Advances in Physics Theories and Applications
ISSN 2224-719X (Paper) ISSN 2225-0638 (Online)
Vol.49, 2015

Studying Variance Method of X-Ray Diffraction Line Profile Then Develop It to Three New Models for Determine New Parameters

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Abstract
In this study have been determined the crystallite size and lattice strain of ZnO nanoparticles by using variance and have been developed the variance method by presenting three new models (UDVM, UDSVM and UDEDVM) to determine lattice parameters such as crystallite size, lattice strain, stress and energy density for the first time. In variance method we have calculated the values of crystallite size, mean square strain and lattice strain (22.276 nm), (0.133473 x 10^{-3}) and (14.479619 x 10^{-3}) respectively. We have calculated the values of crystallite size and lattice strain (22.276 nm) and (14.47962 x 10^{-3}) respectively by using UDVM, the values of crystallite size, stress and lattice strain (22.276 nm), (3.7266 x 10^{-3} TPa) and (14.48006 x 10^{-3}) respectively by using UDSVM and the values of crystallite size, stress, energy density & lattice strain (22.276 nm), (2.9957 x 10^{-3} TPa), (21689.7 KJ/m^3) and (14.48024 x 10^{-3}) respectively by using UDEDVM.

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]. The variance method is a single line method to evaluate the contribution of size and strain broadening. The method was first suggested by Tournarie (1956), and then developed by Wilson (1962a) [4]. 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) [5]. J. I. Langford in 1968 has stated in any attempt to interpret broadened X-ray diffraction peaks in terms of imperfections in polycrystalline specimens, particular attention should be paid to experimental technique and the method of collecting data. The experimental conditions should be arranged to give maximum intensity in as short a time as possible, keeping instrumental effects to a minimum. Of particular importance are the correct choice of receiving slit, incremental change in angle and range of scan for each reflection. All measures of breadth require a knowledge of the background associated with each line, and a reliable estimate of this is given by the variance method [6]. Klug and Alexander in 1974 have developed variance methods [7]. In 1997, the modified application of the variance method, using the pseudo-Voigt function as a good approximation to the X-ray diffraction profiles, is proposed in order to obtain microstructural quantities such as the mean crystallite size and root-mean-square (r.m.s.) strain [8].

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) [9].

2. Theory

2.1 The Variance analysis 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 [10].

$$w(2\theta) = \frac{\int (2\theta - <2\theta>)^2 \, . \, I(2\theta) d(2\theta)}{\int I(2\theta) d(2\theta)} \quad \text{...... (1)}$$

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

$$< 2\theta > = \frac{\int 2\theta . \, I(2\theta) d(2\theta)}{\int I(2\theta) d(2\theta)} \quad \text{...... (2)}$$

May let range of Measurement $\sigma_1 + \sigma_2 = \sigma$ and express the linear of variance-range in for

$$w = w_0 + K\sigma \quad \ldots\ldots (3)$$

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) [10].

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

$$W = W_P + W_S + W_D \quad \ldots\ldots (4)$$

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 [11]

$$W = \frac{\lambda \Delta 2\theta}{2\pi^2 P' cos\theta} + \frac{S\lambda^2}{cos^2\theta} \quad \ldots\ldots (5)$$

S given by equation (6) [12-13].

$$S = \frac{<e^2> - B_D^2/\pi^2}{d^2} \quad \ldots\ldots (6)$$

$$\frac{1}{P'} = \frac{1}{P} + \frac{B_D}{d} \quad \ldots\ldots (7)$$

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 2θ scale over which the measurements are being made. P' Is the apparent crystallite size from variance method; P is true crystallite size [11-12].

From Bragg's law [14]

$$4d^2 sin^2\theta = \lambda^2 \rightarrow d^2 = \lambda^2/4sin^2\theta \quad \ldots\ldots (8)$$

$$2sin\theta = \lambda \rightarrow d = \frac{\lambda}{2sin\theta} \quad \ldots\ldots (9)$$

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

$$W = \frac{\lambda \Delta 2\theta}{2\pi^2 cos\theta}\left[\frac{1}{p} + \frac{B_D}{d}\right] + \frac{<e^2>\lambda^2}{d^2 cos^2\theta} - \frac{{B_D}^2}{\pi^2}\frac{\lambda^2}{d^2 cos^2\theta} \quad \ldots\ldots (10)$$

