# Microstructural characterisation of ZnO nanoparticles using X-ray peak profile analysis- a comparative study

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دراسة البنية الدقيقة لجسيمات أكسيد الزنك النانوية باستخدام تحليل الأشعة السينية - دراسة مقارنة

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#### Abstract:

The applicability of semiconductor crystalline nanomaterials in a wide range of highly performed novel devices is influenced by their microstructural properties. The estimation of these microstructural parameters, including crystallite size, lattice strain, stress, energy density, and lattice parameters has been most frequently carried out using X-ray diffractometry (XRD). In the present work, the crystalline structure of ZnO nanoparticles (ZnO-NPs) was investigated through X-ray peak profile analysis by applying different integral breadth techniques. Therefore, the reliability of different methods namely, the Williamson-Hall (W-H) models which are the uniform deformation model (UDM), the uniform stress deformation model (USDM), and the uniform deformation energy density model (UDEDM), as well as the Halder-Wagner method and the size strain plot Method (SSP) were investigated and compared. In addition, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA) were used to characterize the morphology and chemical structure of synthesized ZnO-NPs. The findings obtained revealed that the lattice strain of the ZnO-NPs estimated from W-H analysis and the SSP method were highly intercorrelated, while the crystallite size calculated from W-H models was almost similar and in better agreement with the previously reported TEM results.

Keywords: ZnO nanoparticles, X-ray peak profile, crystallite size, lattice strain, lattice constants.

الملخص:

تتأثر قابلية تطبيق المواد النانوية البلورية شبه الموصلة في مجموعة واسعة من الأجهزة الحديثة عالية الأداء بخصائصها المجهرية. في هذه الدراسة تم تقدير هذه المعاملات المجهرية، بما في ذلك حجم البلورة، إجهاد الشبكة، الإجهاد، كثافة الطاقة، ومعاملات الشبكة باستخدام حيود الأشعة السينية تم تقدير هذه المعاملات المجهرية، بما في ذلك حجم البلورة، إجهاد الشبكة، الإجهاد، كثافة الطاقة، ومعاملات الشبكة باستخدام حيود الأشعة السينية تم تقدير هذه المعاملات المجهرية، بما في ذلك حجم البلورة، إجهاد الشبكة، الإجهاد، كثافة الطاقة، ومعاملات الشبكة باستخدام حيود الأشعة السينية (XRD). ايضا في هذا العمل، تم التحقيق في البنية البلورية لجسيمات أكسيد الزنك النانوية (ZnO-NPS) من خلال تحليل ملف تعريف قمم الأشعة السينية من خلال تطبيق تقنيات عرض تكاملية مختلفة. بالاضافة الي انه تم التحقيق في موثوقية الطرق التحليلية المختلفة مثل: نماذج ويليامسون-هول السينية من خلال تطبيق تقنيات عرض تكاملية مختلفة. بالاضافة الي انه تم التحقيق في موثوقية الطرق التحليلية المختلفة مثل: نماذج ويليامسون-هول (H-H), نموذج التشوه المنتظم (UDEDN)، نموذج كثافة طاقة التشوه المنتظم (UDEDN)، نموذج كثافة القد التشوه المنتظم (UDEDN)، بالإضافة إلى طريقة هالدر واغنر وطريقة مخطط إجهاد الحجم (SSP)، ومقارنتها جميعا. بالإضافة إلى ذلك، استُخدم المجهر الإلكتروني الماسح (SEM)، نموذج كثافة طاقة التشوه المنتظم (EM-H), نموذج التشوه المنتظم والماسح (SEM)، ومقارنتها جميعا. بالإضافة إلى ذلك، استُخدم المجهر الإلكتروني الماسح (SEM) طريقة منول إلى الأضافة إلى ذلك، استُخدم المجهر الإلكتروني الماسح (SEM) وتحليل الأشعة السيكاني متوافقا بشكل كبير، بينما كان حجم البورة المحسو من نماذج (SEM) مشاهم المربعة. والماسم والتها مرسيكا كبيد الزنك النانوية المُصنعة. وأطهرت النتابع مور ولوجية وتركيب جسيمات أكسيد الزنك النانوية المصنعة. وأظهرت النتائج أن إجهاد الشبكة الأشعة السينية المستنة للطاقة (EDXA) من خلال (SEM) من خال (SEM) من نماذج (SEM) ماسينية المشنتة الطاقة (EM-ظرق النكان وريقة و(SEM) كاني متوافقا بشكل كبير، بينما كان حجم البلورة الأشعر ولارعة وركيك كبيد الزنك البنانوية المصنعة. وأطهرت النتائي والأسبكة وراليكم ورالأسعة السيئة المرسيمات أكسيد الزائك النانوية المقتر من تحليل (H-M) وطريقة (SEM) ماسمن ورالي ا

