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X-ray Peak Broadening Analysis of ZnO Nanoparticles Derived by Precipitation method

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Abstract- In the present report ZnO nanocrystals were prepared by precipitation method from Zinc Chloride and Ammonia in aqueous solutions at a pH value 8.0 .ZnO nanocrystals were then synthesized by heating the precursor in a muffle furnace at temp 350°C for 3 hours and allowed to cool to room temperature. The obtained ZnO nanoparticles have been studied using characterization techniques like X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy dispersive analysis Of X-ray (EDAX). XRD results reveal that the sample is crystalline with a hexagonal wurtzite phase. X-ray peak broadening analysis was used to evaluate the crystallite sizes and lattice strain by the Williamson-Hall (W-H) analysis. Further appropriate physical parameters such as strain, stress, and energy density values were also calculated using W-H analysis with different models, viz, uniform deformation model, uniform deformation stress model and uniform deformation energy density model. SEM and EDAX study confirms the preparation of ZnO nanoparticles.

Index Terms- Nanoparticles, Scanning electron microscopy (SEM), X-ray diffraction (XRD),W-H analysis, ZnO

I. INTRODUCTION

ZnO is a II-VI group semiconductor material with wide band gap (~3.37 eV) and high excitation binding energy (~60 meV) [1, 5] at room temperature. It exhibits numerous

Characteristics suited for various technological applications such as antireflection coatings, transparent electrodes in solar cells [6], piezoelectric devices [7], gas sensors [8], varistors [9], UV and blue light emitters [10] and even thin film transistors [11].

Various chemical synthesis methods have been employed by several workers to synthesize nano / micro crystals such as solvothermal, hydrothermal, self assembly and Sol-gel, etc [12-16]. In this work, ZnO nanoparticles were synthesized using the cost competitive and simple precipitation process. The characterization was done using X-Ray diffraction, SEM, and EDAX.

A perfect crystal would extend in all directions to infinity, so no crystals are perfect due to their finite size. This deviation from perfect crystallinity leads to a broadening of the diffraction peaks. The two main properties extracted from peak width analysis are the crystallite size and lattice strain. Crystallite size is a measure of the size of coherently diffracting domain. The crystallite size of the particles is not generally the same as the particle size due to the presence of polycrystalline aggregates [17]. The most common techniques used for the measurement of particle size, rather than the crystallite size, are the Brunauer Emmett Teller (BET), light (laser) scattering experiment, scanning electron microscopy (SEM) and TEM analysis. Lattice strain is a measure of the distribution of lattice constants arising from crystal imperfections, such as lattice dislocation. The other sources of strain are the grain boundary triple junction, contact or sinter stresses, stacking faults, coherency stresses etc. [18]. X-ray line broadening is used for the investigation of dislocation distribution. Crystallite size and lattice strain affect the Bragg peak in different ways. Both these effects increase the peak width, the intensity of the peak and shift the 2θ peak position accordingly. W-H analysis is a simplified integral breadth method where, both size induced and strain induced broadening are deconvoluted by considering the peak width as a function of 2θ [19]. Although X-ray profile analysis is an average method, they still hold an unavoidable position for grain size determination.

The strain associated with the prepared samples at 350 °C due to lattice deformation was estimated by a modified form of W-H, namely, uniform deformation model (UDM).The other modified models, such as uniform deformation stress model (UDSM) and uniform deformation energy density model (UDEDM), gave an idea of the stress-strain relation and the strain as a function of energy density 'u'. In UDM, the isotropic nature of the crystal is considered, whereas UDSM and UDEDM assume that the crystals are of an anisotropic nature.