Substitute equations (8) and (9) in (10) gives the following equation:

$$W = \frac{\lambda(\Delta 2\theta)}{2\pi^2 p cos\theta} + \frac{(\Delta 2\theta)B_D}{\pi^2}\frac{sin\theta}{cos\theta} - 4\frac{{B_D}^2}{\pi^2}\frac{sin^2\theta}{cos^2\theta} + 4 < e^2 > \frac{sin^2\theta}{cos^2\theta} \quad \ldots\ldots (11)$$

Since $\frac{sin\theta}{cos\theta} = tan\theta$

$$W = \frac{\lambda(\Delta 2\theta)}{2\pi^2 p cos\theta} - \frac{B_D tan\theta}{\pi^2}[4\, B_D tan\theta + (\Delta 2\theta)] + 4 < e^2 > tan^2\theta \quad \ldots\ldots (12)$$

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 [15-16].

$$W_{2\theta} = \frac{\Delta 2\theta\lambda}{2\pi^2 P cos\theta} + 4tan^2\theta < e^2 > \quad \ldots\ldots (13)$$

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

$$\frac{W_{2\theta} cos\theta}{\Delta 2\theta\lambda} = \frac{1}{2\pi^2 P} + \frac{4sin\theta tan\theta}{\Delta 2\theta\lambda} < e^2 > \quad \ldots\ldots (14)$$

The instrumental corrected broadening β_{hkl} [17] corresponding to the diffraction peaks was estimated using the equation

$$\beta_{hkl} = \sqrt{(\beta_{measured})^2 + (\beta_{instrumental})^2} \quad \ldots\ldots (15)$$

2.2 The Uniform Deformation Variance Model (UDVM)

The mean crystallite sizes and microstrain parameters are not defined in the same way; they vary according to the method used to calculate them. The single-line method, where a Voigt shaped peak is assumed, provides the volume-weighted column length and the maximum ("upper") strain, that can be defined as a root-mean-square (RMS) value of strain [18] if a Gauss strain distribution it is assumed.

$$< e^2 >^{1/2} = \sqrt{\frac{2}{\pi}}e \quad \ldots\ldots (16)$$

Where e is the microstrain, and $< e^2 >^{1/2}$ is the root-mean-square of Strain

Can be rewritten equation (16) as the following:

$$e = < e^2 >^{1/2} \sqrt{\frac{\pi}{2}} \quad \ldots\ldots (17)$$

$$e^2 = < e^2 > \frac{\pi}{2} \quad \ldots\ldots (18)$$

$$< e^2 > = e^2 \frac{2}{\pi} \quad \ldots\ldots (19)$$

From equation (19) can be rewritten equation (14) as the following equation:

$$\frac{W_{2\theta} cos\theta}{\Delta 2\theta\lambda} = \frac{1}{2\pi^2 P} + \frac{8sin\theta tan\theta}{\pi\Delta 2\theta\lambda}\, e^2 \quad \ldots\ldots (20)$$

Equation (20) represent the Uniform Deformation Variance Model (UDVM)

2.3 The Uniform Deformation Stress Variance Model (UDSVM)

Generalized Hooke's law refers to the strain, keeping only the linear proportionality between the stress and strain as given by

$\sigma = Ye$ ..... (21)

$e = \sqrt{\frac{\sigma^2}{Y^2}} \rightarrow e^2 = \frac{\sigma^2}{Y^2}$ ..... (22)

Where σ the stress of the crystal and Y is the modulus of elasticity or Young's modulus [19].

Assuming a small strain to be present in nanoparticles, Hooke's law can be used here. With a further increase in the strain, the particles deviate from this linear proportionality. Applying the Hooke's law approximation to the above equation (22), we get the following equation:

$\frac{W_{2\theta}cos\theta}{\Delta 2\theta\lambda} = \frac{1}{2\pi^2 P} + \frac{8sin\theta tan\theta}{\pi Y_{hkl}^2(\Delta 2\theta)\lambda}\sigma^2$ ..... (23)

Equation (23) represent the Uniform Deformation Stress Variance Model (UDSVM)

2.4 The Uniform Deformation Energy Density of Variance Model (UDEDVM)

According to Hooke's law, the energy density u (energy per unit volume) as a function of strain is [9].