الكلمات المفتاحية: جسيمات نانوية من أكسيد الزنك، ملف قمم الأشعة السينية، حجم البلورة، إجهاد الشبكة، ثوابت الشبكة.

## 1. Introduction

Over the last decades, ZnO-NPs have attracted enormous interest in scientific research and nanostructure-based studies due to their multifunctional physical and chemical properties. They pave the way for developing a new generation of nano-scaled devices in a broad range of platforms including electronic [1], photocatalytic [2], optical [3], piezoelectric [4], spintronic [5], solar cells [6], sensing [7], etc. In addition, ZnO-NPs have been promising materials in biomedical, biological, environmental, and agricultural research due to their biodegradability, low toxicity, and biocompatibility. ZnO-NPs can be used as a potential anti-tumour [8], antimicrobial [9], anti-inflammatory and antibacterial [10], bioimaging and drug delivery [11], wound healing [12], and tissue engineering agent [13]. Moreover, ZnO-NPs are considered as large and direct band gap semiconducting metal oxide (3.37 eV) with high excitonic binding energy (60 meV), which makes it efficiently perform well in optical devices at or over room temperature [14]. The interconnections between the structural characteristics of ZnO-NPs and its diverse novel applications have been always a hot topic in today's materials science and bioengineering due to its extraordinary performance is highly affected by these structural parameters. The microstructure can be investigated by applying direct examination microscopy methods to evaluate the deformation of nanocrystalline materials and observe the morphological variations at the macro, micro, and local scales [15]. In general, XRD is a suitable and straightforward technique for providing reasonable accuracy on the crystallite size, lattice strain,

and lattice parameters. One of the biggest advantages of XRD is its ability to examine samples in a less labourintensive way without the need for special sample preparation [16]. On the other hand, indirect characterization microscopy methods, in some cases, are quite convenient for studying crystal anisotropy at highly dense stacking faults [17], compressive stress [18], and dislocation densities [19]. In the present work, X-ray peak profile analysis was used to determine the microstructural parameters of ZnO-NPs in terms of crystallite size, microstrain, lattice stress, lattice strain energy density, and lattice constants. In particular, a qualitative estimation of the causes of Xray peak widening for ZnO-NPs, using modified W–H models including UDM, USDM, UDEDM, and further approaches such as the Halder-Wagner method and SSP, was performed.

