Restriction of Particle Size and Lattice Strain through X-Ray Diffraction Peak Broadening Analysis of ZnO Nanoparticles

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Abstract
In this study have been determined the crystallite size and lattice strain of ZnO nanoparticles as shown in Figure (1) by using variance and integral breadth methods, and also used some other methods such as Scherrer and Williamson-Hall to calculate above parameters. In variance method we have calculated the values of crystallite size, mean square strain and lattice strain are (22.276 nm), (0.133473 x 10^-3) and (14.479 x 10^-3) respectively, and the crystallite size is (25.126 nm) as well as the lattice strain is (2.443 x 10^-3) by using integral breadth method. The other methods such as Scherrer which gives the value of crystallite size is (17.622 nm) and lattice strain is (6.036 x 10^-3), while the Williamson-Hall gives the following values: crystallite size is (22.063 nm) and the lattice strain is (1.192 x 10^-3).

Keywords: X-ray diffraction, Variance analysis method, integral breadth method.

1. Introduction
Diffraction lines of crystalline materials contain a wealth of microstructural information: The amount and distribution of the phases in the material, compositional inhomogeneity, the crystallite size and shape distributions, the crystallographic orientation distribution function. In many cases such information is not easily and statistically assured accessible by methods other than diffraction [1]. Microstructural parameters of a given material, crystallite size, distribution of sizes and crystallite strain, can be determined by X-ray diffraction methods, in combination with other techniques, especially electron microscopy and diffraction [2]. In 1912, the X-ray diffraction by crystals was discovered by Friedrich, Knipping and V. Laue [1]. X-ray diffraction is a convenient method for determining the mean size of nano crystallites in nano crystalline bulk materials. In 1918, the first scientist, Paul Scherrer, published his results in a paper that included what became known as the Scherrer equation. This can be attributed to the fact that “crystallite size” is not synonymous with “particle size”, while X-ray diffraction is sensitive to the crystallite size inside the particles [3]. Laue in 1926 has considered the case of crystallites having the form of a parallelepiped and introduced the general form of the integral breadth, and also used Cauchy and Gaussian functions to model line profiles for the first time [4]. X-ray diffraction peak profile analysis is a powerful tool for the characterization of microstructures in crystalline materials. Diffraction peaks broaden when crystallites are small or the material contains lattice defects. The two effects can be separated on the basis of the different diffraction-order dependence of peak broadening. In 1953, the classical method have evolved during the past five decades: the Williamson-Hall (Williamson and Hall, 1953) procedure [5]. The method was first suggested by Tournarie (1956), and then developed by Wilson (1962a) [6]. Wilson in 1963 has applied the standard measures of position and dispersion used in statistical analysis (i.e. the centroid and variance) to powder diffraction, since the central moments of convoluted functions, can readily be separated. This approach has been reviewed recently by Berti (1993) [7]. Klug and Alexander in 1974 have developed Scherrer, integral breadth and variance methods [7]. In this study to calculate the crystallite size and lattice strain XRD patterns of calcined samples of ZnO nanoparticles in the range of 2θ =30° to 70° were used as shown in Figure (1) [8].

2. Theory
2.1 The Variance method
The variance of the line profiles [W(2θ)] is defined as the second central moment of the distribution of diffracted intensities [I(2θ)] , and is therefore a measure of the line broadening. According to this definition, W(2θ) is calculated on the 2θ scale for a given truncation range (2θ) by the expression [9].

\[ W(2\theta) = \frac{\int_{(2\theta)} (2\theta - \langle 2\theta \rangle)^2 \cdot I(2\theta) d(2\theta)}{\int_{(2\theta)} I(2\theta) d(2\theta)} \] .......................... (1)

With <2θ> being centroid of line profile [7].

\[ <2\theta> = \frac{\int_{(2\theta)} 2\theta \cdot I(2\theta) d(2\theta)}{\int_{(2\theta)} I(2\theta) d(2\theta)} \] .......................... (2)

May let range of Measurement \( \sigma_1, \sigma_2, \sigma \) and express the linear of variance-range in for

\[ w = w_0 + K\sigma \] .......................... (3)

The variance coefficients (w_0 and K) of the line profiles can be evaluated empirically by a linear fit to the set of variance-range pairs determined directly by equation (1) [9].