$u = \frac{e^2 Y_{hkl}}{2}$ ..... (24)

$e^2 = \frac{2u}{Y_{hkl}}$ ..... (25)

$e = \sqrt{\frac{2u}{Y_{hkl}}}$ ..... (26)

Can be rewritten equation (21) as the following:

$\sigma = Y\sqrt{\frac{2u}{Y_{hkl}}} \rightarrow \sigma = \sqrt{2uY}$ ..... (27)

Therefore $Y = \frac{\sigma^2}{2u}$ ..... (28)

Substitute equation (28) in (21) gives the following equation:

$\sigma = e\frac{\sigma^2}{2u} \rightarrow u = \frac{e\sigma}{2}$ ..... (29)

$e = \frac{2u}{\sigma}$ ..... (30)

Substitute equation (25) in (20) gives the following equation:

$\frac{W_{2\theta}cos\theta}{\Delta 2\theta\lambda} = \frac{1}{2\pi^2 P} + \frac{16sin\theta tan\theta}{\pi Y_{hkl}(\Delta 2\theta)\lambda}u$ ..... (31)

Equation (31) represent the Uniform Deformation Energy Density of Variance Model (UDEDVM)

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 2θ and Intensity, $\sum I/I_{(peak)}$, $\sum(2\theta.I(2\theta)$, then used equation (2) to obtain centroid (<2θ>), 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).

We calculated $\sum I/I(peak)$, $\sum(2\theta.I(2\theta)$, <2θ> and $\sum(2\theta-<2\theta>)^2$. I(2θ) 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 $\frac{\boldsymbol{W(2\theta)Cos\theta}}{\boldsymbol{\lambda(\Delta 2\theta)}}$ and $\frac{\boldsymbol{4Sin\theta Tan\theta}}{\boldsymbol{\lambda(\Delta 2\theta)}}$, the results are listed in Table (3).

Where $W_{2\theta}$ is corrected by using equation (15), then transformed to radian. Δ2θ is set to the value of 2 and wavelength λ is 0.154056 nm

The expression $\frac{\boldsymbol{4Sin\theta Tan\theta}}{\boldsymbol{\lambda(\Delta 2\theta)}}$ is the x-axis and $\frac{\boldsymbol{W(2\theta)Cos\theta}}{\boldsymbol{\lambda(\Delta 2\theta)}}$ is the y-axis in variance plot as shown in Figure (2).

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

$< e^2 >= Slope\ ,\ P = \frac{1}{intercept*2\pi^2}$

$< e^2 > = 0.0001334733$

We used equation (17) to calculate strain (e)

$$e = \sqrt{\frac{0.0001334733 * \pi}{2}} = 14.47961 * 10^{-3}$$
$$P = \frac{1}{0.00227412 * 2\pi^2} = 22.276973\ nm$$

3.2 Variance models (UDVM, UDSVM and UDEDVM)

The calculated values of lattice parameter (a, c) are listed in Table (3), found to be in a good agreement with the standard (JCPDS) values [20]. As shown in Table (4).

Young's modulus will use Uniform Deformation Stress Variance Model (UDSVM) and Uniform Deformation energy density Variance Model (UDEDM) models and we can get it from the following equation:

$$Y_{hkl} = \frac{\left[h^2+\frac{(h+2k)^2}{3}+\left(\frac{al}{c}\right)^2\right]^2}{s_{11}\left(h^2+\frac{(h+2k)^2}{3}\right)^2+s_{33}\left(\frac{al}{c}\right)^4+(2s_{13}+s_{44})\left(h^2+\frac{(h+2k)^2}{3}\right)\left(\frac{al}{c}\right)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (32)$$

Y_{hkl} is the Young's modulus in the direction normal to the set of crystal lattice plane hkl. In a hexagonal crystal, Young's modulus is given by [21-22].

In this study we using our lattice parameters a, c and S_{11}, S_{13}, S_{33}, S_{44} in equation (32) for each peak (hkl), we have obtained Young's modulus of ZnO nanoparticles as shown in Table (5).

Where S_{11}, S_{13}, S_{33}, S_{44} are the elastic compliances of ZnO with values of 7.858×10^{-12}, 2.206×10^{-12}, 6.940×10^{-12}, 23.57×10^{-12} $m^2 * N^{-1}$ respectively [9].

In this study we used our data from (Figure 1 and Table 2) to calculate $\frac{W(2\theta)Cos\theta}{\lambda(\Delta 2\theta)}$, $\frac{8Sin\theta Tan\theta}{\pi\lambda(\Delta 2\theta)}$, $\frac{8Sin\theta Tan\theta}{Y^2\pi\lambda(\Delta 2\theta)}$ and $\frac{16Sin\theta Tan\theta}{Y\pi\lambda(\Delta 2\theta)}$ for UDVM, UDSVM and UDEDVM for each peak of XRD pattern of ZnO nanoparticles, the results are listed in the Tables (6-8).

Where $W_{2\theta}$ is corrected by using equation (15), then transformed to radian. Δ2θ is set to the value of 2, wavelength λ is 0.154056 nm, Y^2 is 0.066238 *TPa* and Y is 0.206886166 *TPa*.

