PHASE ANALYSIS AND MICROSTRUCTURE OF ZINC OXIDE NANOPARTICLES

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

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By

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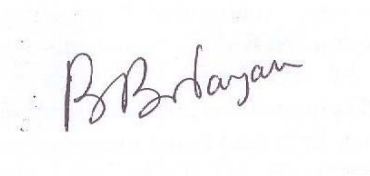
CERTIFICATE

This is to certify that the thesis entitled "Phase analysis and microstructure of zinc oxide nanoparticles", submitted by Mr. Manish Kumar Gupta bearing Roll number: 109CR0672 in partial fulfilment of the requirements for the award of Bachelor of Technology in Ceramic Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university/institute for the award of any Degree or Diploma.



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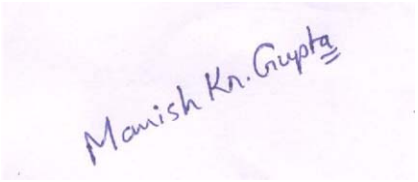

Manish Kumar Gupta

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ABSTRACT

ZnO nanoparticles were prepared by precipitation method and calined at at 400°C, 600°C, and 800°C. The synthesized as well as calcined ZnO nanoparticles were characterized by DSC TG, X-ray diffraction (XRD) and FE SEM. X-ray diffraction result indicates that the sample is having a crystalline wurtzite phase. Crystallite size of ZnO nanoparticles calcined at different temperatures was determined using Scherrer's formula. Field Emission Scanning Electron Microscopy (FE SEM) result reveals that the ZnO sample is spherical in shape, rod like structure and polycrystalline nature. Crystallite sizes and lattice strain were also analyzed using Williamson-Hall (W-H) analysis.

Key words: zinc oxide, FESEM, XRD, crystallite size, Strain, morphology

INTRODUCTION:

Nanostructured materials prepared via different synthesis techniques may lead to different types of structural defects including lattice strain. Crystaline materials having nano meter size particles in the range between 10 nm to 100 nm may lead to broaden the diffraction peaks. The broadening of the diffraction peak determine the crystallite size and lattice strain. Crystallite size can be determined from Scherrer's formula. Other than this methods, there are several other methods such as Williamson-Hall method was also adopted to determine crystallite size. This method also determine the lattice strain. So, in this work, ZnO nanopowders were synthesized using precipitation method and calcined at different temperatures. The crystallite size and lattice strain was determined using Williamson-Hall method.

LITERATURE REVIEW:

Mote et. al [1] have prepared ZnO nanopowders via coprecipitation techniques. The average grain size of about 50 nm was prepared at 450 °C. The physical parameters such as strain, stress, and energy density values were also calculated using W-H analysis with different model for example uniform deformation model, uniform deformation stress model and uniform deformation energy density model.

Prabhu et. al. [2] have prepared Fe-doped ZnO nanoparticles having hexagonal wurtzite structure. The crystallite sizes and lattice strain on the peak broadening of Fe doped ZnO nanoparticles were studied using Williamson- Hall (W-H) analysis and size- strain plot. Strain, stress and energy density parameters were calculated for the XRD peaks of all the samples using (UDM), uniform stress deformation model (USDM), uniform deformation energy density model (UDEDM) and by the size-strain plot method (SSP). The results of mean particle size of Fe doped ZnO-NPs showed an inter correlation with W-H analysis, SSP, and TEM results.

Brandstetter et. al. [3] have also adopted Williamson-Hall analysis for determining grain size and lattice strain using nanocrystalline Ni and Cu powders.

Similarly, Zak et. al. [4] prepared ZnO nanopowders via sol-gel method. The sample is crystalline in nature having hexagonal wurtzite phase. The phase development in the ZnO nanoparticles was studied by XRD. The Williamson-Hall analysis and size-strain plot method were used to study the individual contributions of crystallite sizes and lattice strain on the peak broadening of the ZnO nanoparticles. The TEM image of ZnO-NPs calcined at 750 °C

revealed an average particle size of about 20 nm and a nonuniform strain in the particles. The TEM results were in good agreement with the results of the W-H method.

Prabhu et. al. [5] have also use W-H method to determine lattice strain on ZnO powders prepared via a simple facile surfactant assisted combustion synthesis.

Thool et. al. [6] prepared ZnO flat thin film via chemical bath deposition techniques. The crystallite size and lattice strain from X-ray line broadening were evaluated using the Scherrer method and Williamson–Hall method.

Sarma et. al. [7] have prepared ZnO nanopowders by simple cost competitive precipitation method after annealing the precursor at 350°C. The line broadening of ZnO nanoparticles due to the small crystallite size and strain was analysed by W-H method.

