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Estimation of Elastic Properties of Zinc Oxide Nanomaterial using Williamson Hall Method

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***Abstract*:- Zinc oxide (ZnO) nanoparticles were synthesized by green synthesis using Azadirachta indica (neem) leaves extract. The analysis of the P-XRD results is considered as a convenient and operational method in calculating the crystalline size and the respective lattice strain, Young's modulus, stress and energy density. X- ray diffraction patterns were investigated using Scherrer method and Williamson–Hall method in order to estimate the crystalline size and the mechanical parameters. The XRD pattern confirmed the existence of crystalline hexagonal wurtzite ZnO nanoparticles with average crystallite size in the range 27.7 nm. Morphology and particles size of ZnO nanoparticles was determined by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HR-TEM) studies.**

Keywords : ZnO Nanoparticles, X-Ray Peak Analysis, Lattice Strain, Williamson–Hall Method

1. INTRODUCTION

Zinc oxide nanomaterials have taken excessive attentiveness on account of their specific properties and inclusive applications in different areas of science [1]. ZnO is non-toxic, and chemically sustained metal oxide, which has noble mechanical, optical, electrical properties. It is a metal oxide having semiconductor nature which is considered like n-type semiconductor [2]. Recently it has appeared as a significant material and has extended precise consideration in the scientific research [3-6]. It is utilized like a stabilizer in several fields like cement [7], fire retardent [8], sensors [9], solar cells[10], paints [11], adhesives [12], antimicrobial activity and food packaging applications [13], etc.

Diverse approaches have been utilized to synthesize zinc oxide nanomaterial as hydrothermal [14], sol gel synthesis [15], chemical precipitation [16] and green method. Green synthesis is considered as a unique method in the synthesis of nanomaterial for its significant leads. The biological method, which is represented as a replacement to chemical and physical methods, provides an environment friendly approach of synthesizing nanoparticles [17]. However, this process does not require costly, dangerous and toxic chemicals. In addition, the nanoparticles synthesis by using plant offers several advantages such as safer solvent utilization, decrease use of toxic reagents, milder response conditions. It is a low temperature technique, in which simple apparatus employment is utilized. It is low cost method which is ecofriendly [18]. The estimation of X-ray peaks has been considered in order to estimate the crystalline size, strain, Young's modulus, energy density and stress [19]. Williamson–Hall [20] method is the approach which is applied for determining the crystalline size and related strain.

In continuation of our previous work [21] the present study was aimed to investigate green synthesis of ZnO nanoparticles with an observation regarding change in properties, morphology. From X-ray diffraction patterns using Scherrer formula and Williamson–Hall methods, the crystalline size and the equivalent lattice strain could be determined. The scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) of the obtained nanoparticles were studied to characterize them.

2. EXPERIMENTAL METHODS

The P-XRD analysis was considered out using XPERT-PRO X-Ray Diffractrometer which was operated at a voltage of 45kV and a current of 40 mA through CuKα radiation in a θ-2θ conformation. The high resolution transmission electron microscope studies were carried out on Model JEOL/ JEM 2100, operated at accelerating voltage of 200kV with the resolution-Point 0.23 nm and lattice 0.14 nm. The FESEM has been carried out on the JEOL Model JSM-6100 which was operated at resolution of 4 nm at 8 mm at an accelerating voltage 0.3 to 30 kV and magnification 10 X to 300,000X.

2.1 Synthesis of Zinc Oxide Nanoparticles

The collected *Azadirachta indica* (neem) leaves were thoroughly washed multiple times with double distilled water and dried at room temperature.After that 40 g dried leaves along with 100 ml distilled water was mixed and boiled at 60°C for 25 min. The colour of the solution changed from green to pale yellow. Resulting solution was allowed to cool at room temperature. The extract was filtered by using Whatman filter paper No.1 and stored in a refrigerator for use.