The variance (W) of the X-ray line profile is given by

\[ W = W_p + W_s + W_d \] .......................... (4)
Where \( W_P, W_S, W_D \) is the factor corresponding to crystallite size, lattice strain, layer disorder respectively. The variance of the X-ray line profile is represented by \([10]\).

\[
W = \frac{\Delta 2\theta}{2\pi \rho' \cos \theta} + \frac{\lambda^2}{\cos^2 \theta} \tag{5}
\]

S given by equation (6) \([11-12]\).

\[
\frac{1}{\rho^2} = \frac{d^2}{d} + \frac{B_D}{d} \tag{6}
\]

\[
\frac{1}{\rho^2} = \frac{d^2}{d} + B_D \tag{7}
\]

Where \( B_D \) is the integral width of the defect profile, \( < e^2 > \) is the mean square strain, \( d \) is the inter planer spacing, \( \Delta 2\theta \) = total angular range in 2\( \theta \) scale over which the measurements are being made. \( P' \) Is the apparent crystallite size from variance method; \( P \) is true crystallite size \([10-11]\).

From Bragg’s law \([13]\).

\[
\frac{4}{\rho} \sin \theta = \frac{\lambda}{\rho} \rightarrow \frac{1}{\rho} \sin \theta = \frac{\lambda}{4 \sin \theta} \tag{8}
\]

\[
2 \sin \theta = \lambda \rightarrow d = \frac{\lambda}{2 \sin \theta} \tag{9}
\]

Substitute equation (6) and (7) in (5) gives the following equation:

\[
W = \frac{\Delta 2\theta}{2\pi \rho' \cos \theta} + \frac{\lambda^2}{\cos^2 \theta} \tag{10}
\]

Where \( B_D \) is commonly neglected in practical applications \([7]\). The numerical solution of size and strain parameter is conveniently carried out by neglecting \( B_D \) and arranging equation (12) and become to equation (13). It is assumed that the broadening of the x-ray line is due to the crystallite-size and strain only, the variance can be written as \([14-15]\).

\[
W_{2\theta} = \frac{\Delta 2\theta \lambda}{2\pi \rho' \cos \theta} + 4 \tan^2 \theta < e^2 > \tag{13}
\]

Multiplying equation (13) by \( \frac{\cos \theta}{\Delta 2\theta \lambda} \) we can get the following equation:

\[
\frac{W_{2\theta} \cos \theta}{\Delta 2\theta \lambda} = \frac{1}{2\pi \rho'} + \frac{4 \sin \theta \tan \theta}{\Delta 2\theta \lambda} < e^2 > \tag{14}
\]

Also the relation between root mean square strain and lattice strain is \([16]\).

\[
< e^2 >^{1/2} = \frac{\sqrt{2} e}{\sqrt{\pi}} \tag{15}
\]

The instrumental corrected broadening \( \beta_{int} \) \([17]\) corresponding to the diffraction peaks was estimated using the equation

\[
\beta_{int} = \sqrt{\left( \beta_{measured} \right)^2 + \left( \beta_{instrumental} \right)^2} \tag{16}
\]

2.2 Integral Breadth Method

The integral breadth (IB) method is frequently used in studies of the microstructure of materials for a quick estimation of the so-called ‘size-strain’ line broadening effect, mostly relating to the broadening caused by the average size of the crystallites (coherently scattering domains) and by lattice strains (often denoted as microstrains or lattice distortions) caused by, e.g. the presence of lattice defects \([18]\).

\[
\beta_i = A / I_0 \tag{17}
\]

\( A \) being the peak area and \( I_0 \) the height of observed line profile. In both the relation the peak broadening was attributed to effect of the disfiguring coherent size. When the broadening is solely due to strain effect the following \([19]\).

The peak broadening and its anisotropy were supposed to be caused by the dislocations in the crystals. According to Krivoglaz, the strain-induced part of the integral breadth \( \beta_i \) of a diffraction profile (expressed in S units, \( s = 2 \sin \theta / \lambda \)) related to the arrangement of the dislocations, with weak defect correlation, is given by \([20]\).

\[
\beta_i = 2 \cos \theta e \tag{18}
\]

\[
\beta_i = 4 \cos \theta e \frac{\sin \theta}{\lambda} \tag{19}
\]

Where \( \beta_{2\theta} = \frac{\lambda}{\cos \theta} \beta_i \) integral breadth in the units of S \([21]\).