The expression $\frac{\boldsymbol{8Sin\theta Tan\theta}}{\boldsymbol{\pi\lambda(\Delta 2\theta)}}$ is the x-axis and $\frac{\boldsymbol{W(2\theta)Cos\theta}}{\boldsymbol{\lambda(\Delta 2\theta)}}$ is the y-axis in the uniform deformation variance model (UDVM) plot as shown in Figure (3), the expression $\frac{8Sin\theta Tan\theta}{Y^2\pi\lambda(\Delta 2\theta)}$ is the x-axis and $\frac{\boldsymbol{W(2\theta)Cos\theta}}{\boldsymbol{\lambda(\Delta 2\theta)}}$ is the y-axis in the uniform deformation stress variance model (UDSVM) plot as shown in Figure (4) and the expression $\frac{16Sin\theta Tan\theta}{Y\pi\lambda(\Delta 2\theta)}$ is the x-axis and $\frac{W(2\theta)Cos\theta}{\lambda(\Delta 2\theta)}$ is the y-axis in the uniform deformation energy density of variance model (UDEDVM) plot as shown in Figure (5).

Figure (3) the uniform deformation variance model plot used To calculate the crystallite size P and strain e by equation (20). Graphically, the crystallite size P is obtained from the y-intercept and the strain e is obtained from slope.

$$e^2 = Slope\ , P = \frac{1}{intercept * 2\pi^2}$$
$$e = \sqrt{Slope} = \sqrt{2.096594 * 10^{-4}}$$
$$e = 14.4796202 * 10^{-3}$$
$$P = \frac{1}{0.00227412 * 2\pi^2} = 22.276973\ nm$$

Figure (4) the uniform deformation stress variance model plot that used to calculate the stress σ and crystallite size by equation (23). Graphically, the crystallite size P from the y-intercept and the stress σ is obtained from the slope, then the strain e is obtained by equation (21).

$$\sigma^2 = Slope\ , P = \frac{1}{intercept * 2\pi^2}$$
$$\sigma = \sqrt{Slope} = \sqrt{1.38882914343158 * 10^{-5}}$$
$$\sigma = 3.72669 * 10^{-3}\ \text{TPa}$$
$$P = \frac{1}{0.00227412 * 2\pi^2} = 22.276973\ nm$$

From equation (22) can be obtained the strain

$$e = \sqrt{\frac{1.38882914343158 * 10^{-5}}{0.066238046}}$$
$$e = 14.48006 * 10^{-3}$$

Figure (5) the uniform deformation energy density of variance model plot that used to calculate the energy density u and crystallite size by equation (31). Graphically, the crystallite size P from the y-intercept and the energy density u from the Slope, then the strain e is obtained by equation (25).

$$u = Slope\ , P = \frac{1}{intercept * 2\pi^2}$$
$$u = 0.0000216897\ TPa = 21689.7\ KJ\ .m^{-3}$$

$P = \frac{1}{0.0022741236 * 2\pi^2} = 22.276973\ nm$

Could be obtained the stress by equation (27)

$\sigma = \sqrt{2.16897 * 10^{-5} * 2 * 0.206886166}$

$\sigma = 2.99576 * 10^{-3}$ TPa

Could be obtained the strain by equation (26)

$e = \sqrt{\frac{2 * 0.0000216897}{0.206886166}}$

$e = 14.480249 * 10^{-3}$. And can get the strain by using equation (30) e = 14.4802 also.

We used variance x-ray diffraction line profile method to determine crystallite size and lattice strain of ZnO nanoparticles. In comparison to our models UDVM, UDSVM and UDEDVM to determine crystallite size, lattice strain, stress and energy density. The results are listed in Table (9).

The crystallite size and lattice strain of variance method exactly the same as UDVM, UDSVM and UDEDVM by use different equations for drawing plots that prove our derivation is comparable as shown in Table (9).

The advantage of the uniform deformation variance model (UDVM) is calculate lattice strain directly from slope in UDVM plot while variance method is calculate mean square strain from slope of plot, the uniform deformation stress variance model (UDSVM) is calculate stress directly from slope of UDSVM plot and the uniform deformation energy density variance model (UDEDVM) is calculate energy density directly from slope in UDEDVM plot. That can help who work in experimental of X-ray diffraction by using our program (excel with table and equations) as a tool they can just put W (2θ) and (2θ) of each peak and they will get full data, plot and determined lattice parameter such as crystallite size and strain.

UDEDVM plot has the most accurate results than UDSVM and UDVM plots because of the value of stress which found in UDEDVM plot is σ =2.9957 x 10^{-3} TPa and this value according to Hooke's law σ = eY.