II. EXPERIMENTAL DETAILS

In this experiment 1M $ZnCl_2$ solution was kept under constant stirring using magnetic stirrer for 1 hour to completely dissolve and 25% ammonia solution was added here drop by drop touching the walls of the vessel to make the pH of the solution 8.0. The reaction was allowed to proceed for 45 minutes at temperature 50°C. The beaker was sealed and the solution was allowed to settle for overnight and further the precipitate was filtered using whatman filter for three times. The precipitate was heated to dry it completely in a hot air oven and grinded with a mortar. Next it was heated in a muffle furnace at 350 °C for 3 hrs and allowed to cool to room temperature. X-ray diffraction pattern was recorded using Philips –X'pert Pro X-ray diffractometer using CuK_α radiation of wavelength $\lambda = 0.1541$ nm. Morphology of the sample was investigated using SEM and EDAX.

III. Results and Discussion

3.1. XRD Analysis

The XRD patterns of calcined samples of ZnO nanoparticles in the range of 2θ =30°to 70°are shown in Fig. 1. All evident peaks could be indexed as the ZnO wurtzite structure (JCPDS Data Card No: 36-1451). Wurtzite lattice parameters such as the values of d, the distance between adjacent planes in the Miller indices (hkl) (calculated from the Bragg Equation, $\lambda=2d\sin\theta$), lattice constants *a*, *b*, and *c*, inter- planar angle and unit cell volumes are calculated from the Lattice Geometry equation [20]. The lattice parameters of the powders calcined at 350°c are shown in table 1.

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

$$a = \frac{\lambda}{\sqrt{3}\sin\theta_{100}} \text{-------}(1b)$$

$$c = \frac{\lambda}{\sin\theta_{002}} \text{------}(1c)$$

$$V = \frac{\sqrt{3}a^2c}{2} \text{-------}(1d)$$

Table 1 – The structural parameters of ZnO nanoparticles

data	2θ	hkl	d_{hkl} (Å)	Structure	Lattice parameters(Å)	V (Å^3)
My sample	32.063 34.720	(100) (002)	2.788 2.580	Hexagonal	a =3.219 c =5.161 c/a =1.6033	46.31
Jcpds (36-1451)	31.770 34.422	(100) (002)	2.814 2.603	Hexagonal	a =3.250 c =5.207 c/a =1.6021	47.63

3.2 Crystallite Size and Strain

3.2.1 Scherrer Method

XRD can be utilized to evaluate peak broadening with crystallite size and lattice strain due to dislocation [21]. The crystallite size of the ZnO nanoparticles was determined by the X-ray line broadening method using the Scherer equation:

$$D = \frac{K\lambda}{\beta_{hkl}COS\theta} \text{------}(2)$$

Where k denotes Scherrer constant (the shape factor) =.09, λ= 1.5418 nm is the wavelength of the incident CuK_α radiation; β represents full-width at half maximum of the respective peak and θ is the Bragg diffraction angle.

The breadth of the Bragg peak is a combination of both instrument- and sample-dependent effects. To decouple these contributions, it is necessary to collect a diffraction pattern from the line broadening of a standard material (e.g., silicon) to determine the instrumental broadening. The instrument-corrected broadening β corresponding to the diffraction peak of ZnO was estimated using the relation

$$\beta_{hkl}^{\ 2} = (\beta)^2_{measured} - (\beta)^2_{instrumental} \text{----}(3)$$

3.2.2 Williamson- Hall Method

The strain induced in powders due to crystal imperfection and distortion was calculated using the formula:

$$\varepsilon = \frac{\beta_{hkl}}{4\tan\theta} \text{----}(4)$$

From Equations (2) and (4), it was confirmed that the peak width from crystallite size varies as $\frac{1}{\cos\theta}$, strain varies as tanθ. Assuming that the particle size and strain contributions to line broadening are independent to each other and both have a Cauchy-like profile, the observed line breadth is simply the sum of Equations 2 and 4.

$$\beta_{hkl} = \frac{k\lambda}{D\cos\theta} + 4\varepsilon\tan\theta \text{--------}(5)$$