1.09 g zinc acetate dihydrate was dissolved in 15 mL deionised water in a 100 ml round bottom flask. 20 ml well-preserved *Azadirachta indica* (neem) leaf extract was added drop wise to the above solution with constant stirring on magnetic stirrer. The pH of the solution was adjusted 12 by mixing NaOH (2M) solution. The obtained solution was irradiated with microwaves at 110 W for 15 min at 80 °C in a microwave synthesizer. The obtained resultant precipitate was centrifuged, washed with distilled water and then dried in an oven at 110 °C. Finally, the powder was dried in a vacuum desiccator over anhydrous $CaCl_2$.

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3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction Spectral Studies

X-ray diffraction studies can be employed for estimating peak broadening using crystalline size and strain in lattice caused by disruptions. XRD spectrum indicated that particles were crystalline in nature. Full width at half maximum (β) has been utilized to evaluate the size distribution of particles (Fig.1)[22]. It has been perceived that as the width of peak is increased, the size distribution of nanoparticles is also increased. The crystalline size of nanoparticles was assessed by means of the width of X- ray peaks supposing that these are free from non-uniform strains through Debye-Scherrer's formulation. The average nano crystalline size was evaluated by means of Debye-Scherrer formula as [23-24]:

$$D = \frac{K\lambda}{\beta Cos\theta} \qquad .....(1)$$

Where K = shape factor = 0.9, D= Crystalline size, and λ = Wavelength of Cuk_{α} line =1.54060 Å. From the calculations, the average crystalline size of ZnO nanoparticles was found 27.7 nm.

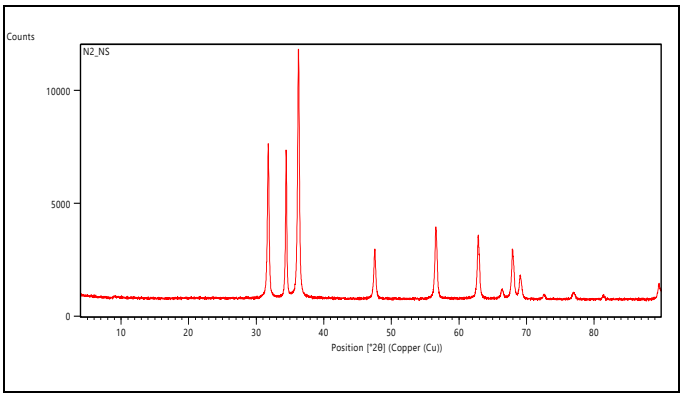


Fig. 1: P-XRD graph of ZnO nanoparticles

Table 1: Cell Parameters for ZnO nanoparticles

Unit Cell Parameter (a) / Å	Unit Cell Parameter (c) / Å	c/a Ratio	Cell Volume ($Å^3$)
3.251	5.209	1.602	47.67

3.2 Transmission electron microscopic studies

TEM results concluded the size of zinc oxide nanoparticles. It has been confirmed from the images (Fig.2) that size of zinc oxide nanoparticles lies in the range of 4.69 to 42.08 nm.