Substitute equation (19) in (20) gives the following equations:

\[
\beta_{2\theta} = \frac{\lambda}{\cos \theta} 4 \cos \theta e \frac{\sin \theta}{\lambda} \tag{20}
\]
\[
(\beta_{20})_{l}^{0} = 4e \tan \theta \tag{22}
\]

Scherer for broadening resulting from small crystallite size alone [22].

\[
P = \frac{k \lambda}{\beta_{20} \cos \theta} \rightarrow (\beta_{20})_{l}^{0} = \frac{k \lambda}{\beta_{20} \cos \theta} \tag{23}
\]

In 2\theta Scale, or

\[
(\beta_{2})^{2} = \frac{K \lambda}{\beta_{20} \cos \theta} \rightarrow (\beta_{2})_{l}^{0} = \frac{K}{D} \tag{24}
\]

On the S Scale

\[
S = \frac{T}{U} \rightarrow (\beta_{2})_{l}^{0} = \frac{T}{U} \tag{25}
\]

Scherrer for broadening resulting from small crystallite size alone [22].

\[
S = \frac{T}{U} \rightarrow (\beta_{2})_{l}^{0} = \frac{T}{U} \tag{23}
\]

In 2\theta Scale, or

\[
(\beta_{2})^{2} = \frac{K \lambda}{\beta_{20} \cos \theta} \rightarrow (\beta_{2})_{l}^{0} = \frac{K}{D} \tag{24}
\]

On the S Scale

\[
S = \frac{T}{U} \rightarrow (\beta_{2})_{l}^{0} = \frac{T}{U} \tag{25}
\]

Wherein K of equation (24) has been set equal to unity [23, 24]. With regard due to effect of size (or due to stacking faults\( (\beta_{20})_{l}^{0} \)) and widening induced by microstrain \( (\beta_{20})_{l}^{0} \), respectively [25].

According to Voigt method, the basic relationships between the integral breadths \( \beta_{i} \) are shown as the following equation: [21, 26].

\[
\beta_{i} = \beta_{SC} + \beta_{DG} \quad \text{(Cauchy/Cauchy)} \quad \tag{25}
\]

\[
\beta_{i}^{2} = (\beta_{SG})^{2} + (\beta_{DG})^{2} \quad \text{(Gaussian/Gaussian)} \quad \tag{26}
\]

Where \( \beta_{SG} \) and \( \beta_{DG} \) are the Cauchy components of size and strain integral breadth respectively and \( \beta_{SG} \) and \( \beta_{DG} \) are the corresponding Gaussian components [21].

Substitute equation (19) and (24) in (25) gives the following equation:

\[
(\beta_{2})_{l}^{0} = \frac{1}{p} + 4e \sin \theta \lambda \tag{27}
\]

Substitute equation (19) and (24) in (26) gives the following equation:

\[
[(\beta_{2})_{l}^{0}]^{2} = \left[ \frac{1}{p} \right]^{2} + 16e^{2} \left[ \sin \theta \lambda \right]^{2} \tag{28}
\]

From equation (20) can obtain the following equation:

\[
(\beta_{2})_{l}^{0} = \frac{1}{p} \tag{29}
\]

Substitute equation (29) in (27) gives equation (30). The basic assumption of this method is that the both size and strain broadened profiles are of Cauchy (Lorentzian) shape. Based on this assumption, a mathematical relation was established between the integral breadth (\( \beta \)), volume weighted average crystallite size (\( P \)), and the lattice strain (\( e \)) as follows [24].

\[
(\beta_{2})_{l}^{0} = \frac{1}{p} + 4e \sin \theta \lambda \tag{30}
\]

Substitute equation (29) in (28) gives equation (31). Gaussian squared method assuming a Gaussian–Gaussian profile, crystallite size and lattice strain parameters can be calculated [26].

\[
[(\beta_{2})_{l}^{0}]^{2} = \left[ \frac{1}{p} \right]^{2} + 16e^{2} \left[ \sin \theta \lambda \right]^{2} \tag{31}
\]

According to Weidenthaler [28], the relationships between the integral breadth \( \beta \) and FWHM for Cauchy and for Gaussian profiles are described by the following equations [29-30]:

\[
\frac{\beta_{FWHM}}{\beta_{i}} = \frac{2}{\pi} = 0.6366 \quad \text{For Cauchy profile} \quad \tag{32}
\]

\[
\frac{\beta_{FWHM}}{\beta_{i}} = \sqrt{\frac{4\pi n}{\pi}} = 0.9394 \quad \text{For Gaussian profile} \quad \tag{33}
\]

If \( \frac{\beta_{FWHM}}{\beta_{i}} \) close to 0.6366, should use the integral breadth (Cauchy profile) equation (30) and if \( \frac{\beta_{FWHM}}{\beta_{i}} \) close to 0.9394, should use the integral breadth (Gaussian profile) equation (31) to determine the crystallite size (\( P \)) and the lattice strain (\( e \)).