By rearranging the above equation, we get

$$\beta_{hkl}\cos\theta = \frac{k\lambda}{D} + 4\varepsilon\sin\theta \text{----(6)}$$

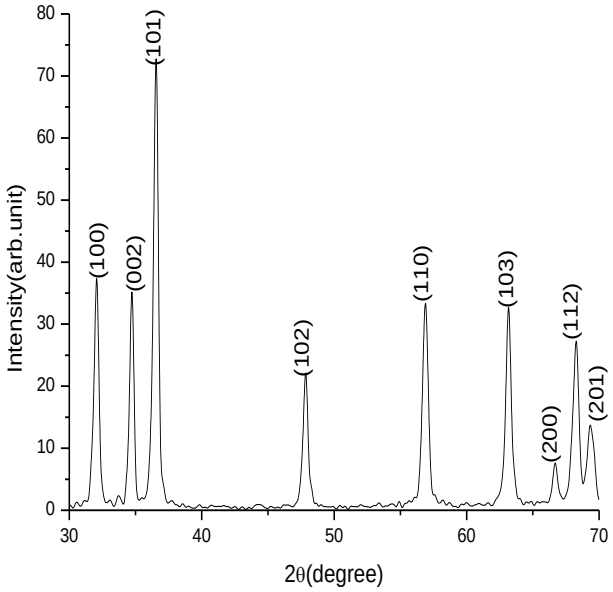

Figure1:XRD of ZnO nanoparticles

The above equations are W-H equations. A plot is drawn with $4\sin\theta$ along the x-axis and $\beta_{hkl}\cos\theta$ along the y-axis for prepared ZnO nanoparticles as shown in Figure 2.

From the linear fit to the data, the crystalline size was estimated from the y-intercept, and the strain ε, from the slope of the fit. Equation 6 represents the UDM, where the strain was assumed to be uniform in all crystallographic directions, thus considering the isotropic nature of the crystal, where the material properties are independent of the direction along which they are measured. The uniform deformation model for ZnO nanoparticles is shown in Figure 2.

In the Uniform Stress Deformation Model, USDM, a generalized Hooke's law refers to the strain, keeping only the linear proportionality between the stress and strain as given by $\sigma = \mathrm{Y}\varepsilon$, where σ is the stress of the crystal and *Y* is the modulus of elasticity or Young's modulus. This equation is valid for a significantly small strain. Assuming a small strain to be present in ZnO 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 (6), we get

$$\beta_{hkl}\cos\theta = \frac{k\lambda}{D} + \frac{4\sigma\sin\theta}{\mathrm{Y}_{hkl}} \text{----(7)}$$

For a hexagonal crystal, Young's modulus is given by the following relation [12, 13]:

$$\mathrm{Y}_{hkl} = \frac{[h^2 + \frac{(h+2k)^2}{3} + \left(\frac{al}{c}\right)^2]^2}{S_{11}\{h^2 + \frac{(h+2k)^2}{3}\} + S_{33}\left(al/c\right)^4 + (2S_{13} + S_{44})\{h^2 + \frac{(h+2k)^2}{3}\}(\frac{al}{c})^2} \text{-----(8)}$$

where S_{11}, S_{13}, S_{33}, S_{44} are the elastic compliances of ZnO with values of 7.858 x10^{-12}, 2.206 x10^{-12}, 6.940x10^{-12}, 23.57 x10^{-12} m^2N^{-1}, respectively [22].