OBJECTIVES

Our prior objective is to prepare ZnO nanparticles and calculate crystallite size and lattice strain using Willium-son Hall method. ZnO nanoparticles were developed by calcining zinc hydroxide at different calcination temperature. The zinc hydroxide was prepared using precipitation method by taking zinc chloride and hydrazine hydrate.

EXPERIMENTAL WORK

3.1 Synthesis of zinc oxide

Zinc oxide was prepared using precipitation method. Anhydrous $ZnCl_2$, hydrazine hydrate (N_2H_5OH) were used as a starting material. 20 ml of 1 M $ZnCl_2$ was prepared using distilled water. 20 ml of hydrazine hydrate was added drop wise in to a beaker containing zinc chloride solution. Starting pH of the precursor was ~ 4. The pH was increased to 12 by addition of hydrazine hydrate. At this pH, precipitates were collected. These precipitate powders were washed properly with hot distilled water and dried in an oven at 60 °C. The dried prepared powders were calcined at 400 °C, 600 °C and 800 °C for 1h. The phase analysis was performed using XRD. Crystallite size was determined from Scherrer's formula. Particle morphology was studied using FESEM. Lattice strain was determined using Willium son hall method.

3.2 General Characterization:

3.2.1 Thermal Analysis:

Thermal decomposition of as-synthesized powder was studied using thermogravimetric and differential scanning calorimetry DSC/TG by heating the sample at 10°C/min in Argon atmosphere in a thermal analyser (Model Netzsch, STA 449C). Alpha alumina was used as reference material.

3.3.3 X-ray Diffraction:

Phase analysis was studied using the X-ray diffraction (Rigaku, Japan) at room temperature with filtered 0.154056 nm Cu-Kα radiation. Samples were scanned in a continuous mode from 200-800 at a scanning rate of 200/min. Crystallite size was determined using Scherrer's formula. Lattice strain and crystallite size was determined using Willian-son Hall method.

3.3.4 Microstructural analysis:

Microstructural features were studied using Felid Emission Scanning Electron Microscope (NOVA, NanoSEM). One pinch of the well-grinded sample powder was deposited on to the carbon tape pasted on the brass plate. This brass plate was coated for 5 minutes and then used for microscopy.

RESULTS AND DISCUSSION

4.1 Thermal Analysis (DSC-TG):

Figure 1 shows the DSC-TG curves of as synthesized zinc hydroxide powder. An endothermic peak was observed at around 150 °C in the DSC curve indicates the removal of absorbed water molecules. The total weight loss from room temperature to 600 °C in TG curve was about 30%. Based on DSC-TG behaviour, the as-synthesized powders were calcined at 400 °C, 600 °C and 800 °C to understand the phase formation of zinc oxide.

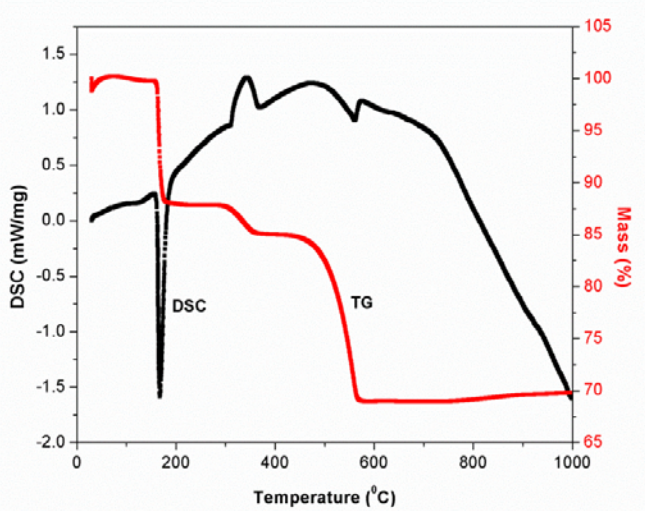

Figure 2: DSC-TG curve of as synthesized zinc hydroxide powder

4.3 Field Emission Scanning Electron Microscopy:

Fig. 2 shows FESEM micrographs of as-synthesized zinc oxide nanopowders. The morphology of zinc oxide seems to be nearly rod-like structure. The length of the rod was around 4 µm and thickness is about 500 nm. The rods like morphology are agglomerated in nature. Further the powders are calcined at 400 °C, the morphology of these powders are studied using FESEM. Fig. 3 show FESEM micrographs of zinc oxide nanopowders calcined at 400 °C. At this temperature, the particles are agglomerated in nature and still rod like morphology was observed at this calcination temperature. However, some particles are seems to be spherical in nature.