2.3 The Peak Position and the Peak Width (Broadening) Determination

There are two important measures in line profile analysis of power diffraction

- The peak position
- The peak width (broadening)

The peak position determined by Klug and Alexander in 1974 [7].

Full-Width at Half-Maximum intensity (FWHM): The overall width of line profile at half-maximum intensity measured above the background as shown in Figure (2).

\[
FWHM = 2\theta_{2} - 2\theta_{1}
\]

2.4 Another analysis methods

2.4.1 Scherrer Method

XRD can be utilized to evaluate peak broadening with crystallite size and lattice strain due to dislocation [31].

The crystallite size determined by the X-ray line broadening method using the Scherer equation

\[
P = \frac{k \lambda}{\beta_{hkl} \cos \theta} \tag{34}
\]
Where $P$ is the crystallite size in nanometers, where $K=0.94$, is the wavelength of the radiation (1.54056 Å for CuKα radiation), $\beta_{hkl}$ is the full width at half maximum (FWHM) of the peak in radians, and $\theta$ is the Bragg angle [32].

Similarly, according to Wilson, the broadening due to lattice strain may be expressed by the relation:

$$ \beta_\theta = \eta \tan \theta \rightarrow e = \frac{\beta_\theta}{4 \tan \theta} \quad \text{(35)} $$

Where $\eta$, is the peak broadening due to lattice strain $\eta$ the strain distribution within the material, $\eta = 4e$ and $\theta$ is the Bragg's angle [33].

### 2.4.2 Williamson-Hall Method

Crystal imperfections and distortion of strain-induced peak broadening are related by $e \approx \beta_s/4\tan\theta$. There is an extraordinary property of equation (34) which has the dependency on the diffraction angle $\theta$. Scherrer-equation follows a $1/\cos\theta$ dependency but not $\tan\theta$ as W-H method. This basic difference was that both microstructural causes small crystallite size and lattice strain occur together from the reflection broadening [34]. Depending on different $\theta$ positions the separation of size and strain broadening analysis is done using Williamson and Hall. The following results are the addition of the Scherrer equation and $e \approx \beta_s/4\tan\theta$ [35].

$$ H_{hkl} = H + H' \quad \text{(36)} $$

$$ H_3 = \frac{\theta_0}{K} + 4* \frac{\theta_0}{\cos \theta} \quad \text{(37)} $$

According to the Williamson-Hall method [36], the individual contributions to the broadening of reflections can be expressed as

$$ \beta_{hkl}\cos \theta = \frac{K^2}{P} + 4esin\theta \quad \text{(38)} $$

Where $P$ is the crystallite size and $e$ is the lattice strain [37].

### 3. Results and Discussion

#### 3.1 Variance analysis method

In this study we have analyzed line diffraction profile by variance method, from Figure (1) we have got $\theta$ and Intensity, $\sum I(\text{peak})$, $\sum(2\theta.I(2\theta))$, then used equation (2) to obtain centroid ($2\theta$), then got $\sum(2\theta-<2\theta>)^2.I(2\theta)$ then used equation (1) to obtain variance ($W_{2\theta}$) for each peak of ZnO nanoparticles, the results are listed in Tables (1-2) as shown in Figures (3).

We calculated $\sum I(\text{peak}), \sum(2\theta.I(2\theta)), <2\theta>$ and $\sum(2\theta-<2\theta>)^2.I(2\theta)$ of peak (100) as shown in Table 1. And the other peaks calculated by the same method.

We used our data from (Figure 1 and Table 2) to calculate $\frac{W(2\theta)\cos \theta}{\lambda(2\theta)}$ and $\frac{4\sin \theta \tan \theta}{\lambda(2\theta)}$, the results are listed in Table (3). Where $W_{2\theta}$ is corrected by using equation (16), then transformed to radian. $\Delta2\theta$ is set to the value of 2 and wavelength $\lambda$ is 0.154056 nm

The expression $\frac{4\sin \theta \tan \theta}{\lambda(2\theta)}$ is the x-axis and $\frac{W(2\theta)\cos \theta}{\lambda(2\theta)}$ is the y-axis in variance plot as shown in Figure (4).