The uniform deformation variance model (UDVM), the uniform deformation stress variance model (UDSVM) and the uniform deformation energy density variance model (UDEDVM) can be applied to any sample not only on oxides or zinc oxide because of variance method applied on many samples with excellent results. So that the (UDVM), (UDSVM) and (UDEDVM) which derived from variance method in this study can be applied on all samples such as metals, alloy, ceramic, polymers and composites to determine crystallite size and strain.

4. Conclusion

1. The variance method gives the accurate results of the crystallite size and lattice strain after correction the instrumental broadening. This method takes into account the total area of the peak using parallel lines of intensity.
2. This study has developed a variance method in order to calculate lattice strain, stress and energy density the results are listed in the Table (9) with a good convergence of the value of strain and at the same crystallite size.

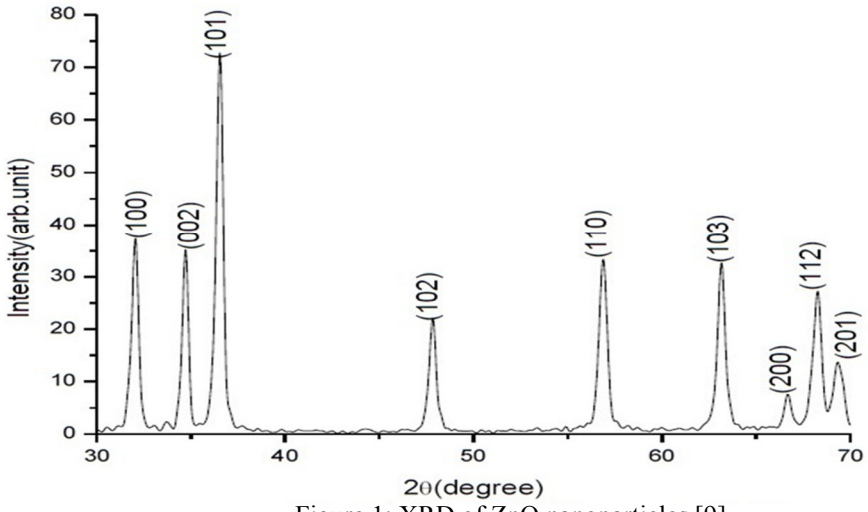

Figure 1: XRD of ZnO nanoparticles [9]

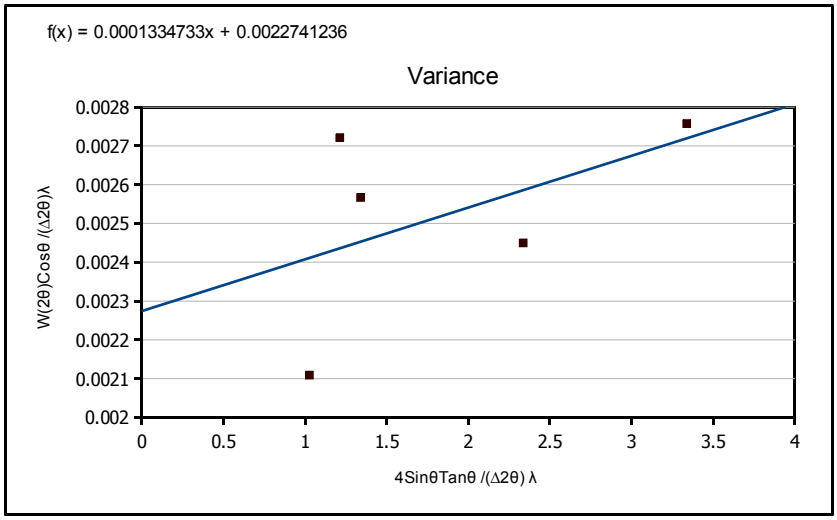

Figure 2: Variance plot of $W_{2\theta}\,Cos\theta/(\Delta 2\theta)\lambda$ VS $4Sin\theta Tan\theta/\pi\ (\Delta 2\theta)\lambda$ of ZnO nanoparticle

