text{FeNiO}_4 \) samples have been mapped on the universal curve. It is clear that there is an excellent agreement between the theoretical and calculated values of \( S_c \) in the present spinels. Similar \( S_c \) results have been reported for the solid solution \( (\text{Fe}_4 \text{O}_4 - \text{Fe}_2 \text{TiO}_4) \) [60] and \( \text{MgGa}_2 \text{O}_4 \) spinels [61].

The sample of the complete randomness should have an ordering parameter \( Q \) of 0 with an inversion factor \( \lambda \) of 2/3 and has maximum configurational entropy \( S_c (\approx 15.861 \text{J/mol.K}) \). The hypothetical samples of perfect normal configuration is going to be the sample \( (\text{Mg}_{1-x} \text{Zn}_{x})_{6} \text{Ni}_{12} \text{O}_{4} \) with \( Q = 1 \), \( \lambda = 0 \), \( \kappa = 1 \) and minimum configurational entropy, \( S_c (\approx 0 \text{J/mol.K}) \). On the other hand the hypothetical sample of perfect inverse configuration is going to be the sample \( (\text{Fe})_{6}[(\text{Mg}_{1-x} \text{Zn}_{x})\text{Ni}]_{12}\text{O}_{4} \) with \( Q = (-0.5) \), \( \lambda = 1 \), \( \kappa = 0 \) with figurational entropy \( S_c (\approx 2R\ln 2 \approx 11.526 \text{J/mol.K}) \). This equation represents the universal function of the ordering, random, inverse factors and the configurational entropy for the present spinels have been calculated and shown in Table 3. Figure 12 shows \( S_c \) as a function of the inverse factor. The \( S_c \) increases first then it tends to saturate for \( \lambda \) values higher than 0.5. The inset in Figure 12 shows that the \( S_c \) decreases as the \( \text{Zn} \) content increases in the sample (i.e. as the structure moves towards the normality phase).

![Figure 10](image1.jpg)

**Figure 10.** The ordering parameters \( Q \), \( \lambda \) and \( \delta \) versus the \( \text{Zn} \) content \((x)\) for the \( \text{Mg}_{1-x} \text{Zn}_{x} \text{FeNiO}_4 \) spinels.

![Figure 11](image2.jpg)

**Figure 11.** The universal configurational entropy curve. Values of \( S_c \) (red points) for the \( \text{Mg}_{1-x} \text{Zn}_{x} \text{FeNiO}_4 \) samples were mapped on the curve.
3.4. The Atomic Structure Factor, \( f \)

The atomic scattering factor, \( f \), has been defined as the ratio of the amplitude of the scattered waves by an atom to the amplitude of the scattered waves by one electron [13], i.e.;

\[
f = \frac{\lambda_{\text{atom}}}{\lambda_{\text{electron}}} \quad (13)
\]

In order to calculate the structure factor, \( F \) for these samples, values of the atomic factor function, \( f \), has to be estimated first. The atomic scattering factor in spinel, \( f_{\text{tot}} \) consists of participation of the cations at the tetrahedral, \( f_{\text{tet}} \) and octahedral, \( f_{\text{oct}} \) sites and the anions, \( f_{\text{ani}} \) can be written as;

\[
f_{\text{tot}} = f_{\text{tet}} + f_{\text{oct}} + 4 f_{\text{ani}}
\]

where \( n \) and \( m \) represent the number of cations at the tetrahedral and octahedral sites respectively, while \( C_k \) and \( f_k \) represent the concentration of the concerned cations and their atomic structural factor respectively. The cations distribution in the \( \text{Mg}_{1-x}\text{Zn}_x\text{FeNiO}_4 \) spinels reveals that there are only three cations; \( \text{Mg}^{2+}, \text{Zn}^{2+} \) and \( \text{Fe}^{3+} \) residing at the tetrahedral sites and four cations; \( \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Fe}^{3+} \) and \( \text{Ni}^{3+} \) residing at the octahedral site. Values of \( f_{\text{atom}} \) for the various atoms as a function of \( \sin(\theta)/\lambda \) have been tabulated in many X-ray books [13, 23]. It is clear that the ratio, \( f_{\text{atom}} \), has its maximum value, which is equal to its atomic number, \( Z \) in the forward direction \((2\theta=0^\circ)\) at which the electron scattered waves are totally in phase. As \( \theta \) increases, the \( f_{\text{atom}} \) decreases because the scattered waves become increasingly out of phase. Values of \( f_{\text{atom}} \) are independent of the unit cell size and shape and it decreases as \( \lambda \) increases. However, the resultant effect of both \( \theta \) and \( \lambda \) on \( f_{\text{atom}} \) is that \( f_{\text{atom}} \) decreases as \( \sin(\theta)/\lambda \) increases. Values of the atomic factor for the different atoms in each \((hkl)\) planes in the \( \text{Mg}_{1-x}\text{Zn}_x\text{FeNiO}_4 \) spinels have been calculated and tabulated in Table 6. Values of \( f_{\text{atom}} \) for the different samples are quite similar. Figure 13-a shows values of \( f_{\text{atom}} \) for the different atoms in the different \((hkl)\) planes of the samples with \( x=0.2 \) as an example. Figure 13-b shows values of \( f_{\text{tet}}, f_{\text{oct}}, f_{\text{ani}} \) and \( f_{\text{tot}} \) for the different \((hkl)\) planes in the \( \text{Mg}_{1-x}\text{Zn}_x\text{FeNiO}_4 \) spinels. Quite similar results have been reported for the spinels \( \text{Mg}_{1-x}\text{Zn}_x\text{FeCrO}_4 \) [31].