# 2. Materials and methods

ZnO-NPs were produced by precipitation techniques using chitosan, which acts as a chelating agent for zinc ions, zinc chloride, and sodium hydroxide. The reaction parameters including the concentrations, pH of the precursor solution, growth temperature, and stirring time were optimized to maximize the nanoparticle production and ease the formation of zinc–chitosan complex. First, one solution was prepared by dissolving 5 g of zinc chloride in 100 ml of acetic acid, and then another reaction mixture of chitosan and acetic acid was made. Two precursor solutions were blended and stirred for 24 h, followed by adding a quantitative amount of sodium hydroxide (5 %) with steady stirring. The solution was kept for 24 h at room temperature to generate a white gel-like precipitate of zinc hydroxide (Zn (OH)<sub>2</sub>). Finally, to eject nonreactive species the prepared gel was filtered and washed with distilled water, and then heated at 500  $^{\circ}$ C for 4 h in the furnace to obtain ZnO-NPs. XRD with Cu-K $\alpha$  X-ray radiation having a characteristic wavelength of 0.15418 nm was used to characterize the synthesized ZnO-NPs. The scan speed of  $2^{0}$ /min was performed from 10<sup>0</sup> to 60<sup>0</sup>. The XRD patterns were analyzed through the X'Pert HighScore software with the assistance of OriginPro data analysis software to estimate the microstructural features of ZnO-NPs. The surface morphology and the elemental composition of the ZnO-NPs sample were examined by SEM and EDXA.

# 3. Results and discussion

The XRD plot of the prepared ZnO-NPs is shown in Fig. 1. It was seen that all the observed peaks were indexed as hexagonal wurtzite structures of ZnO according to the standard data of the Joint Committee on Powder Diffraction Standards (JCPDS), having card no. 01-089-0510 [20]. It was noticed that the diffracted peaks were sharp and narrow, indicating that ZnO-NPs were highly crystalline. There are no other reflected peaks were found in the XRD patterns suggesting that ZnO-NPs samples have good phase purity. In the following subsections, the X-ray peak profile was analyzed to estimate the different structural aspects of ZnO-NPs using various approaches based on the W-H models (three models), the Halder-Wagner Method, and the SSP method.



Fig. 1. The XRD plot of the prepared ZnO-NPs.

#### 3.1. W-H models

The XRD peak broadening is developed because of the crystallite size and lattice strain. According to the Scherrer formula, the contribution of only crystallite size on the peak broadening is included. However, the W-H method is considered both size-induced and strain-induced peak widening [21]. Lattice strain is mainly released due to crystal imperfections, such as lattice dislocations, grain boundary, triple junction, contact or sinter stresses, stacking faults, point defects, and coherency stresses [22]. The W-H method as an easy, straightforward integral breadth approach enables assessing the contributions of the size of the crystal and the microstrain separately. Therefore, the total peak breadth is described by the sum of the crystallite size and lattice strain contributions and can be represented by the following Equation:

## $\beta_{hkl} = (k\lambda/D\cos\theta) + 4\varepsilon\tan\theta$

(1)

where k is the Scherrer constant ( $\approx 0.90$ ),  $\lambda$  the wavelength of the X-rays used (0.15418 nm),  $\theta$  the diffraction angle,  $\beta_{hkl}$  is the full width at half maximum (FWHM; in radians), and  $\varepsilon$  is the microstrain. The first term of Equation (1) represents the size of the crystal (the Scherrer equation), whilst the second represents the strain contribution. According to the W-H approach, the lattice strain is related to the broadening of the X-ray peaks by  $\varepsilon \approx \beta / \tan \theta$ . The only difference between the Scherrer formula and the W-H approach is the former has a 1/cos  $\theta$ dependency, while the latter has tan  $\theta$  dependency [23]. The crystallographic parameters of ZnO-NPs obtained from the XRD line profile are summarized in Table. 1.

2θ(deg)	θ(deg)	4sin (θ)	cos(θ)	β(rad)	β.cosθ	hkl	d-spacing [Å]
31.6698	15.8349	1.09144	0.96205	0.00357	0.00343	100	2.82532
34.3442	17.1721	1.18096	0.95542	0.00391	0.00374	002	2.61119
36.2663	18.1331	1.24488	0.95033	0.00425	0.00404	101	2.48119
38.1532	19.0766	1.30732	0.94508	0.00455	0.00430	102	2.35686
47.5494	23.7747	1.61256	0.91513	0.00496	0.00454	110	1.91549
56.5664	28.2832	1.89532	0.88061	0.00530	0.00467	103	1.62569

Table. 1. The crystallographic parameters of ZnO-NPs extracted from the XRD peak profile.