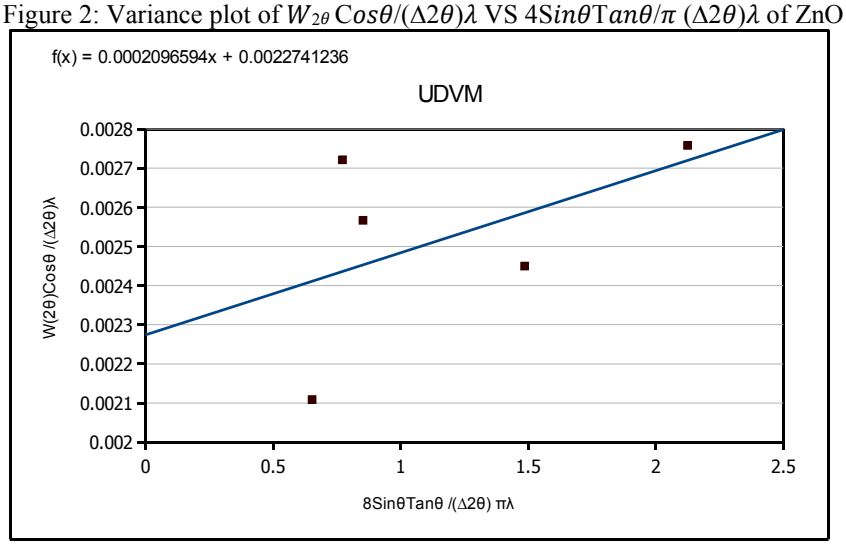

Figure 3: UDVM plot of $W_{2\theta}\,cos\theta/(\Delta 2\theta)\lambda$ VS $8sin\theta tan\theta)/\pi\ (\Delta 2\theta)\lambda$ of ZnO nanoparticles

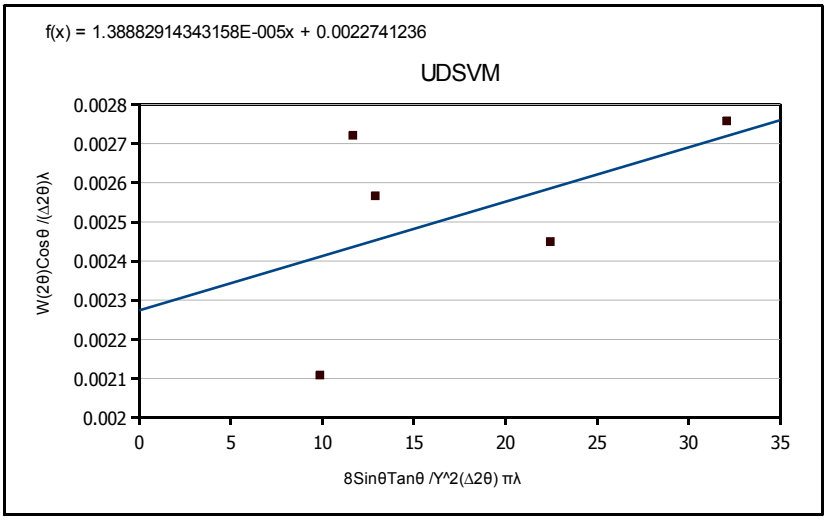

Figure 4: UDSVM plot of $W_{2\theta}\,cos\theta/(\Delta 2\theta)\lambda$ VS $8sin\theta tan\theta/\pi Y_{hkl}^2(\Delta 2\theta)\lambda$ of ZnO nanoparticles

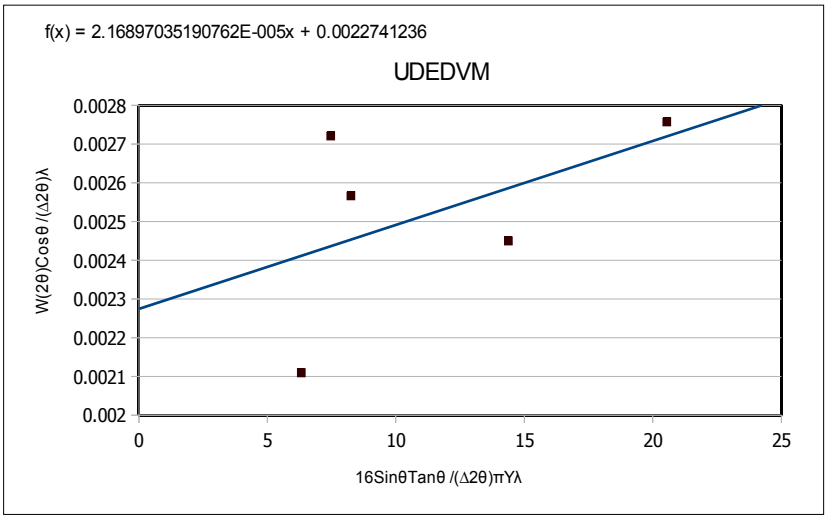

Figure 5: UDEDVM plot of $W_{2\theta}\,cos\theta/(\Delta 2\theta)\lambda$ VS $16sin\theta tan\theta/\pi Y_{hkl}\,(\Delta 2\theta)\lambda$ of ZnO nanoparticles