Figure 4 the variance plot used to calculate the crystallite size $P$ and mean square strain $\langle e^2 \rangle$ by equation (14). Graphically, the crystallite size $P$ is obtained from the y-intercept and the strain is obtained from $\langle e^2 \rangle$ which in turn is obtained from the slope.

$$ \langle e^2 \rangle = \text{Slope}, \quad P = \frac{1}{\text{intercept}+2\pi^2} $$

$$ \langle e^2 \rangle = 0.0001334733 $$

We used equation (15) to calculate strain ($e$)

$$ e = \sqrt{\frac{1}{2}} \times 14.47961 \times 10^{-2} = 22.76973 \text{ nm} $$

#### 3.2 Integral breadth analysis method

In this study we have analyzed line diffraction profile by integral breadth method, we have used Figure (1) to get $2\theta$ and intensity, then used equation (17) to obtain integral breadth $\beta_i$ for 20 steps to get ($\beta_i$)$_{\text{Average}}$ for each peak of ZnO nanoparticles, the results are listed in Tables (4) and as shown in Figure (5).

We calculated ($\beta_i$)$_{\text{Average}}$ of peak (100) as shown in Table 3. And the other peaks calculated by the same method.

We have used equations (32-33) for each peak of ZnO nanoparticles to confirm if our peaks are Cauchy or Gaussian profiles, the the results are listed in Table (5).

In this study all peaks are following Gaussian profile as shown in Table (5).
In this study we used our data from (Figure 1 and Table 5) to calculate \( \left( \frac{\beta_i \cos \theta}{\lambda} \right)^2 \) and \( \left( \frac{\sin \theta}{\lambda} \right)^2 \), the results are listed in Table (6).

Where \( \beta_i \) is corrected by using equation (16), then transformed to radian. \( \lambda \) is set to the value of 0.154056 nm.

The expression \( \left( \sin \theta / \lambda \right)^2 \) is the x-axis and \( \left( \beta_i \cos \theta / \lambda \right)^2 \) is the y-axis in integral breadth plot as shown in Figure (6).

Figure 6 the Integral breadth plot have been used to calculate the crystallite size \( P \) and strain \( e \) by equation (31), since all the values of \( \beta_i \) follow Gaussian profile. Graphically, the crystallite size \( P \) is obtained from the y-intercept and the strain \( e \) is obtained from \( e^2 \) which in turn is obtained from the slope.

\[
16 \ e^2 = \text{Slope}, \quad P = \frac{1}{\sqrt{\text{intercept}}}
\]

\[
4e = \sqrt{\text{Slope}} \rightarrow e = \frac{\sqrt{\text{Slope}}}{4} = \frac{\sqrt{0.5563 \times 10^{-3}}}{4}
\]

\[
e = 2.443 \times 10^{-3}
\]

\[
P = \frac{1}{0.001589568}
\]

\[
P = 25.126 \text{ nm}
\]

### 3.3 Analysis methods

#### 3.3.1 Scherrer method

In this study we have used equations (34-35) to determine the crystallite size \( (P) \) and lattice strain \( (e) \) respectively, we have used Figure (1) to calculate FWHM as shown in Figure (2) and the results of crystallite size, lattice strain and FWHM are listed in Table (7).

The advantage of Scherrer method is the easiest method to apply it in order to calculate crystallite size and lattice strain.

#### 3.3.2 Williamson-Hall method

In this study we have used equations (34-35) to determine the crystallite size \( (P) \) and lattice strain \( (e) \) respectively, we have used Figure (1) to calculate FWHM as shown in Figure (2) and the results of crystallite size, lattice strain and FWHM are listed in Table (7).

The advantage of Williamson-Hall method is the easiest method to apply it in order to calculate crystallite size and lattice strain.

#### 3.4 Comparison among Variance, integral breadth, Scherrer and Williamson-Hall methods to determine crystallite size and lattice strain of ZnO nanoparticles

We have determined crystallite size and lattice strain of ZnO nanoparticles by using variance, integral breadth, Scherrer & Williamson-Hall X-ray diffraction line profile methods. The results are listed in Table (9).