#### 3. 1.1. Uniform Deformation Model (UDM)

In UDM, the crystal lattice is presumed to be naturally isotropic, and the strain is uniformly distributed in all crystallographic directions [24]. By rearranging Equation (1) the UDM can be expressed as:

$$\beta_{hkl}$$
.  $\cos\theta = k\lambda/D + 4\varepsilon.\sin\theta$ 

(2)

Equation (2) illustrates a straight-line equation and can be represented by plotting the term  $(4Sin\theta)$  on the x-axis as a function of  $(\beta_{hkl}, \cos\theta)$  on the y-axis for all diffraction peaks of ZnO-NPs. The microstrain and crystallite size contributions can be estimated from the linear fitting of the plot, where the strain is obtained from the slope and the size of the crystal from the intercept with the *y*-axis. The size of the crystal estimated by the UDM is approximately 36.88 nm, while the microstrain is determined to be  $1.41 \times 10^{-3}$ . The positive value of the slope suggested the expansion of the crystal lattice [25]. The plot showed a good linear fitting as the correlation coefficient value of R<sup>2</sup> is 0.89. The UDM plot for the ZnO-NPs is shown in Fig. 2.



Fig. 2. The UDM plot for the ZnO-NPs.

## 3.1.2. Uniform stress deformation model (USDM)

Due to the UDM analysis assumes the strain to be uniformly and linearly dependent on the inverse of the atomic spacing  $(d^{-1} = 2 \sin \theta / \lambda)$ , therefor it can be noted that lattice deformation is heterogenous within the crystalline planes producing a reasonable anisotropy through planes. Hence, an anisotropic effect is considered by modifying the W–H equation to include anisotropic strain. This modified model is USDM in which the uniform deformation stress along all the lattice plane directions is used to estimate the lattice microstrain by considering the elastic constants [26]. According to USDM, the strain is evaluated from Hooke's law where stress and strain are linearly proportional by the following equation:

$$\sigma = \varepsilon. Y_{hkl} \tag{3}$$

Here,  $\varepsilon$  is the anisotropic stain,  $\sigma$  is the deformation stress, and  $Y_{hkl}$  is the modulus of elasticity or Young's modulus. It is worth mentioning that Hook's law is only valid when a sample holds a small amount of microstrain, otherwise the linear proportion of the stress and strain no longer exist. Thus, by substituting Hooke's law  $\varepsilon = \sigma / Y_{hkl}$  to Equation (2) the USDM equation can be expressed as:

$$\beta_{hkl}$$
.  $\cos\theta = k\lambda/D + 4 \sigma . \sin\theta/Y_{hkl}$ 

Young's modulus Y<sub>hkl</sub> can be given for a hexagonal crystal by the following Equation [27].

$$Y_{hkl} = \frac{[h^2 + \frac{(h+2k)^2}{3} + (\frac{al}{c})^2]^2}{S_{11}(h^2 + \frac{(h+2k)^2}{3})^2 + S_{33}(\frac{al}{c})^4 + (2S_{13} + S_{44})(h^2 + \frac{(h+2k)^2}{3})(\frac{al}{c})^2}$$
(5)

Where  $s_{11}$ ,  $s_{13}$ ,  $s_{33}$  and  $s_{44}$  are the elastic compliances of ZnO with values  $7.858 \times 10^{-12}$ ,  $-2.206 \times 10^{-12}$ ,  $6.940 \times 10^{-12}$  and  $23.57 \times 10^{-12}$  m<sup>2</sup> N<sup>-1</sup>, respectively, and 'a' and 'c' are lattice constants [28]. Using the compliance values, Young's modulus for ZnO-NPs was estimated as ~127 GPa.



Fig. 3. The USDM plot for the ZnO-NPs.