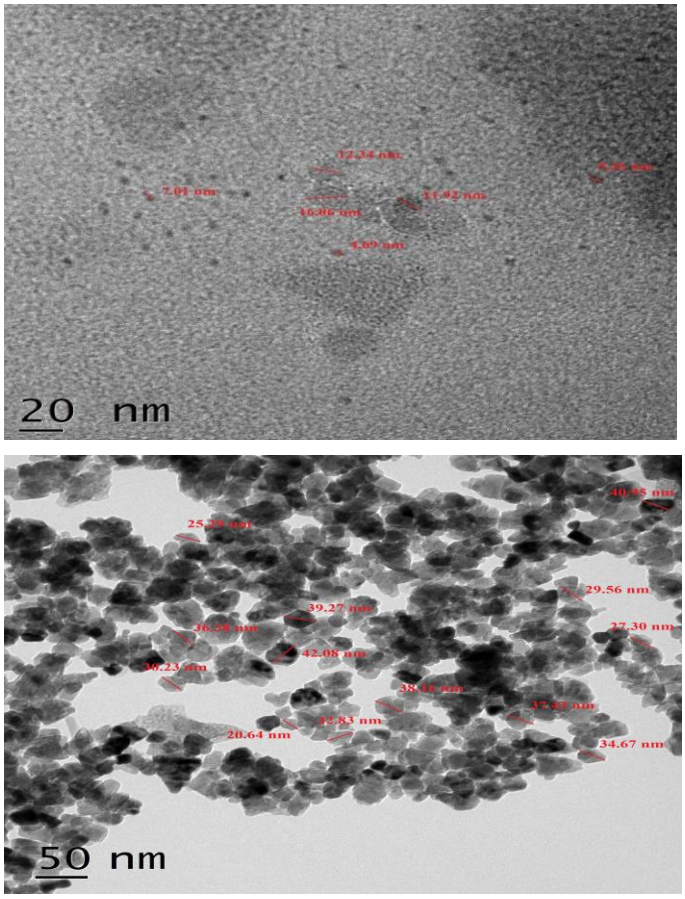
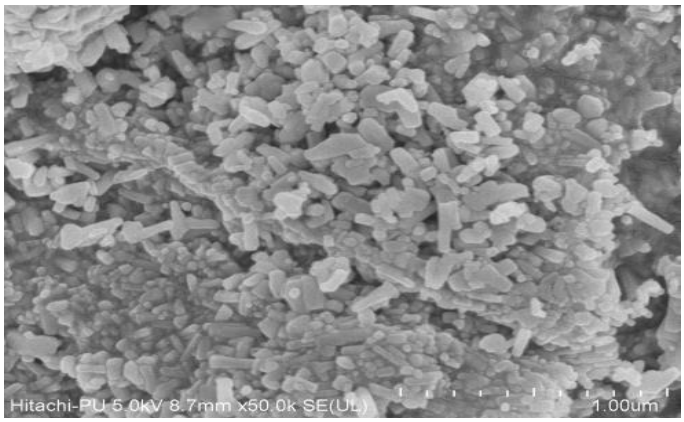


Fig. 2: TEM images of ZnO nanoparticles

3.3 FESEM Analysis

FESEM (Fig.3) was used to evaluate surface morphological characteristics of zinc oxide nanoparticles. SEM micrographs markedly specified that zinc oxide nanoparticles are almost hexagonal symmetry.



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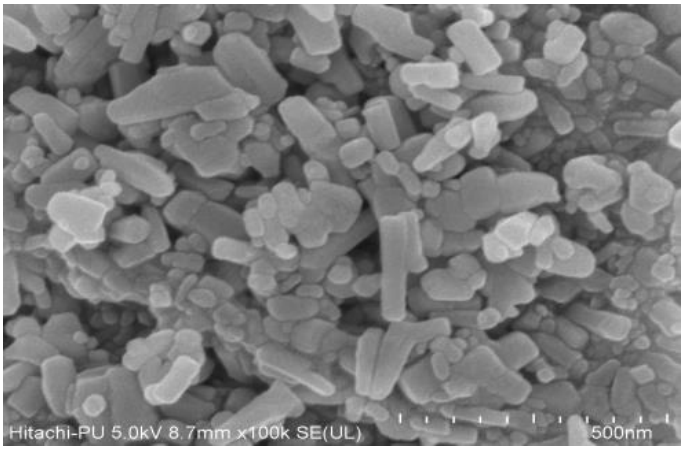

Fig. 3: FESEM images of ZnO nanoparticles

3.4 *Williamson Hall Method*

In Williamson-Hall method, crystalline size D and micro strain ε are related and the slope of the plot among $4\sin\theta$ and $\beta\cos\theta$ gives the micro strain and the crystalline size value [25, 26]. The strain which is prompted because of crystal defectiveness and distortion was evaluated by means of the formula :

$$\varepsilon = \frac{\beta}{4Tan\theta} \quad \text{....(2)}$$

It was analyzed from equations (1) and (2) that peak breadth from crystalline size diverges by means of $\frac{1}{\cos\theta}$, strain diverges with $\tan\theta$. Supposing that both the particle size and strain contributions to line widening are freefrom each other and together have a Cauchy-like profile, the perceived line extent is basically the sum of equations (1) and (2).