Methods of Variance and Integral breadth give the most accurate results than Scherrer and Williamson-Hall methods due to these two methods of Variance and Integral breadth dependent on the total area of the peak (peak + Tails) due to tails of peak is increase the variance value \( (W_{2\theta}) \) thus increase the strain while integral breadth takes the area of peak and both Scherrer and Williamson-Hall take the full width at half maximum (FWHM) of the peak which it is Approximation method because of this method is relying on only two lines to calculate the intensity.

The results indicate that the variance is very sensitive to the range of integration \( \Delta 2\theta = (2\theta_2 - 2\theta_1) \) The variance method give us higher Strain than integral breadth and Williamson-Hall methods due to the slope of the variance of the line profile as a function of the range of integration.

Variance method takes into account the total area of the peak (peak + Tails) due to tails of peak is increase the variance value \( (W_{2\theta}) \) thus increase the strain while integral breadth takes the area of peak and both Scherrer and Williamson-Hall take the full width at half maximum (FWHM) of the peak.
used total area under the curve of the peak.
2. The integral breadth determined the crystallite size and lattice strain after remove the instrumental broadening and used rectangular area of the peak. Therefore this method is accurate to analysis of the line profile XRD.
3. The Scherrer and Williamson-Hall methods give less accurate results of the crystallite size and lattice strain than variance and integral breadth methods. These methods are used the full width at half maximum (FWHM) of the peak which it is Approximation method.
4. All above methods give a good results to determine crystallite size and lattice strain but the variance method give the most accurate results because it is cover all the area of the peak and we know the value of high intensity give not accurate results to determine lattice parameters of structure lattice.

Figure 1: XRD of ZnO nanoparticles [8]

![XRD of ZnO nanoparticles](image1)

Figure 2: A diffraction line profile illustrating the definition of peak, centroid and full-width at half-maximum intensity (FWHM) [7]
Figure 3: Peak (100) of ZnO nanoparticles for 40 steps

Figure 4: Plot of $W2\theta \cos \theta / (\Delta 2\theta)\lambda$ vs $4\sin \theta / \pi (\Delta 2\theta)\lambda$ of ZnO nanoparticles

Figure 5: Peak (100) of ZnO nanoparticles for 20 steps

Figure 6: Integral breadth plot of $(\beta_1 \cos \theta) / \lambda^2$ vs $(\sin \theta / \lambda)^2$ of ZnO nanoparticles

Figure 7: Williamson-hall plot of $\beta_{hk\ell} \cos \theta$ vs $4\sin \theta$ of ZnO nanoparticles
Table 1: Variance method for peak (100) of ZnO nanoparticles

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<tr>
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<td>1.77409E-05</td>
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<tr>
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</tr>
<tr>
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<td>0.029993487</td>
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<td>0.040411255</td>
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<td>0.051500933</td>
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<tr>
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<td>0.047067707</td>
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<td>0.030645342</td>
</tr>
<tr>
<td>27</td>
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<td>0.125</td>
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<td>0.206369763</td>
<td>0.02579622</td>
</tr>
<tr>
<td>28</td>
<td>57.35</td>
<td>3</td>
<td>0.09375</td>
<td>5.3765625</td>
<td>0.254297701</td>
<td>0.02384041</td>
</tr>
<tr>
<td>29</td>
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<td>2.5</td>
<td>0.078125</td>
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<td>0.30722564</td>
<td>0.024002003</td>
</tr>
<tr>
<td>30</td>
<td>57.45</td>
<td>2</td>
<td>0.0625</td>
<td>3.590625</td>
<td>0.365153579</td>
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<tr>
<td>31</td>
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<td>3.234375</td>
<td>0.428081518</td>
<td>0.024079585</td>
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<tr>
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<td>1.5</td>
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<td>0.019557223</td>
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<tr>
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<td>0.022766229</td>
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<td>38</td>
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<td>0.015759017</td>
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<td>0.009375</td>
<td>0.5428125</td>
<td>1.111505029</td>
<td>0.01042036</td>
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<tr>
<td>40</td>
<td>57.95</td>
<td>0.05</td>
<td>0.0015625</td>
<td>0.090546875</td>
<td>1.219432967</td>
<td>0.001903564</td>
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<tr>
<td>41</td>
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<td>0.0003125</td>
<td>0.018125</td>
<td>1.332360906</td>
<td>0.000416363</td>
</tr>
</tbody>
</table>

\[ \sum \frac{I(I_{peak})}{I(I_{(peak)})} = 12.914375 \]
\[ \sum 20.1(I(2θ)) = 734.1269531 \]
\[ \sum (2θ-<2θ>)² \cdot I(2θ) = 0.986043966 \]
### Table 2: Calculated the variance of the line profile $W_{2\theta}$ for each peak of ZnO nanoparticles