Plotting  $\beta_{hkl}$ . cos $\theta$  on the y-axis versus 4sinh/Y<sub>hkl</sub> on the x-axis, then the uniform deformation stress and the crystallite size can be calculated from the slope of the fitted line and the y-intercept, respectively. The measured crystallite size at 37.5 nm was similar to that obtained from UDM, while the anisotropic stress was nearly 193 MPa. The USDM plot for ZnO-NPs is shown in Fig. 3, it can be indicated from the higher value of the goodness-of-fit R<sup>2</sup> that the lattice strain produced by dislocations is monotonous in sin  $\theta$ .

#### 3.1.3. Uniform deformation energy density model (UDEDM)

As mentioned earlier, in some cases, when the anisotropic nature is considered, the concept of crystal homogeneity and isotropy is unfitted. So, when anisotropic lattice energy density e.g., energy per unit volume (u) is considered another modified UDEDM must be adopted. Therefore, u as a function of strain based on Hooke's law can be expressed as:

 $u = (\epsilon^2 Y_{hkl})/2$ 

(6)

(4)

As stress and strain are related by Equation (3), thus the lattice strain can be described as a function of the anisotropic energy density,

$$\varepsilon = \sigma. \left( 2.u/Y_{hkl} \right)^{1/2} \tag{7}$$

Then, by substituting Equation (7) into Equation (2) the UDEDM equation can be expressed as [29],

$$\beta_{hkl.}\cos\theta = k\lambda/D + 4.\sin\theta.(2.u/Y_{hkl})^{1/2}$$

Then, by plotting the term  $\beta_{hkl}$ . cos $\theta$  on the y-axis versus  $4 \sin\theta (2/Y_{hkl})^{1/2}$  on the x-axis, the Y-intercept of the fitted line represents the crystallite size as 35 nm, while the slope provides the anisotropic energy density value which is approximately 41 KJm<sup>-3</sup>. The plot of UDEDM for the ZnO-NPs is shown in Fig. 4. Notably, all W-H models provide nearly similar findings of the lattice strain and crystallite size.

(8)



Fig. 4. The UDEDM plot for the ZnO-NPs.

#### 3.2. Halder-Wagner Method

The Halder-Wagner approach is an integral broadening method in which the low-angle reflections, where the overlapping of the diffracting peaks is much less, are particularly targeted in the XRD line profile analysis. In this model, the size and the strain breadth are described as Lorentz, and Gaussian functions, respectively, and the peak broadening is a symmetric Voigt function [30]. Therefore, according to the Voigt function,  $\beta_{hkl}$  can be given as:

$$\beta_{hkl}^2 = \beta_L \cdot \beta_{hkl} + \beta_G^2 \tag{9}$$

Where  $\beta_L$  and  $\beta_G$  are the full width at half maximum of the Lorentzian and Gaussian functions. The broadening of reciprocal lattice points ( $\beta^*$  and the interatomic spacing for the reciprocal cell ( $d^*$ ) are included in the following Equation to provide the crystalline size and the lattice strain.

$$\left(\frac{\beta^*}{d^*}\right)^2 = \frac{\kappa\beta^*}{D(d^*)^2} + (2\varepsilon)^2 \tag{10}$$

 $\beta^*$  and  $d^*$  can be given as

$$\beta^* = \beta \cos\theta / \lambda \tag{11}$$

$$d^* = 2\sin\theta/\lambda \tag{12}$$

Now, using Equations (11) and (12) Equation (10) can be rewritten as:

$$\left(\frac{\beta}{\tan\theta}\right)^2 = \frac{\kappa\lambda}{D} \cdot \frac{\beta}{\tan\theta\sin\theta} + 16\varepsilon^2 \tag{13}$$

The plot of Equation (13), with the term( $\beta^*/d^{*2}$ ) along the x-axis and ( $\beta^*/d^*$ )<sup>2</sup> along the y-axis for all the XRD data is shown in Fig. 5. Based on the linear fitting of Equation (13), the slope gives the crystalline size while the

intercept represents the microstrain of ZnO-NPs. The size of the crystal estimated from the Halder-Wagner model is 27.97 nm, which approximately matches with those extracted from the W-H models, whilst, according to the negative value of the intercept the lattice strain cannot be calculated.