![Figure 12. The configurational entropy, Sc versus the inversion factor, \( \lambda \). The inset shows the Sc versus for Zn content \((x)\) for the \( \text{Mg}_{1-x}\text{Zn}_x\text{FeNiO}_4 \) spinels.](image)

**Figure 12.** The configurational entropy, \( Sc \) versus the inversion factor, \( \lambda \). The inset shows the \( Sc \) versus for Zn content \((x)\) for the \( \text{Mg}_{1-x}\text{Zn}_x\text{FeNiO}_4 \) spinels.

**Figure 13.** (a): The atomic function factor for Mg, Zn, Fe, Ni and O atoms versus \( \sin(\theta)/\lambda \) in the \( \text{Mg}_{1-x}\text{Zn}_x\text{FeCrO}_4 \) spinels. (b): The total atomic function factor for the tetrahedral, \( f_{\text{tet}} \), octahedral, \( f_{\text{oct}} \) and \( f_{\text{ani}} \) sites as a function of the Zn contents \( x \).

**Table 6.** Atomic function factor of the different atoms as a function of \( x \) and \( \sin(\theta)/\lambda \) for the \( \text{Mg}_{1-x}\text{Zn}_x\text{FeNiO}_4 \) spinels.

| \( \sin(\theta)/\lambda \) | \( X = 0.0 \) | \( \text{Mg} \) | \( \text{Zn} \) | \( \text{Fe} \) | \( \text{Ni} \) | \( \text{O} \) |
|-----------------|----------------|--------|--------|--------|--------|--------|
| \( 0.169505 \)  | 220 | 9.17941 | 23.74179 | 20.18080 | 22.01130 | 5.84809 |
| \( 0.198738 \)  | 311 | 8.62398 | 22.45552 | 18.95300 | 20.75426 | 5.30227 |
| \( 0.207049 \)  | 222 | 8.44707 | 22.13214 | 18.66739 | 18.23289 | 5.20132 |
| \( 0.239086 \)  | 400 | 8.07467 | 20.91472 | 17.61015 | 17.42386 | 4.75279 |
| \( 0.293451 \)  | 422 | 6.82443 | 18.84886 | 15.81612 | 17.42922 | 3.99169 |
The scattered waves by the individual atoms can be represented by the structure factor \( F \), which can be written as:

\[
F_{hk\ell} = \sum f_{\text{atom}} e^{2\pi i(hu_n + kv_n + \ell w_n)}
\]  

(15)

Where \( f_{\text{atom}} \) represents the atomic scattering factor of the \( n \)th atom and \( N \) represents the total number of atoms in the unit cell each with fractional coordinates \( u_n, v_n \) and \( w_n \). The \( u_n, v_n \) and \( w_n \) coordinates for the face centered cubic (FCC) structure can be calculated using the following relations, which takes into account the small effects of the oxygen positional parameter, \( u [10-57] \):

\[
F_{hk\ell} = 4 f_{\text{atom}} (h k l \text{ are all even or all odd (unmixed)})
\]

(16)

The structure factors of the FCC planes have been calculated using the following relations, which takes into account the small effects of the oxygen positional parameter, \( u [10-57] \):
\[ F_{111} = 4\sqrt{2}F_A - BF_B + 16\sqrt{2}F_0 \left( \cos^2(2\nu u) + \sin^2(2\nu u) \right) \]
\[ F_{220} = BF_A + 32F_0 \cos^2(4\nu u) \]
\[ F_{311} = 4\sqrt{2}F_A + BF_B + 16\sqrt{2}F_0 \left( \cos^2(2\nu u) \cos(6\nu u) - \sin^2(2\nu u) \sin(6\nu u) \right) \]
\[ F_{222} = 16F_A + 32F_0 \cos^2(4\nu u) \]
\[ F_{333} = 4\sqrt{2}F_A + BF_B + 16\sqrt{2}F_0 \left( \cos^2(2\nu u) \cos(6\nu u) - \sin^2(2\nu u) \sin(6\nu u) \right) \]
\[ F_{400} = 8F_A + 32F_0 \cos(8\nu u) \]
\[ F_{422} = 8F_A + 32F_0 \cos(8\nu u) \]
\[ F_{511} = 4\sqrt{2}F_A + BF_B + 16\sqrt{2}F_0 \left( \cos^2(2\nu u) \cos(10\nu u) - \sin^2(2\nu u) \sin(10\nu u) \right) \]
\[ F_{440} = BF_A + 16F_B + 32F_0 \cos^2(8\nu u) \]

Values of the structure factors, \( F_{\text{obs}} \) for the different (hkl) planes are shown in Table 7.