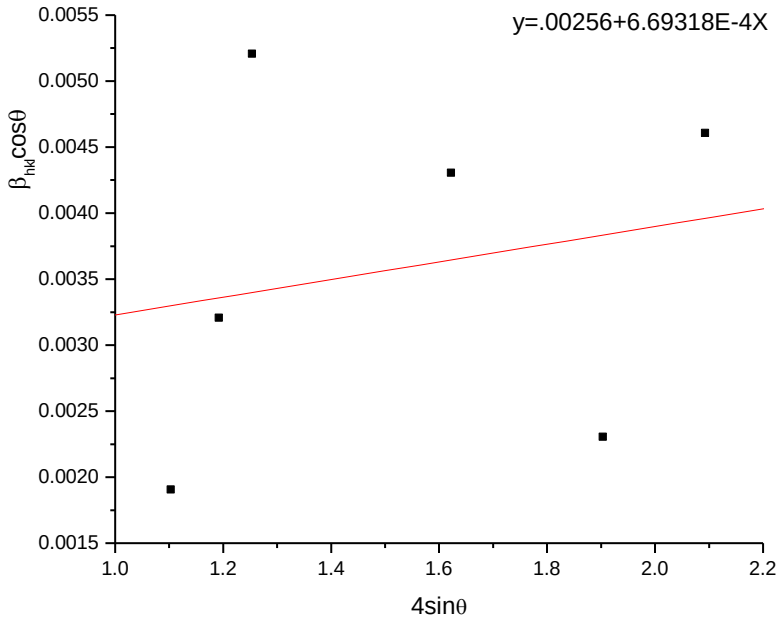

Figure2: Plot of β_{hkl}cosθ vs 4sinθ Of ZnO nanoparticles

Young's modulus, *Y*, for hexagonal ZnO nanoparticles was calculated as ~ 127 GPa. Plots were drawn with $\frac{4\sin\theta}{Y_{hkl}}$ on the x-axis and $\beta_{hkl}\cos\theta$ on the y-axis for the ZnO-nanoparticles. The USDM plots for ZnO nanoparticles calcinations at 350°C are shown in Fig. 3.The stress is calculated from the slope of the fitted line.

There is another model that can be used to determine the energy density of a crystal called the Uniform Deformation Energy Density Model, UDEDM. In Equation (7), the crystals are assumed to have a homogeneous, isotropic nature. However, in many cases, the assumption of homogeneity and isotropy is not justified. Moreover, the constants of proportionality associated with the stress -strain relation are no longer independent when the strain energy density *u* is considered. According to Hooke's law, the energy density u (energy per unit volume) as a function of strain is $u = \frac{\varepsilon^2 Y_{hkl}}{2}$. Therefore, Equation (7) can be modified to the form

$$\beta_{hkl}\cos\theta = \frac{k\lambda}{D} + \{4\sin\theta(\frac{2u}{Y_{hkl}})^{\frac{1}{2}}\} ----(9)$$

The uniform deformation energy density (UDEDM) can be calculated from the slope of the line plotted between $\beta_{hkl}\cos\theta$ and $4\sin\theta(2/Y_{hkl})^{\frac{1}{2}}$. The lattice strain can be calculated by knowing the Y_{hkl} values of the sample. W-H equations modified assuming UDEDM and the corresponding plot is shown in Figure 4.