Table 1: Variance method for peak (100) of ZnO nanoparticles

No.	2θ	I(2θ)={I-B}	I/I(peak)	2θ. I(2θ)	$(2\theta-\langle 2\theta\rangle)^2$	$(2\theta-\langle 2\theta\rangle)^2$. I(2θ)
1	56	0.8	0.025	1.4	0.715243353	0.017881084
2	56.05	1	0.03125	1.7515625	0.633171292	0.019786603
3	56.1	1.5	0.046875	2.6296875	0.556099231	0.026067151
4	56.15	1.8	0.05625	3.1584375	0.48402717	0.027226528
5	56.2	2	0.0625	3.5125	0.416955108	0.026059694
6	56.25	2.5	0.078125	4.39453125	0.354883047	0.027725238
7	56.3	3.5	0.109375	6.1578125	0.297810986	0.032573077
8	56.35	4.6	0.14375	8.1003125	0.245738925	0.03532497
9	56.4	6	0.1875	10.575	0.198666864	0.037250037
10	56.45	8	0.25	14.1125	0.156594803	0.039148701
11	56.5	11	0.34375	19.421875	0.119522741	0.041085942
12	56.55	14	0.4375	24.740625	0.08745068	0.038259673
13	56.6	21.5	0.671875	38.028125	0.060378619	0.040566885
14	56.65	27	0.84375	47.7984375	0.038306558	0.032321158
15	56.7	29.2	0.9125	51.73875	0.021234497	0.019376478
16	56.75	31	0.96875	54.9765625	0.009162436	0.008876109
17	56.8	32	1	56.8	0.002090374	0.002090374
18	56.85	31	0.96875	55.0734375	1.83132E-05	1.77409E-05
19	56.9	30.5	0.953125	54.2328125	0.002946252	0.002808146
20	56.95	30	0.9375	53.390625	0.010874191	0.010194554
21	57	25	0.78125	44.53125	0.02380213	0.018595414
22	57.05	23	0.71875	41.0046875	0.041730068	0.029993487
23	57.1	20	0.625	35.6875	0.064658007	0.040411255
24	57.15	17.8	0.55625	31.7896875	0.092585946	0.051500933
25	57.2	12	0.375	21.45	0.125513885	0.047067707
26	57.25	6	0.1875	10.734375	0.163441824	0.030645342
27	57.3	4	0.125	7.1625	0.206369763	0.02579622
28	57.35	3	0.09375	5.3765625	0.254297701	0.02384041
29	57.4	2.5	0.078125	4.484375	0.30722564	0.024002003
30	57.45	2	0.0625	3.590625	0.365153579	0.022822099
31	57.5	1.8	0.05625	3.234375	0.428081518	0.024079585
32	57.55	1.5	0.046875	2.69765625	0.496009457	0.023250443
33	57.6	1.1	0.034375	1.98	0.568937396	0.019557223
34	57.65	1	0.03125	1.8015625	0.646865334	0.020214542
35	57.7	1	0.03125	1.803125	0.729793273	0.02280604
36	57.75	1	0.03125	1.8046875	0.817721212	0.025553788
37	57.8	0.8	0.025	1.445	0.910649151	0.022766229
38	57.85	0.5	0.015625	0.90390625	1.00857709	0.015759017
39	57.9	0.3	0.009375	0.5428125	1.111505029	0.01042036
40	57.95	0.05	0.0015625	0.090546875	1.219432967	0.001905364
41	58	0.01	0.0003125	0.018125	1.332360906	0.000416363
			$\sum I/I_{(peak)}$ =12.914375	$\sum 2\theta.I(2\theta)$ =734.1269531		$\sum(2\theta-\langle 2\theta\rangle)^2$ .I(2θ) =0.986043966

Table 2: Calculated the variance of the line profile W_{20} for each peak of ZnO nanoparticles

Peak	$\sum I/I_{(peak)}$	$\sum(2\theta.I(2\theta)$	$<2\theta>$	$\sum(2\theta-<2\theta>)^2 .I(2\theta)$	$W_{2\theta}$
100	11	351.7663	31.97875	0.657048616	0.0597317
002	10.8482	377.2806	34.77818	0.773965278	0.0713451
101	10.81111	394.5528	36.49512	0.742892332	0.0687156
102	12.02	575.2312	47.85617	0.821170649	0.068317
110	12.91438	734.127	56.84572	0.986043966	0.0763524