Table 7. Values of the structure factors of the different (hkl) planes and of the tetrahedral, octahedral and onion sites as a function of the Zn contents and the oxygen positional factor \( u_{os} \)

| x   | \( u_{os} \) | FA   | FB   | FO   | F220 | F311 | F222 | F400 | F422 | F511 | F440 |
|-----|-------------|------|------|------|------|------|------|------|------|------|------|
| 0.0 | 0.3780      | 67.0815 | 69.2023 | 23.3636 | -555.479 | 925.6678 | 361.3603 | -1315.870 | 354.5831 | 984.7769 | 2386.840 |
| 0.2 | 0.3787      | 70.7640 | 66.8131 | 21.2091 | -564.522 | 926.3642 | 392.7017 | -1178.410 | 564.5298 | 992.0778 | 2307.470 |
| 0.4 | 0.3792      | 77.3515 | 62.9670 | 20.8053 | -616.822 | 932.1586 | 344.6864 | -1050.450 | 616.8338 | 1004.7083 | 2284.117 |
| 0.6 | 0.3798      | 77.9750 | 62.6379 | 19.0112 | -621.447 | 932.6773 | 397.3761 | -982.056 | 621.4648 | 1008.0269 | 2224.986 |
| 0.8 | 0.3800      | 70.6644 | 64.0464 | 15.9668 | -563.176 | 903.7879 | 517.0129 | -966.085 | 563.1935 | 969.6004 | 2092.472 |
| 1.0 | 0.3801      | 68.1899 | 66.4176 | 15.1503 | -543.409 | 909.0293 | 581.0315 | -997.754 | 543.4277 | 972.6756 | 2084.610 |

### 3.6. Debye-Waller Factor (DWF)

The thermal vibrations of atoms about their positions attenuate the X-ray diffracted intensities. A correction for these disruptions can be achieved by employing the Debye-Waller factor (DWF) or the temperature factor [13]. The intensity of the diffracted X-ray spectra from the powder sample is related to the Debye-Waller factor, \( B \)

\[ B = 2\pi^2 k \rho \sigma^2 \]

These disruptions can be achieved by employing the Debye-Waller factor, \( B \)

\[ \frac{I_{\text{obs}}}{I_{\text{cal}}} = K + K - \frac{2\nu u \sin^2(\theta)}{h} \]

(18)

Where \( I_{\text{cal}} \) and \( I_{\text{obs}} \) represent the calculated and observed intensities respectively and \( K \) represents the scale factor. The DWF can be estimated from the least square fittings of the \( \frac{I_{\text{obs}}}{I_{\text{cal}}} \) versus \( -2\sin^2(\theta)h \) of the X-ray intensities of the concerned (hkl) planes. The \( I_{\text{cal}}(\text{hkl}) \) have been estimated employing the following relation [13, 23]:

\[ I_{\text{cal}} = |F|^2, (MF), (LP), (AF), (TF) \]

where \( F \), \( MF \), \( LP \), \( AF \) and \( TF \) represent the structure factor, the multiplicity factor, Lorentz-Polarization factor, absorption factor and temperature factor respectively. The absorption (AF) and temperature (TF) factors vary in opposite directions with temperature and they were usually omitted especially for the problems where relative intensity calculations are concerned [23-26]. Therefore, equation (16) will be reduced to the following simple approximate form:

\[ I_{\text{hkl}} = |F_{\text{hkl}}|^2, (MF), (LP) \]
Figure 15 shows DWF values versus the microstrain in these spinels. The extrapolation of this relation to zero value of ε gives the effective DWF for these samples, which equals to 0.513Å². A value of 0.896Å² has been reported for the normal ZnFeₓCrₓO₄ spinels [22]. The relation between the Debye Waller factor and the crystallite sizes has been shown in Figure 16. This figure shows that both D and DWF decrease as x increases in the region of the “largely normal” spinels while they behaves quite differently in the region of the “largely inverse” spinels. The behaviours of the DWF with the oxygen parameter, u is quite similar to the relation between D and DWF.

Table 8. Relative diffracted intensities and relative areas of the different (hkl) planes for the Mg₁₋ₓZnₓFeNiO₄ spinels.

| Relative Intensities (Iᵢ/İ₁₁) | x | (220) | (222) | (400) | (422) | (511) | (440) |
|-------------------------------|---|-------|-------|-------|-------|-------|-------|
| 0.0  | 2.19 | 0.14  | 0.42  | 1.65  | 1.79  | 2.18  |
| 0.2  | 0.77 | 0.13  | 0.31  | 1.88  | 1.70  | 1.85  |
| 0.4  | 0.88 | 0.08  | 0.22  | 2.39  | 1.85  | 1.77  |
| 0.6  | 0.94 | 0.10  | 0.19  | 2.44  | 1.83  | 1.89  |
| 0.8  | 0.79 | 0.18  | 0.22  | 2.02  | 1.82  | 2.11  |
| 1.0  | 0.74 | 0.20  | 0.24  | 1.82  | 1.75  | 1.87  |

| Relative Areas (Aᵢ/𝐴₁₁) | x | (220) | (222) | (400) | (422) | (511) | (440) |
|-------------------------|---|-------|-------|-------|-------|-------|-------|
| 0.0  | 0.30 | 0.34  | 1.02  | 0.10  | 0.32  | 0.91  |
| 0.2  | 0.31 | 0.42  | 1.06  | 0.10  | 0.33  | 0.33  |
| 0.4  | 0.31 | 0.54  | 1.16  | 0.09  | 0.31  | 0.96  |
| 0.6  | 0.31 | 0.64  | 1.27  | 0.09  | 0.31  | 1.08  |
| 0.8  | 0.31 | 0.65  | 1.20  | 0.09  | 0.31  | 1.11  |
| 1.0  | 0.30 | 0.79  | 1.24  | 0.08  | 0.33  | 1.22  |