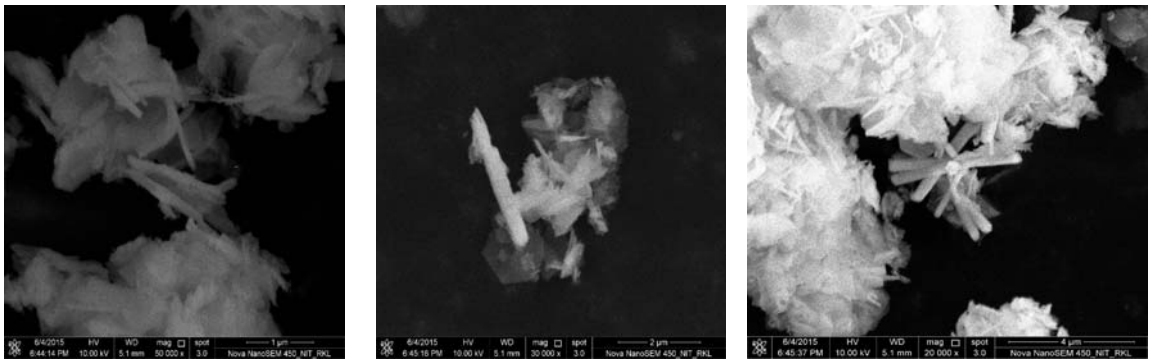

Figure 2: FESEM images of as-synthesized zinc oxide

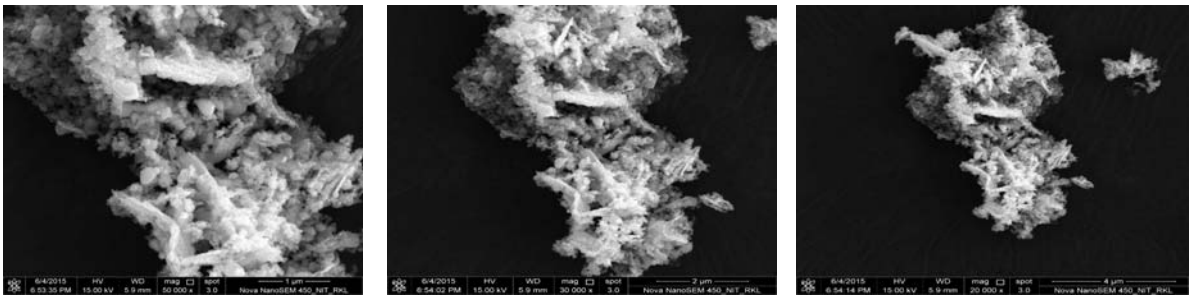

Figure 3: FESEM images of zinc oxide calcined at 400 °C.

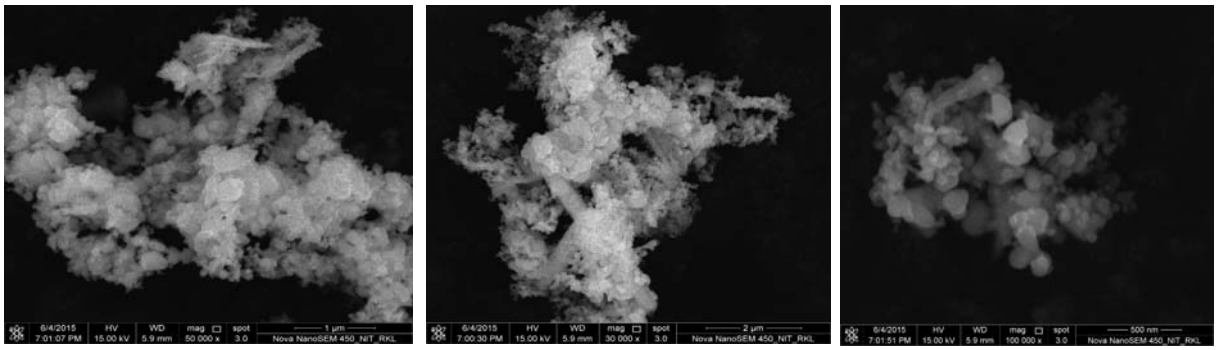

Figure 4: FESEM images of zinc oxide calcined at 600 °C.

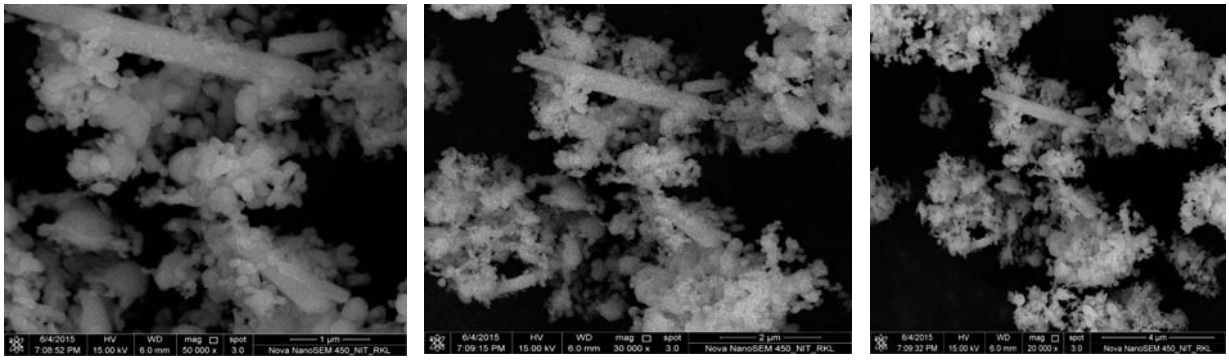

Figure 5: FESEM images of zinc oxide calcined at 800 °C.