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

Peak	$W(2\theta)_{corrected}$	$W(2\theta)_{radian}$	(2θ)	$W(2\theta)Cos\theta/\lambda(\Delta 2\theta)$	$4Sin\theta Tan\theta/\lambda(\Delta 2\theta)$
(100)	0.038732	0.000676	32	0.002109018	1.026091031
(002)	0.050345	0.000879	34.75	0.002721712	1.213067162
(101)	0.047716	0.000833	36.5	0.002566958	1.340628558
(102)	0.047317	0.000826	47.85	0.002450015	2.335806952
(110)	0.055352	0.000966	56.8	0.002758108	3.338643746

Table 4: The structural parameters of ZnO nanoparticles

Data	(2θ)	hkl	Structure	a(Å)	c(Å)	V(Å)
theory	32 34.75	(100) (002)	Hexagonal	3.227	5.159	46.52
JCPDS (36-1451)	31.770 34.422	(100) (002)	Hexagonal	3.25	5.207	47.63

Table 5: Young's modulus and Square Young's modulus *of ZnO* nanoparticles

Peak	a	c	Y_{hkl} N/m^2	Y_{hkl} TPa	Y_{hkl}^2 TPa
100	3.227	5.159	1.7 x 10^{11}	0.169678459	0.02879078
002	3.227	5.159	1.44 x 10^{11}	0.144092219	0.020762568
101	3.227	5.159	1.14 x 10^{11}	0.113791794	0.012948572
102	3.227	5.159	9.78 x 10^{10}	0.097832981	0.009571292
110	3.227	5.159	5.09 x 10^{11}	0.509035378	0.259117016
				(Y_{hkl}) Average = 0.206886166	(Y_{hkl}^2) Average = 0.066238046

Table 6: The uniform deformation variance model (UDVM) for each peak of XRD pattern of ZnO nanoparticles

Peak	$W(2\theta)_{corrected}$	$W(2\theta)_{radian}$	(2θ)	$W(2\theta)Cos\theta/\lambda(\Delta 2\theta)$	$8Sin\theta Tan\theta/\pi\lambda(\Delta 2\theta)$
(100)	0.038732	0.000676	32	0.002109018	0.653229838
(002)	0.050345	0.000879	34.75	0.002721712	0.77226254
(101)	0.047716	0.000833	36.5	0.002566958	0.853470647
(102)	0.047317	0.000826	47.85	0.002450015	1.48702089
(110)	0.055352	0.000966	56.8	0.002758108	2.125446622

Table 7 : The uniform deformation stress variance model (UDSVM) for each peak of XRD pattern of ZnO nanoparticles

Peak	W(2θ) corrected	W(2θ)radian	(2θ)	$W(2\theta)Cos\theta/\lambda(\Delta 2\theta)$	$8Sin\theta Tan\theta/Y^2\pi\lambda(\Delta 2\theta)$
(100)	0.038732	0.000676	32	0.002109018	9.861241177
(002)	0.050345	0.000879	34.75	0.002721712	11.65817407
(101)	0.047716	0.000833	36.5	0.002566958	12.88410203
(102)	0.047317	0.000826	47.85	0.002450015	22.44825751
(110)	0.055352	0.000966	56.8	0.002758108	32.08601401

Table 8: The uniform deformation energy density of variance model (UDEDVM) for each peak of XRD pattern of ZnO nanoparticles

Peak	W(2θ) corrected	W(2θ)radian	(2θ)	$W(2\theta)Cos\theta/\lambda(\Delta 2\theta)$	$16Sin\theta Tan\theta/Y\pi\lambda(\Delta 2\theta)$
(100)	0.038732	0.000676	32	0.002109018	6.314322888
(002)	0.050345	0.000879	34.75	0.002721712	7.464930024
(101)	0.047716	0.000833	36.5	0.002566958	8.249912855
(102)	0.047317	0.000826	47.85	0.002450015	14.37400665
(110)	0.055352	0.000966	56.8	0.002758108	20.54522844

Table 9: The value of strain, stress and energy density of variance method and the new models of this method

Variance method		UDVM	UDSVM		UDEDVM		
$< e^2 > x\ 10^{-3}$	$e\ x\ 10^{-3}$	$e\ x\ 10^{-3}$	$e\ x\ 10^{-3}$	$\sigma\ x\ 10^{-3}$ (TPa)	$e\ x\ 10^{-3}$	$\sigma\ x\ 10^{-3}$ (TPa)	$u\ (KJm^{-3})$
0.1334733	14.479619	14.47962	14.48006	3.7266	14.48024	2.9957	21689.7

at the same crystallite size (P = 22.276 nm).

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