<table>
<thead>
<tr>
<th>Peak</th>
<th>$\Sigma I_{(peak)}$</th>
<th>$\Sigma (20.12\theta)$</th>
<th>$&lt;2\theta&gt;$</th>
<th>$\Sigma (20-&lt;2\theta&gt;)2 \cdot I(2\theta)$</th>
<th>$W_{2\theta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>11</td>
<td>351.7663</td>
<td>31.97875</td>
<td>0.657048616</td>
<td>0.0597317</td>
</tr>
<tr>
<td>002</td>
<td>10.8482</td>
<td>377.2806</td>
<td>34.77818</td>
<td>0.773965278</td>
<td>0.0713451</td>
</tr>
<tr>
<td>101</td>
<td>10.81111</td>
<td>394.5528</td>
<td>36.49512</td>
<td>0.742892332</td>
<td>0.0687156</td>
</tr>
<tr>
<td>102</td>
<td>12.02</td>
<td>575.2312</td>
<td>47.85617</td>
<td>0.821170649</td>
<td>0.068317</td>
</tr>
<tr>
<td>110</td>
<td>12.91438</td>
<td>734.127</td>
<td>56.84572</td>
<td>0.986043966</td>
<td>0.0763524</td>
</tr>
</tbody>
</table>

### Table 3: Variance method for each peak of XRD pattern of ZnO nanoparticles

<table>
<thead>
<tr>
<th>Peak</th>
<th>$W(2\theta)$</th>
<th>$W(2\theta)_{\text{radian}}$</th>
<th>$&lt;2\theta&gt;$</th>
<th>$4\sin\theta\tan\theta/\lambda(\Delta2\theta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>0.038732</td>
<td>0.000676</td>
<td>32</td>
<td>1.026091031</td>
</tr>
<tr>
<td>(002)</td>
<td>0.050345</td>
<td>0.000879</td>
<td>34.75</td>
<td>1.213067162</td>
</tr>
<tr>
<td>(101)</td>
<td>0.047716</td>
<td>0.000833</td>
<td>36.5</td>
<td>1.340628558</td>
</tr>
<tr>
<td>(102)</td>
<td>0.047317</td>
<td>0.000826</td>
<td>47.85</td>
<td>2.335806952</td>
</tr>
<tr>
<td>(110)</td>
<td>0.055352</td>
<td>0.000966</td>
<td>56.8</td>
<td>3.338643746</td>
</tr>
</tbody>
</table>

### Table 4: Integral breadth $\beta_i$ for peak (100) of ZnO nanoparticles

| No. | $2\theta$ | $I(2\theta)=|1-\text{Background}|$ | $\beta_i$ |
|-----|-----------|-----------------------------------|----------|
| 1   | 31.45     | 2.5                               | 0.0714286|
| 2   | 31.5      | 4.5                               | 0.1285714|
| 3   | 31.55     | 6                                 | 0.1714286|
| 4   | 31.6      | 8.5                               | 0.2428571|
| 5   | 31.65     | 11.5                              | 0.3285714|
| 6   | 31.7      | 15                                | 0.4285714|
| 7   | 31.75     | 18                                | 0.5142857|
| 8   | 31.8      | 20.5                              | 0.5857143|
| 9   | 31.85     | 25                                | 0.7142857|
| 10  | 31.9      | 32                                | 0.9142857|
| 11  | 31.95     | 34                                | 0.9714286|
| 12  | 32        | 35                                | 1        |
| 13  | 32.05     | 35                                | 1        |
| 14  | 32.1      | 32.5                              | 0.9285714|
| 15  | 32.15     | 29.5                              | 0.8428571|
| 16  | 32.2      | 21.5                              | 0.6142857|
| 17  | 32.25     | 15.5                              | 0.4428571|
| 18  | 32.3      | 13                                | 0.3714286|
| 19  | 32.35     | 5                                 | 0.1428571|
| 20  | 32.4      | 3.5                               | 0.1      |
| 21  | 32.45     | 2.7                               | 0.0771429|