Further the particles are calcined at 600 °C and 800 °C for 1h. Figure 4 and 5 show FESEM micrographs of zinc oxide calcined at 600 °C and 800 °C, resepctively. In these two samples, shape of the particles are found to be nearly spherical in shape. The agglomerated spherical shape of the particles are in the range of 500 nm to 1 µm. However, the rod-like morphology in these two calcined powders are also observed. The length of the rod shape of zinc oxide 4 µm and thickness was found to be 500 nm.

In order to find out the phase evolution of zinc oxide from as-synthesized powder, XRD analysis of as-synthesized and calcined powders are performed. Fig. 6 shows XRD patterns of as-synthesized and calcined zinc oxide nanopowders calcined at 400 °C, 600 °C and 800 °C, respectively.

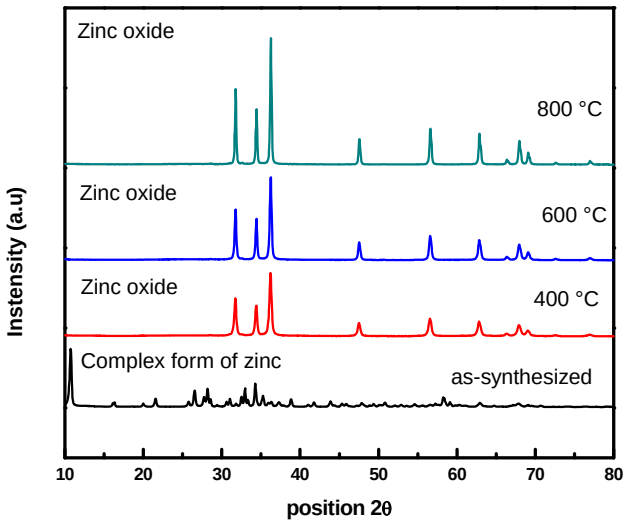

Figure 6: XRD patterns of as synthesized and calcined zinc oxide powders.

The XRD example of the calcined ZnO powder as demonstrated in Figure 6 was having a wurtzite structure. No additional peaks are identified in the calcined powders. However, in the as-synthesized powders, lots of impurity phases are still present. This may be the complex form of zinc. Using XRD data, lattice parameters were calculated and found to be 'a' = 3.25 Å and 'c' = 5.22 Å. The crystallite size of zinc oxide calcined at 400 °C, 600 °C and 800 °C was calculated using Scherrer's formula and are given in Table 1, 2 and 3, respectively .

Table 1: Peak position, FWHM and crystallite size of zinc oxide calcined at 400 °C.

PEAK	$2\theta(^0)$	β	D (nm)
1	31.75	0.3025	27.2
2	34.41	0.2810	29.7
3	36.23	0.3281	25.4
4	47.52	0.3553	24.4
5	56.55	0.4385	20.5
6	62.80	0.4381	21.2

The average crystallite size was 24.7 nm.

Table 2: Peak position, FWHM and crystallite size of zinc oxide calcined at 600 °C.

PEAK	$2\theta(^0)$	β	D (nm)
1	31.76	0.2446	33.7
2	34.43	0.2328	35.7
3	36.25	0.2766	30.2
4	47.53	0.3294	26.3
5	56.66	0.3586	24.5
6	62.57	0.3972	22.7

The average crystallite size was 28.8 nm.

Table 3: Peak position, FWHM and crystallite size of zinc oxide calcined at 800 °C.

Peak	$2\theta(^0)$	β	D (nm)
1	31.78	0.1947	42.4
2	34.45	0.2044	40.6
3	36.27	0.2045	40.8
4	47.66	0.2745	31.1
5	56.73	0.3109	28.2
6	62.59	0.3140	28.7

The average crystallite size was 35.2 nm.

The significance of the broadening of peaks indicates there may be the presence of large strain associated with the powder. So, the strain was determined using Williamson-Hall method. This procedure for calculating strain using W-H method was as follows.

The average nanocrystalline size was calculated using Debye-Scherrer's formula:

$D = k\lambda / \beta\cos\theta$

where D = crystalline size, K = shape factor (0.9), and λ = wavelength of Cukα radiation.