$$\beta = \frac{K\lambda}{DCos\theta} + 4\varepsilon Tan\theta \quad \text{....(3)}$$

By rearranging the above equations

$$\beta Cos\theta = \frac{K\lambda}{D} + 4\varepsilon Sin\theta \quad \text{....(4)}$$

These equations are Williamson-Hall equations. A graph is plotted through $4\sin\theta$ and $\beta\cos\theta$ along X and Y-axis correspondingly for synthesized zinc oxide nanoparticles as presented in Fig. 4. Particle size is evaluated from Y-intercept and strain is evaluated as of slope of the fitted line correspondingly. Now an equation (4) is considered for UDM (Table 2) in which it is presumed that strain is constant in each crystallographic direction. This strain might be due to the lattice contraction or dislocations.

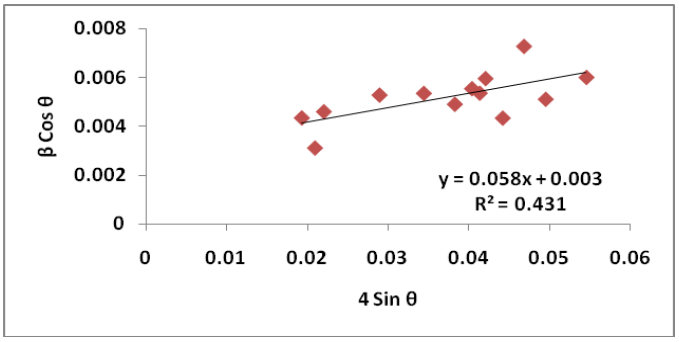

Fig. 4: The Williamson-Hall study using UDM

Uniform stress deformation model (USDM) (Table 2.) is used to calculate strain by means of Hook's law which is represented by $\sigma = Y\varepsilon$ where σ =Stress, Y= Young's modulus. This law withstands the linear proportionality. Hook's law is effective at considerably minor strain. In view of that a minor strain is existing in zinc oxide, Hooke's law can be utilized. Relating Hooke's law estimation in Equation (4) –

$$\beta Cos\theta = \frac{K\lambda}{D} + \frac{4\sigma Sin\theta}{Y} \quad \text{.... (5)}$$

For the hexagonal structure, Young's modulus (Y) is specified through consequent equation (6), in which S_{11}= 7.858×10^{-12} m^2 N^{-1}, S_{33}=6.940×10^{-12} m^2 N^{-1} S_{13} = -2.206×10^{-12} $m^2N^{-1,}$, S_{44} = 23.57×10^{-12} m^2 N^{-1} are elastic constant [27] for zinc oxide. Young's modulus (Y) of zinc oxide was evaluated ≈ 127 GPa. A graph between $4Sin\theta/Y$, $\beta\cos\theta$ were plotted on X and Y-axis respectively. The USDM plot meant for zinc oxide is as presented in Fig 5. The stress is evaluated from slope

$$Y = \left(\frac{\left[h^2 + \frac{(h+2k)^2}{3} + \frac{(al)^2}{c} \right]^2}{S_{11}\left(h^2 + \frac{(h+2k)^2}{3} \right)^2 + S_{33}\left(\frac{al}{c} \right)^4 + (2S_{13} + S_{44})\left(h^2 + \frac{(h+2k)^2}{3} \right)\left(\frac{(al)^2}{c} \right)} \right) \quad \text{....(6)}$$