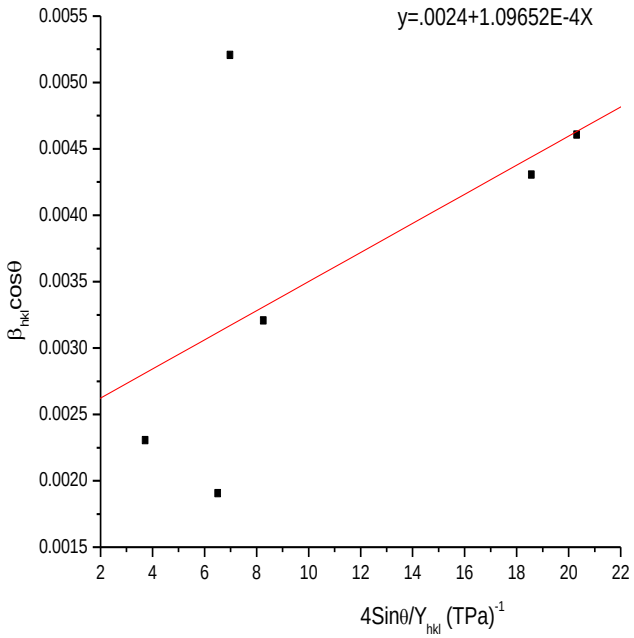

Figure3: Plot of β_{hkl}cosθ vs 4sinθ/Y_{hkl} of ZnO nanoparticles

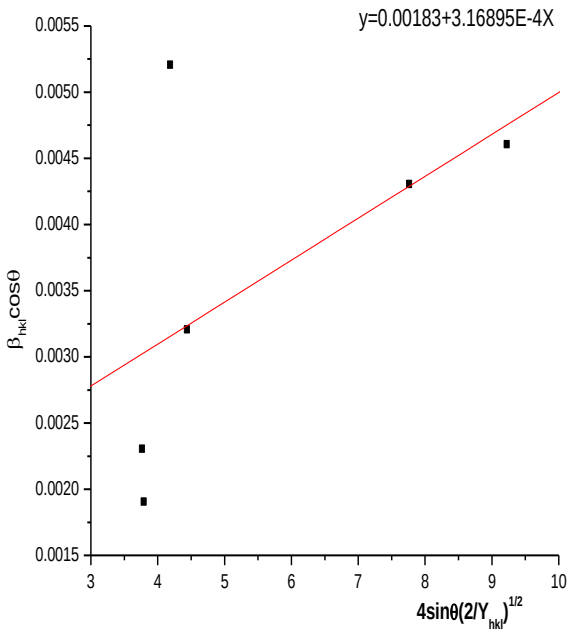

Figure4: Plot of $\beta_{hkl}\cos\theta$ vs $4\sin\theta(2/Y_{hkl})^{1/2}$ of ZnO nanoparticles

From Equations (7) and (9), the energy density and the stress can be related with UDSM and UDEDM, but approaches are different, based on the assumption of uniform deformation stress, according to Equation (7). The assumption of uniform deformation energy is as per Equation (9), even though both models consider the anisotropic nature of the crystallites. From Equations (7) and (9), the deformation stress and deformation energy density are related as $u = \sigma^2 / Y_{hkl}$. It may be noted that though both Equations (7) and (9) are taken into account in the anisotropic nature of the elastic constant, they are essentially different. This is because in Equation (4), it is assumed that the deformation stress has the same value in all crystallographic directions allowing u to be anisotropic, while Equation (9) is developed assuming the deformation energy to be uniform in all crystallographic directions treating the deformation stress σ to be anisotropic. Thus, it is clear that from Williamson-Hall plots using Equations (7) and (9), a given sample may result in different values for lattice strain and crystallite size [23].

Table 2 – The geometric parameters of prepared ZnO nanoparticles

Scherer method	**Williamson method UDM**		**UDSM**			**UDEDM**			
***D* nm**	***D* nm**	**ε x10^{-3}**	**D nm**	**ε x10^{-3}**	**σ (MPa)**	**D nm**	**ε x10^{-3}**	**σ (MPa)**	**u (KJm^{-3})**
36.2	53.3	0.70	57.7	0.85	109	75.7	1.25	159	100

3.3 SEM & EDAX Study

The morphology of the prepared nanoparticles was examined using scanning electron microscopy. Figure 5 shows the surface morphology of the particles prepared in our report. The shapes of the particles are nearly spherical and obviously demonstrate aggregation of the particles. The aggregation of particles should had been originated from the large specific surface area and high surface energy of ZnO nanoparticles [24].The aggregation occurred probably during the process of drying [25,26] .

The EDAX Study of the prepared sample is shown in Figure 6. This shows that the sample contains only Zinc and Oxygen and no other impurity are present in the sample.