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

$\varepsilon = \beta / 4\tan\theta$

By rearranging the above equation, we get

$\beta\cos\theta = (k\lambda / D) + 4\varepsilon \sin\theta$

The above equations are W-H equations. A plot is drawn with 4sinθ along the x-axis and β cosθ along the y-axis. 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.

Uniform deformation stress and uniform deformation energy density were also taken into account; the anisotropic nature of Young's modulus of the crystal is more realistic. The generalized Hook's law referred to the strain, keeping only the linear proportionality between the stress and strain, i.e., σ = E. Here, the stress is proportional to the strain , with the constant of proportionality being the modulus of elasticity or Young's modulus, denoted by E. In this approach, the Williamson-Hall equation is modified by substituting the value of ε , we get

$B\cos\theta = (k\lambda/D) + 4\sin\theta\ \sigma / E_{hkl}$

Ehkl is Young's modulus in the direction perpendicular to the set of the crystal lattice plane (hkl). The uniform stress can be calculated from the slope line plotted between 4sinθ/Ehkl and β cosθ. The strain can be measured if Ehkl of hexagonal ZnO nanoparticles is known. For samples with a hexagonal crystal phase, Young's modulus Ehkl is related to their elastic compliances Sij as :

$$E_{hkl} = \frac{\left[\mathbf{h^2}+\frac{(\mathbf{h+2k})^2}{3}+\left(\frac{\mathbf{al}}{\mathbf{c}}\right)^2\right]^2}{\mathbf{S11}\left(\mathbf{h^2}+\frac{(\mathbf{h+2k})^2}{3}\right)+\mathbf{S33}\left(\frac{\mathbf{al}}{\mathbf{c}}\right)^4+(\mathbf{2S13}+\mathbf{S44})\left(\mathbf{h^2}+\frac{(\mathbf{h+2k})^2}{3}\right)\left(\frac{\mathbf{al}}{\mathbf{c}}\right)^2}$$

Where , S11, S13, S33, and S44 are the elastic compliances of ZnO, and their values are 7.858 × 10−12, 2.206×10−12, 6.940 × 10−12, and 23.57×10−12 m2N−1, respectively [1].

Plotting the values of β cosθ as a function of 4sinθ/Ehkl, the uniform deformation stress can be calculated from the slope of the line and from lattice strain.

According to Hooke's law, the energy density u (energy per unit volume) as a function of strain is u = ε2Ehkl/2. where u is the energy density (energy per unit volume):

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

The uniform deformation energy density can be calculated from the slope of the line plotted between β cosθ and 4sinθ (2/Ehkl)1/2. The lattice strain can be calculated by knowing the Ehkl values of the sample.

For plotting 4sinθ along the x-axis and β cosθ along the y-axis, β cosθ as a function of 4sinθ/Ehkl, and β cosθ versus 4sinθ (2/Ehkl)1/2, different parameters for zinc oxide calcined at 400 °C, 600 °C and 800 °C are calculated and are shown in Table 4, 5 and 6, respectively.

Table 4: Different parameters for zinc oxide calcined at 400 °C.

Peak	$2\theta(^0)$	hkl	β	βcosθ	4sinθ	E_{hkl} $(\times10^{11})$	$4\sin\theta/E_{hkl}$ $(\times10^{-11})$	$4\sin\theta(2/E_{hkl})^{1/2}$ $(\times10^{-6})$
1	31.75	100	0.3025	0.2909	1.09	1.27	0.858	4.31
2	34.41	002	0.2810	0.2684	1.18	1.44	0.819	4.38
3	36.23	101	0.3281	0.3118	1.24	1.00	1.23	5.51
4	47.52	102	0.3553	0.3251	1.61	0.94	1.71	7.42
5	56.55	110	0.4385	0.3861	1.89	1.28	1.47	7.46
6	62.80	103	0.4381	0.3739	2.08	1.01	2.05	9.23

Table 5: Different parameters for zinc oxide calcined at 600 °C.

Peak	$2\theta(^0)$	hkl	β	βcosθ	4sinθ	E_{hkl} $(\times 10^{11})$	$4\sin\theta/E_{hkl}$ $(\times 10^{-11})$	$4\sin\theta(2/E_{hkl})^{1/2}$ $(\times 10^{-6})$
1	31.76	100	0.2446	0.2352	1.09	1.27	0.858	4.31
2	34.43	002	0.2328	0.2336	1.18	1.44	0.819	4.38
3	36.25	101	0.2766	0.2628	1.24	1.00	1.23	5.51
4	47.53	102	0.3294	0.3014	1.61	0.94	1.71	7.42
5	56.66	110	0.3586	0.3150	1.89	1.28	1.47	7.46
6	62.57	103	0.3972	0.3394	2.08	1.01	2.05	9.23

Table 6: Different parameters for zinc oxide calcined at 800 °C.