Figure 14. (a): The relative intensity of the (hkl) reflections as a function of Zn content (x). (b): The relative areas under the (hkl) reflections as a function of Zn content (x) for Mg₁₋ₓZnₓFeNiO₄ spinels.

Figure 15. The Debye-Waller factor (DWF) versus Zn content (x). The inset shows the DWF versus strain for the Mg₁₋ₓZnₓFeNiO₄ spinels.

Figure 16. The crystallite sizes and DWF versus the versus the Zn content (x) for the Mg₁₋ₓZnₓFeNiO₄ spinels.
3.7. The Effective Debye Temperature, \( \theta_D \)

An important parameter of the thermal properties and heat capacity in particular the effective Debye temperature, \( \theta_D \), which is related to the Debye-Waller factor \( B_T \) and can be roughly estimated using the following relations [13];

\[
\theta_D = \left( \frac{6 \hbar^2 N \lambda}{M_k h^2} W(y) \right)^{1/2}
\]

\[
W(y) = \left( \phi(y) + \frac{\gamma}{4} \right)
\]

This equation can be simplified to have the following form at \( T=300 \) K;

\[
\frac{\theta_{D(M_{1-x}Zn_4FeNiO_4)}}{\theta_{D(M_{1-x}Zn_4FeCrO_4)}} = \left( \frac{M_{M_{1-x}Zn_4FeNiO_4}}{M_{M_{1-x}Zn_4FeCrO_4}} \right)^{1/2}
\]

The calculated values of \( \theta_D \) for the \( M_{1-x}Zn_4FeNiO_4 \) spinels are shown in Table 4 together with \( \theta_D \) from the FTIR relation. Figure 17-a shows that values of \( \theta_D \) decrease as the \( Zn^{2+} \) contents increase in the sample. This might be caused by the enhancements of the lattice vibrations, which causes reduction in the values of the Debye temperatures, another reason might be the increase of the average molecular mass, which has an inverse relation with \( \theta_D \). Values of \( \theta_D \) are in the range (321–378 K) compare well with those reported for other spinels such as \( ZnFe_{2-x}CrO_4 \) (284–355 K) [22] CuFe_{2-x}AlO_4 (282–472 K) [65] \( Ni_{1-x}Zn_{x}Fe_{2}O_4 \) (260–330 K) [70] and \( NiFe_{2-x}Cr_{x}O_4 \) (650–675K) [41]. The substitution of the \( \theta_D \) values in the equations allows for the estimation of the DWF for these spinels. The average values of the Debye temperature have been plotted versus the average force constants, \( K_{avg} \) in Figure 17-b. This figure shows clearly the inverse relation between \( \theta_D \) and \( K_{avg} \). Knowing values of the effective Debye temperatures and the function \( W(y) \) allows for the calculation of the effective Debye-Waller factor \( B_T \) and the temperature factor \( M_T \).

\[
B_T = \frac{1.15 \times 10^4 \times 300 \times (\phi(y) + \frac{\gamma}{4})}{\theta_D^2}
\]

(22)

where \( B_T \), \( \phi(y) \), \( K_0 \), \( h \) and \( M \) represent Debye-Waller factor, Boltzmann’s constant, Plank’s constant, absolute temperature and molecular mass of the \( M_{1-x}Zn_{4}FeNiO_4 \) spinels. Values of the \( \phi(y) \) function can be found in standard tables [67]. It is clear that the calculations of \( B_T \) require the estimation of the Debye temperature \( \theta_D \). Values of the Debye temperatures for the present \( M_{1-x}Zn_{4}FeNiO_4 \) spinels can be estimated using known values of \( \theta_D \) for similar \( M_{1-x}Zn_{4}FeCrO_4 \) spinels [68] using scaling law, which relates Debye temperatures of the closely related compounds to their molecular masses as in the following relations [69];

\[
\frac{\theta_{D(M_{1-x}Zn_4FeNiO_4)}}{\theta_{D(M_{1-x}Zn_4FeCrO_4)}} = \left( \frac{M_{M_{1-x}Zn_4FeNiO_4}}{M_{M_{1-x}Zn_4FeCrO_4}} \right)^{1/2}
\]

(23)

Table 9. Debye temperature, the function, Debye-Waller factor, Temperature factor as a function of \( x \) and \( \sin(\theta)/\lambda \) for the \( M_{1-x}Zn_4FeNiO_4 \) spinels.