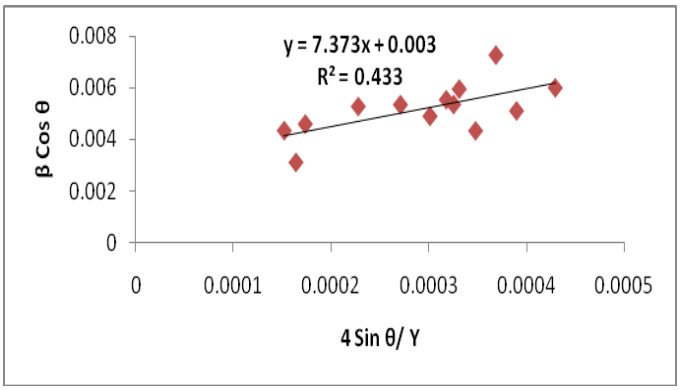

Fig. 5: The W-H study using USDM

Another model is utilized to evaluate the energy density of synthesized ZnO nanoparticles. This model is known as Uniform Deformation Energy Density Model (UDEDM) (Table 3). According to Eq. (5), the crystals are considered to

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have regular and isotropic behavior. Though, in several considerations, the consideration of isotropy and homogeneity is not reliable. Furthermore, the constants of proportionality related with the stress and strain relation are no longer free as soon as the strain energy density u is measured. For an elastic system following Hooke's law, and the energy density u can be computed by $u = (\sigma^2 / 2Y)$ hence Eq. (5) can be rewritten conferring to the energy density and strain relation

$$\beta Cos\theta = \frac{K\lambda}{D} + (4Sin\theta\left(\frac{2u}{Y}\right)^{1/2}) \quad .....(7)$$

Plots of $\beta \mathrm{Cos}\,\theta$ versus $4\,\mathrm{Sin}\,\theta\left(\frac{2}{Y}\right)^{1/2}$ were plotted and the data fitted to lines. The anisotropic energy density u was calculated by the slope of line, and the crystalline size from the y-intercept (Fig. 6).

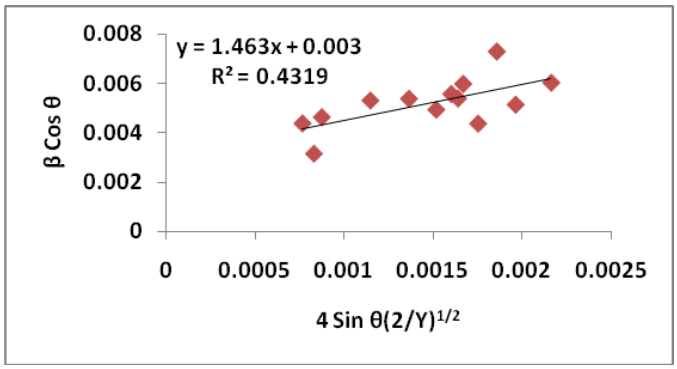

Fig. 6 : The W-H study using UDEDM

Calculated elastic parameters using various models are-

Table 2: Strain & size by UDM & USDM

Williamson - Hall Method				
(UDM)		(USDM)		
D (nm)	ε	D (nm)	ε	σ (GPa)
46.2	0.058	46.2	0.058	7.37

Table 3: Energy density, strain & size by UDEDM

Williamson-Hall Method (UDEDM)			
D (nm)	u (KJm^{-3})	ε	σ (GPa)
46.2	2.14×10^{5}	0.058	7.37

We have effectively synthesized nano crystalline zinc oxide nano powder using *Azadirachta indica* (neem) leaves extract. Average particle size of crystalline material, estimated from XRD data is 27.7 nm is in good agreement with TEM records. It has been concluded that micro strain arises due to crystal imperfections or dislocations. Peak broadening has been observed in XRD results. This broadening was due to strain in lattice. Developed strain, stress and energy density and crystalline size have been estimated using Scherrer formula and Williamson Hall analysis. The TEM records were in noble agreement by means of the corresponding results of Williamson Hall method.

4. CONCLUSIONS

The zinc oxide nanoparticles have been successfully synthesized by using neemextract. As such a synthesis is chemically non-hazardous. Prepared ZnO material was characterized using several analytical techniques like P-XRD, SEM and TEM. P-XRD result reveals the peak broadening and morphology of the sample was characterized by SEM which proved the hexagonal shape. This analysis is important for evaluation of microstrain arising due to dislocations. Hence the mechanical application of the zinc oxide nanomaterial can be improved.

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