$\overline{(\beta_i)}_{\text{Average}} = 0.504354$
Table 5: $\beta_i$ and $\beta_{hkl}$ for each peak of ZnO nanoparticles

<table>
<thead>
<tr>
<th>Peak</th>
<th>$\beta_i$</th>
<th>$\beta_{hkl}$</th>
<th>$\beta_{hkl}/\beta_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>0.504354</td>
<td>0.5</td>
<td>0.991367</td>
</tr>
<tr>
<td>(002)</td>
<td>0.492272</td>
<td>0.4729</td>
<td>0.960648</td>
</tr>
<tr>
<td>(101)</td>
<td>0.48413</td>
<td>0.4693</td>
<td>0.969368</td>
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<tr>
<td>(102)</td>
<td>0.540816</td>
<td>0.4993</td>
<td>0.923235</td>
</tr>
<tr>
<td>(110)</td>
<td>0.576042</td>
<td>0.602</td>
<td>1.045063</td>
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</tbody>
</table>

Table 6: Integral breadth method for each peak of XRD pattern of ZnO nanoparticles

<table>
<thead>
<tr>
<th>Peak</th>
<th>$\beta_i$</th>
<th>$\beta_i$ radian</th>
<th>(20)</th>
<th>$(\beta_i \cos \theta / \lambda)^2$</th>
<th>$(\sin \theta / \lambda)^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>0.4180122</td>
<td>0.007296</td>
<td>32</td>
<td>0.0020723</td>
<td>3.201245016</td>
</tr>
<tr>
<td>(002)</td>
<td>0.4033521</td>
<td>0.00704</td>
<td>34.75</td>
<td>0.001902</td>
<td>3.757451119</td>
</tr>
<tr>
<td>(101)</td>
<td>0.3933706</td>
<td>0.006866</td>
<td>36.5</td>
<td>0.0017913</td>
<td>4.132242372</td>
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<td>(102)</td>
<td>0.46135</td>
<td>0.008052</td>
<td>47.85</td>
<td>0.0022826</td>
<td>6.929647743</td>
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<tr>
<td>(110)</td>
<td>0.5021808</td>
<td>0.008765</td>
<td>56.8</td>
<td>0.0025046</td>
<td>9.531706674</td>
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Table 7: Calculate FWHM and determine the crystallite size ($P$) and lattice strain ($\epsilon$) by Scherrer method for each peak of ZnO nanoparticles

<table>
<thead>
<tr>
<th>Peak</th>
<th>FWHM</th>
<th>FWHM radian</th>
<th>(20)</th>
<th>$P_{nm}$</th>
<th>$\epsilon \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>0.5</td>
<td>0.00872665</td>
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<td>17.26304736</td>
<td>7.608358</td>
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<td>(002)</td>
<td>0.4729</td>
<td>0.00825366</td>
<td>34.75</td>
<td>18.3841131</td>
<td>6.594449</td>
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<td>0.4693</td>
<td>0.00819083</td>
<td>36.5</td>
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<td>0.00871443</td>
<td>47.85</td>
<td>18.17961628</td>
<td>4.910521</td>
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<td>0.602</td>
<td>0.01050688</td>
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$P$ (average) = 17.622 nm
$\epsilon$ (average) = 6.03624 x $10^{-3}$

Table 8: Williamson-Hall method for each peak of XRD pattern of ZnO nanoparticles

<table>
<thead>
<tr>
<th>Peak</th>
<th>$\beta_{hkl}$</th>
<th>$\beta_{hkl}$ radian</th>
<th>(20)</th>
<th>$\beta_{hkl} \cos \theta$</th>
<th>$4 \sin \theta$</th>
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<td>1.252655226</td>
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<tr>
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<tr>
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Table 9: The results of variance, integral breadth methods and other methods

<table>
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<tr>
<th>Variance method</th>
<th>Integral breadth method</th>
<th>Scherrer method</th>
<th>Williamson-Hall method</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{nm}$ &lt; $\epsilon^2$ x $10^{-3}$</td>
<td>$P_{nm}$ x $10^{-3}$</td>
<td>$P_{nm}$ x $10^{-3}$</td>
<td>$P_{nm}$ x $10^{-3}$</td>
</tr>
<tr>
<td>22.276</td>
<td>14.479</td>
<td>25.126</td>
<td>6.036</td>
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</tbody>
</table>

Reference