| \( x \) | \( \theta_D(K) \) average | \( Y=\theta_D/300 \) | \( \phi(y) \) | \( y/4 \) | \( B_T \) | \( \sin(\theta)/\lambda \) | \( \sin(\theta)/\lambda \times 2 \) | \( M_T \) | \( \exp(-2M_T) \) |
|---|---|---|---|---|---|---|---|---|---|
| 0.0 | 577 | 1.9217 | 0.6185 | 0.4804 | 0.05624 | 0.169063 | 0.028582 | 0.00161 | 0.99679 |
| 0.2 | 562 | 1.8733 | 0.6260 | 0.4683 | 0.05664 | 0.198213 | 0.039289 | 0.00223 | 0.99556 |
| 0.4 | 555 | 1.8500 | 0.6295 | 0.4625 | 0.05578 | 0.206480 | 0.042634 | 0.00238 | 0.99526 |
| 0.6 | 549 | 1.8283 | 0.6328 | 0.4571 | 0.05494 | 0.238428 | 0.056848 | 0.00312 | 0.99377 |
| 0.8 | 540 | 1.8000 | 0.6370 | 0.4500 | 0.05456 | 0.292640 | 0.085638 | 0.00467 | 0.99070 |
| 1.0 | 530 | 1.7650 | 0.6426 | 0.4413 | 0.05468 | 0.310421 | 0.095257 | 0.00527 | 0.98952 |

Table 9 shows values of the concerned parameters; \( B_T \), \( y \), \( \phi(y) \), \( M \), \( \theta_D \) and \( M_T \). It is clear that values of \( B_T \) using Debye temperatures are lower than those obtained using the integrated intensities of the scattered Bragg XRD reflections. This might be caused by the high values of Debye temperatures \( \theta_D \), which have an inverse relation with the Debye Walle factors. The temperature factor \( (M_T) \) is related to the effective Debye-Waller factor \( (B_T) \) through the following relation [13];

\[
e^{-2M_T} = e^{-2B_T \left( \frac{\sin(\theta)}{\lambda} \right)^2}
\]

\[
M_T = B_T \left( \frac{\sin(\theta)}{\lambda} \right)^2
\]

(24)

The temperature factors of these samples have been calculated and shown in Table 9. Figure 18 shows the temperature factor as a function of \( \sin(\theta)/\lambda \) for the sample with \( x=0.4 \) as an example. It is clear that values of \( M_T \) decrease as the \( \sin(\theta)/\lambda \) increases. Similar results have been shown by the Cr metal [13] and \( ZnFe_{2-x}Cr_{x}O_4 \) spinel [22]. Moreover, Debye temperature \( \theta_D \) is related to the average infrared primary bands frequency \( v_{avg} \) through the following relations [71, 72];

\[
\theta_D = \frac{hc v_{avg}}{K_B}
\]

\[
\theta_D = 1.439 \times v_{avg}
\]

(25)
average force constant $K_{\text{avg}}$ is shown in Figure 18. It is clear that there are two separate regions in these spinels. Values of $\theta_D$ from the heat capacity scaling and infrared spectroscopy are not the same. Similar results have been reported for other spinels. It has been well established that values of Debye temperatures obtained from different experimental measurements such as elastic constant, heat capacity and infrared spectroscopy are generally in differences [46].

### 3.8. The FT-IR Analysis

The infrared (FT-IR) transmission spectra of the $\text{Mg}_{1-x}\text{Zn}_x\text{FeNiO}_4$ spinels are shown in Figure 19-a. The main distinctive features of these spectra are the two dominant metal–oxygen absorption bands at $\nu_1$ and $\nu_2$. These bands appear in the IR spectra of most spinels [73]. Values of $\nu_1$ and $\nu_2$ for the $\text{Mg}_{1-x}\text{Zn}_x\text{FeNiO}_4$ spinels fall in the range (600–570 cm$^{-1}$) and (420–430 cm$^{-1}$) respectively. These bands are caused by the intrinsic valence vibrations of the metal cations at the tetrahedral and octahedral sites, $\text{M}_{\text{tet}}$–$\text{O}$ and $\text{M}_{\text{oct}}$–$\text{O}$ respectively. Values of $\nu_1$ and $\nu_2$ shift to lower values as the Zn content increases. Similar results have been reported for the spinels $\text{Mg}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ [21] and $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ [33]. This is an indication of the weakening of the cation-anion bonds at the tetrahedral and octahedral sites. The replacement of the Mg with Zn causes redistributions of the cations at the A and B sites. This might be linked with the variations of the average cation radii at the A- and B-sites. It is clear that both $r_A$ and $r_B$ increase with x. Values of the band positions $\nu_1$ and $\nu_2$ are listed in Table 10 as a function of Zn content. The absorption bands $\nu_1$ and $\nu_2$ correspond to the stretching vibrations of the $\text{Mg}^{2+}$–$\text{O}^2$-, $\text{Zn}^{2+}$–$\text{O}^2$-, $\text{Fe}^{3+}$–$\text{O}^2$- and $\text{Ni}^{3+}$–$\text{O}^2$ bonds at the tetrahedral and octahedral sites. There are many factors responsible for the differences in position of the two bands such as differences in the average metal-oxygen distances, electronegativity, ionic radii and the force constants at the A- and B- sites. Similar results have been reported for the $\text{Mg}_{1-x}\text{Zn}_x\text{FeCrO}_4$ [31-34] and $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$ [39-42] spinels. But they are differing from those of the $\text{ZnFe}_{2-x}\text{Cr}_x\text{O}_4$ [22-25] and $\text{MgFe}_{2-x}\text{Cr}_x\text{O}_4$ [24-27] spinels, in which the values of the bands $\nu_1$ and $\nu_2$ shift to higher values (increase) with the Cr content. Figure 19-b shows details of the other absorption bands. The bands at 1638 and 2730 cm$^{-1}$ correspond to other O–H group confirming the presence of interlayer water and the oscillations of the H–O–H bonds and they are independent of the sample compositions. These bands might be assigned to the formation of hydrogen bonds between the hydroxyl groups, which might be caused by the water absorption by the samples during the compaction of the sample powders with KBr as pellets. The wide absorption band appeared at (3450–3470 cm$^{-1}$) corresponds to O–H bond stretching vibrations of $\text{H}_2\text{O}$ present in the interlayer space. Similar results have been reported for most of the spinels such as the Co-Zn ferrites [28].
Table 10. The absorption bands, molecular weight and force constants at the tetrahedral and octahedral sites of the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels.