IV. CONCLUSIONS

The ZnO nanoparticles with hexagonal structure have been synthesized by simple cost competitive precipitation method after annealing the precursor at 350°C. The prepared ZnO particles were characterized by XRD, SEM, and EDAX.The line broadening of ZnO nanoparticles due to the small crystallite size and strain was analysed by Scherrer's formula. The size and strain contributions to line broadening were analyzed by the

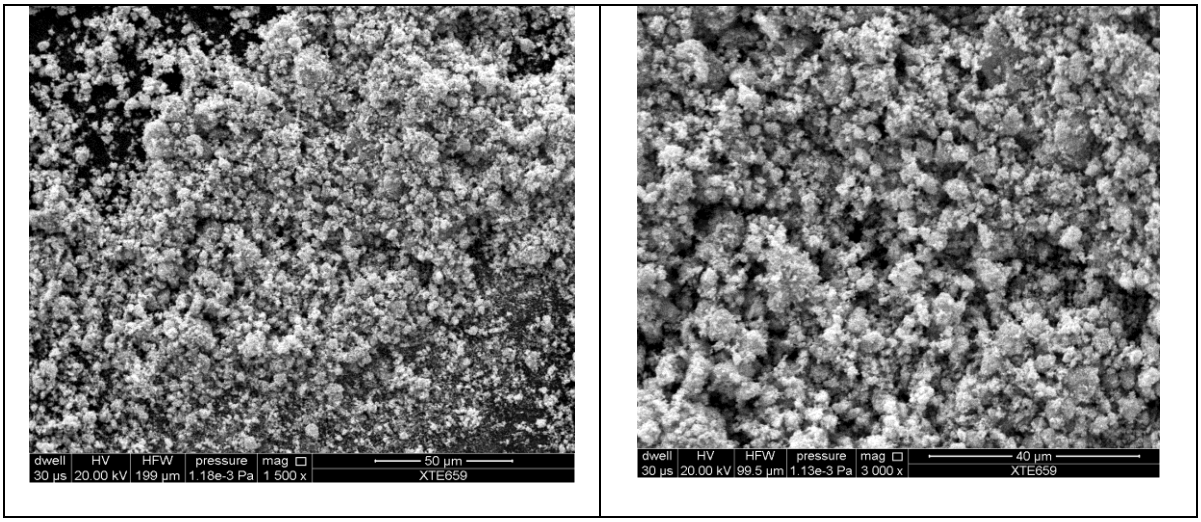

Fig5: SEM image of ZnO nanoparticles

Element	Weight percentage	Atomic percentage
O K	18.96	48.87
Zn K	81.04	51.13
Total	100	100

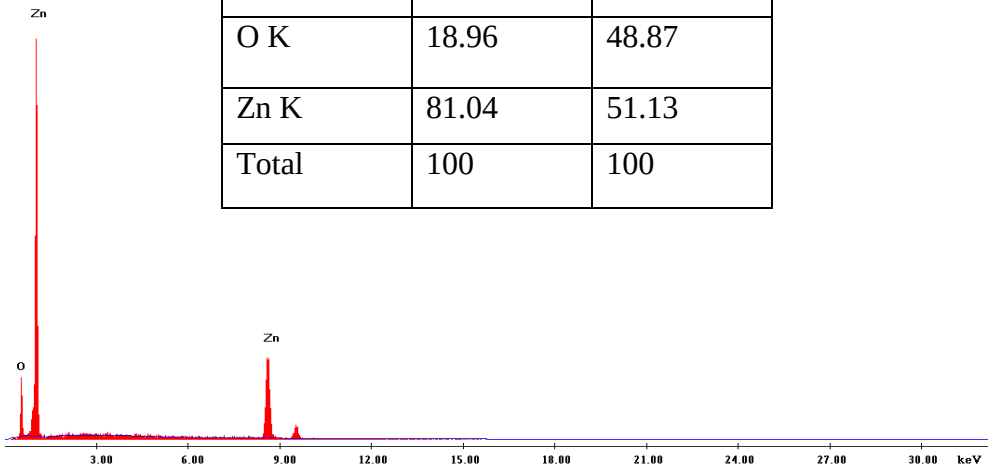

Fig 6: EDAX of ZnO nanoparticles

method of Williamson and Hall using uniform deformation, uniform deformation stress, and uniform deformation energy density models. The three modified forms of W-H analysis were helpful in determining the strain, stress, and energy density value with a certain approximation, and hence, these models are highly preferable to define the crystal perfection.