Fig. 5. The plot of Halder-Wagner model for ZnO-NPs.

#### 3.3. SSP method

In comparison to the W-H methods, SSP is another approach that enables a better determination of the crystallite size and the lattice strain based on the isotropic line broadening of the diffracted peaks. Hence, in this method, much more attention is given to data from reflections at low angles, owing to higher values of the peak position and the intensity resulting in overlapping peaks where the accuracy is extremely declined, and the quality is quite poor. It was demonstrated that the XRD profile is a contribution of Lorentzian function (crystallite size) and Gaussian function (microstrain) [27]. The SSP method can be represented as,

$$(d_{hkl}.\beta_{hkl}.\cos\theta)^2 = \frac{k\lambda}{D} . (d_{hkl}^2.\beta_{hkl}.\cos\theta) + \frac{\varepsilon^2}{4}$$
(14)

In the same way, the plot of  $(d_{hkl}^2, \beta_{hkl}. cos\theta)$  and  $(d_{hkl}, \beta_{hkl}. cos\theta)^2$  can be drawn along x and y axes, respectively, so that the size of the crystal is evaluated from the slope of the fitted line while the lattice strain is estimated from the root of the y-intercept (see Fig. 6). Hence, the estimated crystallite size is 51 nm and in good agreement with the previously reported TEM data for ZnO-NPs [31], while the lattice strain of ZnO-NPs is approximately  $1.1 \times 10^{-3}$ .



Fig. 6. The SSP plot of ZnO-NPs.

The lattice strain evaluated from the SSP, and W-H models was comparable and agreeable (see Table. 2). However, the estimated crystallite size from the SSP model was higher compared to that obtained by the W-H models and the Halder-Wagner approach.

Method	D (nm)	ε (unit ×10- <sup>3</sup> )	σ (Mpa)	u (KJm <sup>3</sup> )	TEM [D(nm)]
W-H (UDM)	36.88	1.41			30 [32]
W-H (USDM)	37.5	1.52	193		30 [33]
W-H (UDEDM)	35	0.802	101.8	41	—
SSP	51	1.1	139.7	77	50 [31]
Halder-Wagner	27.97				

Table. 2. Geometric parameters for the synthesized ZnO-NPs

# 3.4. Lattice parameter

To study the crystal structure and its physical properties it is essential to precisely evaluate the lattice parameters which are free from all systematic errors such as inaccuracy in the measurement of  $\theta$  and hence in the estimation of the interplanar spacing d. Different methods such as the Cohen method and Lutts method were used for measuring the lattice parameters from the X-ray peak profile. Herein, a simple and straightforward quantitative method based on The Nelson-Riley extrapolation function and least squares analysis [34] was used to estimate the lattice parameter. The Nelson-Riley Function F( $\theta$ ) is given as:

$$(\theta) = [(\cos 2\theta / \sin \theta) + (\cos 2\theta / \theta)]/2$$

It was shown that this proposed extrapolation function is extremely accurate at lower angles ( $\theta$ ) not only at higher values of the peak position. The lattice constants 'a' and 'c' of the ZnO hexagonal structure were related to Miller indices and the d-spacing by the following Equation [35],

(15)

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$
(16)

The lattice constants vary from each other at various Miller indices due to unexpected adjustment errors, which can be eliminated by extrapolating  $\cos^2(\theta)/\sin(\theta) \rightarrow 0^\circ$ . Based on the Bragg's law and at the first-order approximation (n=1),

$$d = \lambda/2sin\theta \tag{17}$$

By using Equation (17) Equation (16) can be rewritten as,

$$\sin\theta^{2} = \frac{\lambda^{2}}{4a^{2}} \left[ \frac{4}{3} \left( h^{2} + k^{2} + hk \right) + \left( \frac{a}{c} \right)^{2} l^{2} \right]$$
(18)