| x  | v1  | v2  | vavg | M1         | M2         | Kt      | Ko      | Kavg     | Kt/Ko |
|----|-----|-----|------|------------|------------|---------|---------|----------|--------|
| 0.0| 600 | 431 | 515.5| 46.0676    | 46.3879    | 126373  | 45757   | 86065    | 2.7619 |
| 0.2| 588 | 425 | 506.5| 51.7594    | 47.6495    | 136364  | 45702   | 91033    | 2.9838 |
| 0.4| 598 | 417 | 507.5| 57.4512    | 48.9111    | 156551  | 49942   | 105420   | 3.4664 |
| 0.6| 587 | 429 | 508.0| 51.1042    | 50.6495    | 159342  | 45162   | 106785   | 3.0470 |
| 0.8| 585 | 425 | 505.0| 55.0210    | 51.1042    | 160898  | 52772   | 106785   | 3.2217 |
| 1.0| 581 | 417 | 499.0| 61.9474    | 58.9855    | 159342  | 54464   | 106903   | 2.9526 |

Figure 19. (a): The FTIR spectra for the samples of the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels in the range (400-4000) cm$^{-1}$. (b): the IR spectra showing details of the absorption bands of the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels.

The force constants $K_t$ and $K_o$ at the tetrahedral and octahedral sites respectively have been calculated using the following equations [73]:

$$K_t = 7.62 \cdot M_1 \cdot v_1^2 \cdot 10^{-3} \left( \text{dyn cm}^{-1} \right)$$

$$K_o = 10.62 \left( \frac{M_2}{2} \right) v_2^2 \cdot 10^{-3} \left( \text{dyn cm}^{-1} \right)$$

(26)

where $M_1$ and $M_2$ are the average molecular mass of the cations at the tetrahedral and octahedral sites respectively. Values of the force constants $K_t$ and $K_o$ have been listed in Table 10 as a function of Zn$^{2+}$ content. It is clear that values of $K_t$ and $K_o$ increase as Zn content increases. It is clear that values of $K_t$ are higher than those for $K_o$ by more than 3 times. This difference can be attributed to the differences in band stretching between $v_1$ and $v_2$ bands. The high force constants have been attributed to the band stretching at the tetrahedral sites rather than at the octahedral sites [74]. The force constants at the tetrahedral and octahedral sites increase in spite of the increases in the bond length at the two sites. These behaviors have been attributed to the oxygen ability in forming strong bonds with cations even at larger bond lengths [75]. Moreover, the force constants in spinels are largely influenced by the nature of the cation distributions. Since these spinels are mixed spinels it is hard to establish the normal direct relationships between the bond lengths and the force constants because the other factors such as the molecular mass, bond lengths, electronegativity and the ionic radii were left free to change and not fixed. The average values of the force constants, $K_{avg}$, electronegativities, $\chi_{avg}$ and bond lengths, $R_{avg}$ increase as the Zn content increase in the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels as shown in Figure 20.

![Figure 20. The average values of the force constants, electronegativities and bond lengths in the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels.](image)