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REFERENCES

[1] Yoshitake Masuda, Naoto Kinoshita,Fuyutoshi Sato, Kunihito Koumoto, Cryst.Growth Des. 6, 75 (2006).
[2] M. Singhai, V. Chhabra, P. Kang, D.O. Shah, Mater. Res.Bull. 32, 239 (1997).
[3] Hongyan Xu, Xiulin Liu, Deliang Cui, Mei Li, Minhua Jiang, Sensor. Actuat. B 114, 301 (2006).
[4] M.S. Tokumoto, S.H. Pulcinelli, C.V. Santilli, V. Briois, J. Phys. Chem. B 107, 568 (2003).
[5] N.S. Minimala, A. John Peter, J. Nano- Electron. Phys. 4 No 4, 04004 (2012)
[6] R. R. Potter, solar cells 16 (1986) 521.
[7] S. C. Ko, Y. C. Kim, S. S. Lee, S. H. Choi, S. R. Kim, Sens. Actuators, A 103 (2003) 130.
[8] D. H. Yoon, G. M. Choi, Sens. Actuators, B 45 (1997) 251.
[9] D. Fernández-Hevia, J. de Frutos, A. C. Caballer, J. F. Fernández, Appl. Phys. Lett. 82 (2003) 212.

[10] D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, S Koyama, M. Y. Shen, T. Goto, Appl. Phys. Lett. 70 (1997) 2230.

[11] R. L. Hoffman, B. J. Norris, J. F. Wager, Appl. Phys. Lett. 82 (2003) 733.

[12] B. B. Lakshmi, C. J. Patrissi and C. R. Martin, Chem. Mater., 9, 2544, 1997.

[13] L. Vayssieres, K. Keis, A. Hagfeldt and S. E. Lindquist, Chem. Mater., 13, 4395, 2001.

[14] C. Pacholski, A. Kornowski, H. Weller, Angew. Chem. Int. Edn. Engl., 41, 1188, 2002.

[15] L. Vayssieres, Adv. Mater., 15, 464, 2003.

[16] B. Liu and H. C. Zeng, J. Am. Chem. Soc., 125, 4430, 2003.

[17] K. Ramakanth, Basics of X-ray Diffraction and its Application(I.K. International Publishing House Pvt. Ltd.: New Delhi: 2007).

[18] T. Ungar, J. Mater. Sci, 42, 1584 (2007).

[19] C. Suryanarayana, M. Grant Norton, X-ray Diffraction: APractical Approach (New York: 1998).

[20] B.D. Cullity, Elements of X-ray Diffraction (Addison- Wesley Publishing Company Inc.: California: 1956).

[21] R. Yogamalar, R. Srinivasan, A. Vinu, K. Ariga, A.C. Bose, Solid State Commun. 149, 1919 (2009).

[22] Nye, JF: Physical Properties of Crystals: Their Representation by Tensors and Matrices. Oxford, New York (1985)

[23] Mote et al. Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles. Journal of Theoretical and Applied Physics, 2012, 6:6

[24] Davood Raoufi, Journal of luminescence 134 (2013) 213-219

[25] R.Y. Hong, J.Z. Qian, J.X. Cao, Powder Technol. 163 (2006) 160.

[26] R.Y. Hong, J.H. Li, L.L. Chen, D.Q. Liu, H.Z. Li, Y. Zheng, J. Ding, Powder Technol. 189 (2009) 426.

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