Now, the lattice parameters 'a' and 'c' of the ZnO-Nps can be estimated by Equation (18). The linear plot of Nelson-Riley function  $f(\theta)$  and lattice parameters 'a' and 'c' of the ZnO-NPs for different diffracted planes can be performed along the x and y axes (see Fig. 7), respectively. The intercept of the fitted line provides the precise values of lattice parameters 'a<sub>0</sub>' and 'c<sub>0</sub>' which are extrapolated as nearly 0.31513 nm and 0.50329 nm, respectively. These estimated lattice parameters of the synthesized ZnO-NPs sample are typically less than their bulk counterparts, which could be attributed to the high surface area and nanoscale size of the nanoparticles.



Fig. 7. The Nelson-Riley plots to estimate the lattice parameters of ZnO-NPs by a linear regression.

## 3.5. Estimation of RMS strain

The credibility of devices based on nanostructured semiconductor materials in different applications is highly influenced by the introduction of lattice imperfections as their existence and activity reduce the efficiency of these nanodevices [36, 37]. Therefore, the growth of high-quality crystals with less defect density and uniform diffusion of doping and background impurities are highly demanded to produce much more efficient micro and nanodevices. When the crystal lattice is in the proximity of a deformation and dislocation, it would elastically strain causing the breadth of the diffraction peaks [38]. The presence of defects in the crystals is unavoidable since these imperfections have already developed during the epitaxial growth methods of semiconductor materials. Moreover, special phases of the growth process such as doping, thermal annealing, coating, e-beam lithography, and chemical etching boost the density of defects within the semiconductor materials [39]. The maximum microstrain  $\epsilon_{hkl}$ , was derived mathematically from Bragg's law using the Stokes and Wilson method [40]. The root-mean-square (RMS) microstrains  $\epsilon_{RMS}$  along the <hkl> crystallographic directions were calculated using the maximum microstrain with the presumption of a Gaussian distribution of the lattice strain using the following Equations:

$$\varepsilon_{hkl} = \left(\frac{\Delta d_{hkl}}{d_{0hkl}}\right) \tag{19}$$

$$\langle \varepsilon_{RMS} \rangle = \left(\frac{2}{\pi}\right)^{1/2} \varepsilon_{hkl} \tag{20}$$

It is worth mentioning that the appearance of lattice strains on the <hkl> crystallographic direction indicates the introduction of the interplanar d-spacings distribution which leads to broadening the hkl Bragg reflection without shifting. Now, Equation (20) can be rearranged using Equation (19) as,

$$\langle \varepsilon_{RMS} \rangle = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{\Delta d_{hkl}}{d_{0hkl}}\right) \tag{21}$$

The  $\varepsilon_{RMS}$  is a measure of the maximum lattice distortion [40, 27]. The value of each interplanar spacing d is extracted from the X-ray peak profile, while d<sub>0</sub> represents the standard interplanar spacing values [20]. According

to these interplanar spacings data,  $\varepsilon_{hkl}$  and  $\varepsilon_{RMS}$  for each crystallographic direction were calculated using Equations (19) and (20) and shown in Table. 3. Here  $\varepsilon_{RMS}$  was computed for six crystallographic planes of ZnO-NPs (100), (002), (101), (102), (110) and (103).

(hkl)	d-observed (nm)	dostandard (nm)	Ehki	ERMS
100	.282532	.2814300	.0039157	.00312
002	.261119	.2603320	.0030231	.00241
101	.248119	.2475920	.0021285	.00170
102	.235686	.1911140	.233222	.18613
110	.191549	.1624720	.178966	.14283
103	.162569	.1477120	.100581	.08027

Table. 3. The  $\varepsilon_{hkl}$  and  $\varepsilon_{RMS}$  of ZnO-NPs as a function of the Miller indices of the Bragg reflections.