3.9. The Electronegativity, $\chi$

The electronegativity describes the tendency of an atom to attract the charge density towards itself. The Pauling electronegativity difference $\Delta \chi$ provides measure of the cationic bond strength and its variations reflect the bond length changes. The electronegativity differences $\Delta \chi$ can be estimated at the tetrahedral $\chi_A$ and octahedral $\chi_B$ sites of spinels using the following relations [22, 76]:

$$\Delta \chi = \chi_A - \chi_B$$

...
\[
X_A = \left( C_{Mg^{2+}}^A (X_{Mg^{2+}}) + \left( C_{Zn^{2+}}^A (X_{Zn^{2+}}) \right) + \left( C_{Fe^{3+}}^A (X_{Fe^{3+}}) \right) \right) \\
X_B = \left( C_{Mg^{2+}}^B (X_{Mg^{2+}}) + \left( C_{Zn^{2+}}^B (X_{Zn^{2+}}) \right) + \left( C_{Fe^{3+}}^B (X_{Fe^{3+}}) \right) \right) \\
\Delta X_A = X_A - \frac{X_A}{4} \text{ and } \Delta X_B = X_B - \frac{X_B}{6} 
\]

where \(X_A\) and \(X_B\) represent the Pauling electronegativities of the cations at the tetrahedral and octahedral sites respectively. Values of the Pauling electronegativity for the Mg\(^{2+}\), where \(X_A\) and \(X_B\) represent the Pauling electronegativities of the cations at the tetrahedral and octahedral sites respectively.

Values of the Pauling electronegativity for the Mg\(^{2+}\), Fe\(^{3+}\) and Ni\(^{3+}\) ions have been taken as 1.31, 1.65, 1.83 and 1.91 respectively and 3.44 for the oxygen. The calculated values of \(X_A\), \(X_B\), \(\Delta X_A\) and \(\Delta X_B\) are shown in Table 11.

Table 11. The electronegativities and force constants at the tetrahedral and octahedral sites in the Mg\(_{1-x}\)Zn\(_x\)FeNiO\(_4\) spinels.

| x   | \(X_A\) | \(X_B\) | \(X_{avg}\) | \(\Delta X_A\) | \(\Delta X_B\) | K\(_{AA}\) | K\(_{AB}\) | K\(_{BB}\) | K\(_{AB}/K_{BB}\) |
|-----|--------|--------|-------------|----------------|----------------|----------|----------|----------|----------------|
| 0.0  | 1.6688 | 1.6096 | 1.6797      | 3.0228         | 3.1582         | 2.7849   | 2.8213   | 2.8588   | 0.9871         |
| 0.2  | 1.6952 | 1.7114 | 1.7033      | 3.0162         | 3.1548         | 2.8737   | 2.9012   | 2.9289   | 0.9905         |
| 0.4  | 1.7216 | 1.7322 | 1.7269      | 3.0096         | 3.1513         | 2.9639   | 2.9822   | 3.0005   | 0.9939         |
| 0.6  | 1.7274 | 1.7633 | 1.7454      | 3.0082         | 3.1461         | 2.9839   | 3.0459   | 3.1092   | 0.9796         |
| 0.8  | 1.7202 | 1.8009 | 1.7606      | 3.0010         | 3.1399         | 2.9591   | 3.0979   | 3.2432   | 0.9552         |
| 1.0  | 1.7148 | 1.8376 | 1.7762      | 3.0113         | 3.1337         | 2.9405   | 3.1511   | 3.3768   | 0.9332         |

Figure 21 shows that the electronegativities at the A- and B- sites behave differently as the Zn content increase. The migration of Zn\(^{2+}\) cations from A- sites to the B- sites contributes negatively to \(X_A\) and positively to \(X_B\). The values of \(X_A\) passing through maxima centered at about x=0.6, while \(X_B\) kept increasing as x increases.

The bond stretching forces K\(_{AB}\) in spinels between the cations at the tetrahedral and octahedral sites has been defined as a function of the electronegativities of these cations as in the following equation [39, 77];

\[
K_{AB} = a N \left( \frac{X_A - X_B}{r_e^2} \right) + b 
\]

where a and b are constants, N is the bond order and \(r_e\) is the equilibrium distance. This expression has been simplified by assuming that a, N and \(r_e\) values are approximately constant, while b is small and can be neglected. These simplifications result in quite simple expression for the force constant K\(_{AB}\) as in the following simple forms [39];

\[
\begin{align*}
K_{AA} &= X_A X_A \\
K_{AB} &= X_A X_B \\
K_{BB} &= X_B X_B 
\end{align*}
\]

The bond forces K\(_{AA}\), K\(_{AB}\) and K\(_{BB}\) have been considered as a qualitative measure of the repulsive (or attractive) forces between A-A, A-B and B-B cations respectively. It has been argued that the spinel structure will be preferred for small K\(_{AB}/K_{BB}\) ratio. Values of K\(_{AA}\), K\(_{AB}\), K\(_{BB}\) and the ratio K\(_{AB}/K_{BB}\) have been calculated for the Mg\(_{1-x}\)Zn\(_x\)FeNiO\(_4\) spinels and presented in Table 11. Values of the K\(_{AB}/K_{BB}\) Ratio is less than 1 satisfying the argument. Moreover, the relation between the bond forces K\(_{AB}\) and the ionic radii ratio \(r_A/r_B\) has been plotted for large number of spinels and other compounds [39]. This relation has been reshown in Figure 22. The calculated values of K\(_{AB}(=0.22)\) and the ratio \(r_A/r_B(=1.01)\) for the present spinels Mg\(_{1-x}\)Zn\(_x\)FeNiO\(_4\) have been mapped on this Figure The symbol “X” indicates the location of present spinels among others on this plot. It clear that it lies in the inverse spinel region. Moreover mapping values of K\(_{AB}(=0.22)\) against the ratios \(r_A/r_e(=0.51)\) and \(r_B/r_e(=0.50)\) on the three dimensional surface plot (Figure 3 in ref. [39]) proves that the present Mg\(_{1-x}\)Zn\(_x\)FeNiO\(_4\) samples have the spinel type structure. It has also been argued that the ionic radius ratio plays the dominant role in determining the spinel structure. The radius ratios for large number of spinels fall within the following limits; \(r_A/r_f(=0.36–0.65)\) and \(r_B/r_f(=0.35–0.69)\). The present results shows that \(r_A/r_f(=0.483–0.505)\) and \(r_B/r_f(=0.494–0.497)\) satisfying the argument.