Peak	$2\theta(^0)$	hkl	β	βcosθ	4sinθ	E_{hkl} $(\times 10^{11})$	$4\sin\theta/E_{hkl}$ $(\times 10^{-11})$	$4\sin\theta(2/E_{hkl})^{1/2}$ $(\times 10^{-6})$
1	31.78	100	0.1947	0.8172	1.09	1.27	0.858	4.31
2	34.45	002	0.2044	0.1952	1.18	1.44	0.819	4.38
3	36.27	101	0.2045	0.1943	1.24	1.00	1.23	5.51
4	47.66	102	0.2745	0.2510	1.61	0.94	1.71	7.42
5	56.73	110	0.3109	0.2735	1.89	1.28	1.47	7.46
6	62.59	103	0.3140	0.2683	2.08	1.01	2.05	9.23

Fig. 7, 8 and 9 indicates the different plot for zinc oxide nanopowders calcined at 400 °C, 600 °C and 800 °C, respectively.

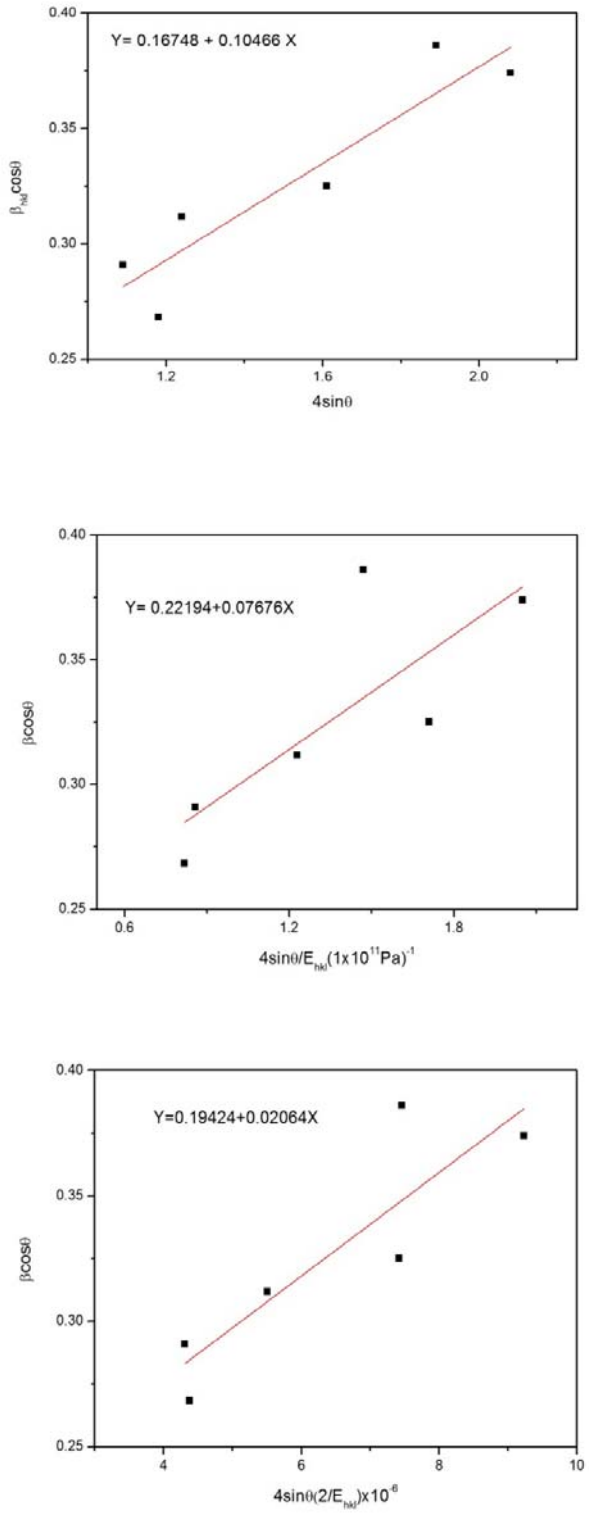

Figure 7: Different plots of zinc oxide powders, calcined at 400 °C..