The linear relationship between  $\varepsilon_{RMS}$  and  $\varepsilon_{hkl}$  is shown in Fig. 8. It can be noted that the estimated values of  $\varepsilon_{RMS}$  for each crystallographic plane vary from those evaluated by W-H models which could be ascribed to that W-H methods can produce higher values of crystallite size and lower values of the lattice strain [41]. It was demonstrated that when the lattice strain values match, each point should almost be located on a straight line making an angle of 45° to the x-axis, which is seen in Fig. 8 and shown by the correlation coefficient (R<sup>2</sup> =1) [42-46]. The  $\varepsilon_{RMS}$  changes linearly with respect to  $\varepsilon_{hkl}$ , indicating that there is no discrepancy in the (hkl) crystallographic planes in the nanocrystalline nature [47]. In the case of the presence of scattered points in the plot with lower values of R<sup>2</sup>(< 0.80), more crystallographic planes should be considered for precise estimation of the structural parameters [48]. In general, the induction of lattice strain is generated by the displacement differences of the atoms with respect to their reference-lattice positions. In ZnO-NPs the lattice strains can be raised in several ways such as the excess density of grain boundaries, dislocations, vacancies, and lattice imperfection [49, 50].



Fig. 8. The linear correlation between  $\varepsilon_{RMS}$  and  $\varepsilon_{hkl}$  of ZnO-NPs.

# 3.6. The SEM and EDXA analysis

Lastly, the surface morphology of the synthesized ZnO-NPs was investigated by SEM. As can be observed in Fig. 9 the SEM image demonstrates that the prepared particles have approximately an inhomogeneous shape. In addition, the aggregation of particles was noted which commonly takes place when physical processes gather particle surfaces to attach under short-term thermodynamic interactions [51]. Due to the large specific surface area and high surface energy ZnO-NPs are more likely to agglomerate and form large particles [52, 53].



Fig. 9. SEM image of ZnO-NPs.

It was reported that the aggregation of nanoparticles arises apparently through the process of heating [54]. The elemental composition of the ZnO-NPs sample was analysed by EDXA (see Fig.10). The EDXA spectra show that only two elements Zn and O are found in the fabricated sample. There are no other impurities which is completely consistent with the XRD data.



Fig. 10. EDXA spectra of ZnO-NPs.

# 4. Conclusion

In the present study, ZnO-NPs were synthesized by precipitation methods using chitosan, zinc chloride, and sodium hydroxide and characterized using XRD, SEM, and EDXA. A qualitative estimation of microstructural properties and crystallinity of ZnO-NPs using X-ray peak broadening analysis was demonstrated. Several elastic properties of ZnO-NPs including the lattice strain, lattice stress, lattice strain energy density and crystallite size were evaluated by different methods of W-H models, SSP model and Halder-Wagner approach. All suggested models were compared, and it was found that the values of the crystallite size obtained from UDM which considers the homogeneous isotropic nature of the crystal, were nearly similar and highly intercorrelated with the crystal sizes obtained by UDSM, and UDEDM, which consider the anisotropic nature of the crystallites, indicating that including of lattice strain in the three models of W-H minorly influences the crystallite size of ZnO-NPs.

Besides, the crystallite sizes estimated by all models of W-H were matched very well with the crystal size obtained by TEM analysis [32, 33]. The calibrated crystallite size value obtained by the SSP method was larger than that of the W-H models and Halder Wagner methods, while the lattice strain evaluated from the SSP, and W-H models

was well-correlated and agreeable. The RMS lattice strain changes linearly with respect to the strain resulting from the interplanar spacing, showing that there is no discrepancy in the (hkl) crystallographic planes in the nanocrystalline nature. It was found that the estimated values of the RMS lattice strain for each crystallographic plane differ from those calculated by W-H models which could be ascribed to that W-H methods can produce higher values of crystallite size and lower values of the lattice strain [41]. This study confirms that all proposed integral breadth methods are simplified and consistent for the study of the microstructural features of ZnO-NPs from X-ray peak profile analysis. In particular, the W-H models can produce valuable details on the qualitative source of X-ray peak broadening for ZnO-NPs.

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