Figure 21. The electronegativities at the tetrahedral and octahedral sites of the Mg\(_{1-x}\)Zn\(_x\)FeNiO\(_4\) spinels.

The bond stretching forces K\(_{AB}\) in spinels between the cations at the tetrahedral and octahedral sites has been defined as a function of the electronegativities of these cations as in the following equation [39, 77];
The samples surface morphology has been characterized using analytical scanning electron microscope (ASEM) model JSM-6510LA-JEOL and transmission electron microscope model JEM-1400-JEOL. The samples were prepared by drop coating from alcohol dispersion on the copper grids using ultrasound. The SEM and TEM micrographs of the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels are shown in Figure 23 and Figure 24 respectively. It appears that the sample surfaces composed of approximately spherical to cubic grains. It also shows a well-packed and continuous grain structure with porosity and small holes at the grains boundaries. There is agglomeration phenomenon in the grains, which forms large grains. The SEM micrographs clearly showed aggregates of well-defined stacked grains of up to few mm in size, which might be caused by the high temperatures (>1000°C) heat treatment for long time (24h). Grain sizes obtained from SEM and TEM micrographs are larger than those obtained from the XRD calculations using Debye-Scherer’s equation and Williamson-Hall plot [45]. Similar results have been shown by other spinels such as Mg$_{1-x}$Zn$_x$Fe$_2$O$_4$ [21] spinels such as ZnFe$_2$, Cr$_2$O$_3$ [22], MgCr$_{2-x}$O$_4$ [24], Zn$_{1-x}$Cd$_x$Fe$_2$O$_4$ [48] and Mg$_{1-x}$Zn$_x$FeCrO$_4$ [34].
Figure 24. The TEM images for the Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels.

4. Conclusions

The Mg$_{1-x}$Zn$_x$FeNiO$_4$ spinels have been prepared using the solid state sintering techniques with sintering temperatures about 1100°C. Both the XRD and FTIR analyses confirm the formation of the face centered cubic spinel phase. The replacement of Mg ions with Zn ions influences the properties of these spinels. Most of the structural parameters such as the lattice constant, bond lengths, the infrared band centers, the oxygen positional parameter and the inversion factor increase as Zn content increases. Values of the ordering, inverse and randomness parameters moves towards the spinel structure normality as the Zn content (x) increases in the sample. The sample MgFeNiO$_4$ has the complete randomness configuration with an order parameter of about (2/3) and its composition can be written as (Mg$_{2/3}$Fe$_{1/3}$)$_A$(Mg$_{1/3}$Fe$_{2/3}$Ni)$_B$O$_4$. This satisfies the fact that the more inverse the spinel the more the disorder. The lattice constant increases with increase in Zn content. This has been attributed to the replacement of smaller Mg$^{2+}$ (0.66Å) cations with a larger cation, the Zn$^{2+}$ of ionic radius (0.74Å). The estimated crystallite sizes were found to depend on the type of estimation method and on the Zn constant (x). Values of the crystallite sizes were found to be in the ranges (26-34) nm, (61-102) nm and (of order of few mm) for the D-S, W-H and SEM methods respectively. Values of the relative integrated areas under the peak vary in the same manner, the areas increase as Zn content increases. Unlike the areas the ratios of the calculated to the observed diffracted X-ray intensities vary in different manner with Zn contents. The Debye-Waller factors were estimated to be in the range (0.77-1.44 Å$^2$) with a free strain DWF value of (0.513Å$^2$) in these spinels. Values of Debye temperature decrease as the Zn$^{2+}$ content increase in the sample. This might be caused by the enhancements of the lattice vibrations, which causes reduction of the Debye temperatures. Another reason might
be the increase of the average masses, which have an inverse relation with \( \theta \) values. Most of the investigated properties such as the oxygen positional factor, Debye Waller factor, crystallite sizes and many others parameters were found to fall into two separate regions; the first region (largely normal) at (0.0 – 0.6) and the second region (largely inverse) at (0.6 – 1.0). These behaviours reflect the differences in nature of the structural phases between the two regions in these samples.

**Declaration**

1) The article is original.
2) The article has been written by the stated authors who are ALL aware of its contents and approve its submission.
3) The article has not been published previously.
4) The article is not under consideration for publication elsewhere
5) No conflict of interest exists, or if such conflict exists, the exact nature must be declared.
6) If accepted, the article will not be published elsewhere in the same form, in any language, without the written consent of the publisher.

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