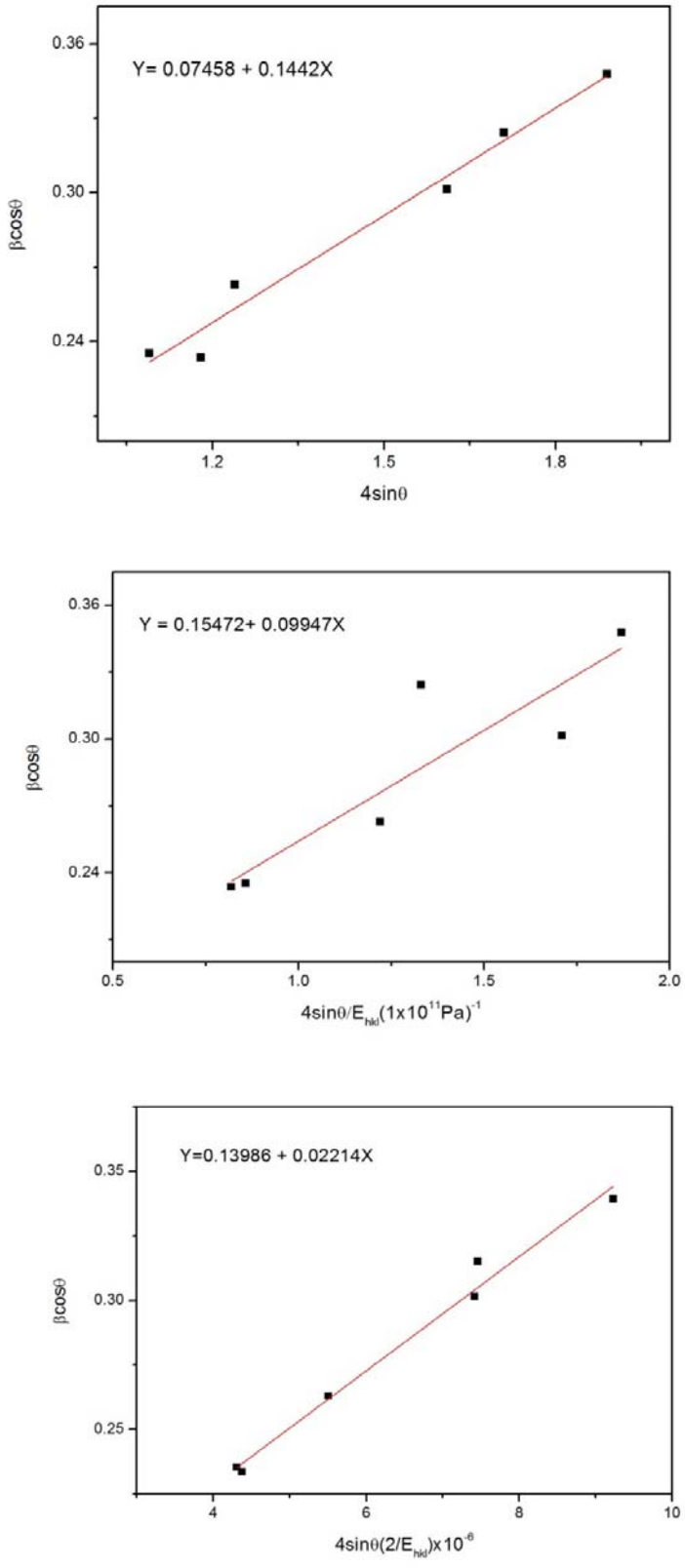

Figure 8: Different plots of zinc oxide powders, calcined at 600 °C.

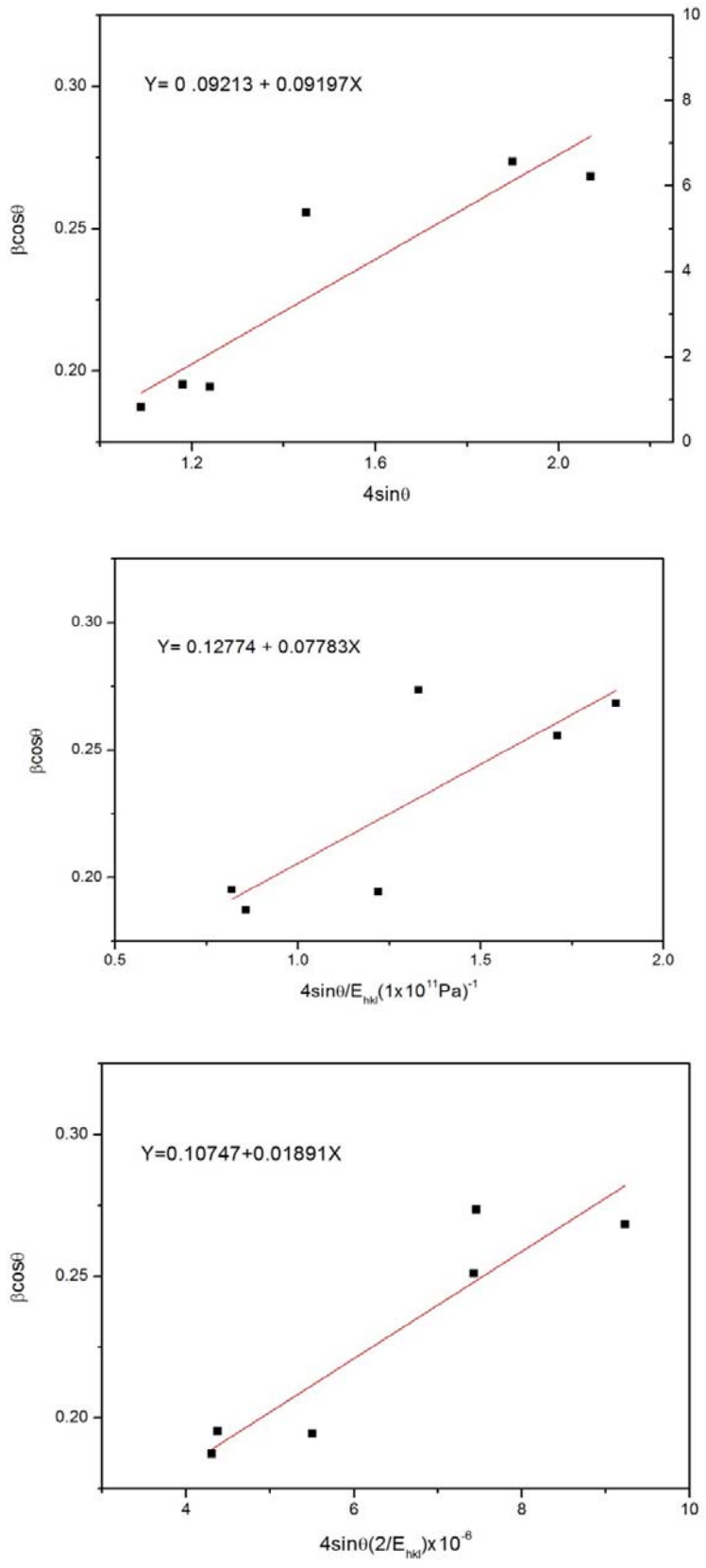

Figure 9: Different plots of zinc oxide powders, calcined at 800 °C.

CONCLUSIONS:

ZnO nanoparticles were prepared by precipitation and anlyzed using DSC-TG, XRD and FE SEM. The as-synthesized powders are nearly rod-like morpholgy and also agglomerated in nature. When the powders are calcined at different calcination temperature, the nature of particle morphology was found to be nearly spherical along with rod-like. The size of the spherical particle was found to be nearly 500 nm . The length of the rod is about 4μm. The crystallite size of the zinc oxide at 400 °C was found to be 24.7 nm and increased to 35. 2 nm at 800 °C. The lattice strain was calculated using W-H method and found to be 0.104 at 400 °C and 0.091 at 800 °C. lattice strain was also determined using different methods and also well-correlated with the strain determined from W-H method.

REFERENCES:

1. Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles. [VD Mote, Y Purushotham and BN Dole], Journal of Theoretical and Applied Physics 2012, 6:6.

2. X-ray Analysis of Fe doped ZnO Nanoparticles by Williamson-Hall and Size-Strain Plot Methods. [Y. T. Prabhu, K. Venkateswara Rao, V. Sesha Sai Kumar, B. Siva Kumari], International Journal of Engineering and Advanced Technology (IJEAT) ISSN: 2249 – 8958, Volume-2, Issue-4, April 2013.

3. Williamson–Hall anisotropy in nanocrystalline metals : X-ray diffraction experiments and atomistic simulations. [S. Brandstetter, P.M. Derlet, S. Van Petegem, H. Van Swygenhoven], Acta Materialia 56 (2008) 165–176.

4. X-ray analysis of ZnO nanoparticles by Williamson-Hall and size-strain plot methods. [A. Khorsand Zak , W.H. Abd. Majid , M.E. Abrishami , Ramin Yousefi], Solid State Sciences 13 (2011) 251e256.

5. X-Ray Analysis by Williamson-Hall and Size-Strain Plot Methods of ZnO Nanoparticles with Fuel Variation. [Yendrapati Taraka Prabhu, Kalagadda Venkateswara Rao, Vemula Sesha Sai Kumar, Bandla Siva Kumari], World Journal of Nano Science and Engineering, 2014, 4, 21-28.

6. Facile synthesis of flat crystal ZnO thin films by solution growth method: A micro-structural investigation. [Gautam Sheel Thool , Ajaya Kumar Singh , R.S. Singh , Ashish Gupta , Md. Abu Bin Hasan Susan], Journal of Saudi Chemical Society, Volume 18, Issue 5, November 2014, Pages 712–721

7. X – ray peak broadening analysis of ZnO nanoparticles derived by precipitation method. [Hiten Sarma , K.C. Sarma], International Journal of Scientific and Research Publications, Volume 4, Issue 3, March 2014.